EFFECTS OF ULTRA-THIN GERMANIUM LAYERS AT THE SILICON-OXIDE INTERFACE DURING OXIDATION REACTIONS ON INJECTION OF INTERSTITIALS

By

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This work is dedicated to those who've come before me, and the genius required in making the integrated circuits that allowed me to write this on a computer rather than a typewriter.

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LIST OF ABBREVIATIONS

BJT	Bipolar Junction Transistor
CMOS	Complimentary Metal Oxide Semiconductor
EDS	Energy Dispersive X-ray Spectrometry
FEG	Field Emission Gun
FIB	Focused Ion Beam
Fin-FET	Fin Field Effect Transistor
FLOOPS	Florida Object Oriented Device and Process Simulator
HAADF-STEM	High Angle Annular Dark Field Scanning TEM
HBT	Heterojunction Bipolar Transistor
HR-TEM	High Resolution TEM
LTE	Low Temperature Epitaxy
MOCVD	Metal Oxide Chemical Vapor Deposition
Nanowire FET	Nanowire based field effect transistor
OED	Oxidation Enhanced Diffusion
OED OSF	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault
OED OSF PTEM	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy
OED OSF PTEM PTFE	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy Poly-tetrafluoro-ethylene (trade name Teflon)
OED OSF PTEM PTFE SiGe	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy Poly-tetrafluoro-ethylene (trade name Teflon) An alloy consisting of a mixture of silicon and germanium
OED OSF PTEM PTFE SiGe SiGeol	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy Poly-tetrafluoro-ethylene (trade name Teflon) An alloy consisting of a mixture of silicon and germanium Silicon-Germanium on insulator
OED OSF PTEM PTFE SiGe SiGeol SiGeOx	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy Poly-tetrafluoro-ethylene (trade name Teflon) An alloy consisting of a mixture of silicon and germanium Silicon-Germanium on insulator Mixed oxides consisting of both silicon and germanium oxides
OED OSF PTEM PTFE SiGe SiGeol SiGeOx SRIM	Oxidation Enhanced Diffusion Oxidation Induced Stacking fault Plan-view Transmission Electron Microscopy Poly-tetrafluoro-ethylene (trade name Teflon) An alloy consisting of a mixture of silicon and germanium Silicon-Germanium on insulator Mixed oxides consisting of both silicon and germanium oxides Stopping Range of lons In Matter
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XTEM Cross-Sectional TEM

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

EFFECTS OF ULTRA-THIN GERMANIUM LAYERS AT THE SILICON-OXIDE INTERFACE DURING OXIDATION REACTIONS ON INJECTION OF INTERSTITIALS

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It is well known that the oxidation of silicon will inject interstitial atoms into the bulk, causing various effects such as OED and OSF. The presence of germanium at this oxidizing interface has long been known to suppress this interstitial injection. Previously it was believed that only the top monolayer at the oxidizing interface was responsible for this effect or could participate in the reaction, but the effects of monolayer and sub-monolayer germanium in this region have never been studied. These doses can be introduced through ion implantation and the interstitial injection quantified through bound interstitials captured by buried loops. Results show that partial suppression can be observed for doses as low as 1.7 x10¹⁴ cm⁻² (0.25 monolayers) but that total suppression requires in excess of 1.4x10¹⁵ cm⁻² (2 monolayers). This opens up new possibilities in modulating or eliminating the degree of injection through controlling the dose of germanium using low energy ion implantation. It is also shown that germanium introduced directly at the surface using ultra-low energy 200eV ion implantation shows similar behavior to germanium introduced through higher energy implantations and subsequent condensation.

CHAPTER 1 INTRODUCTION AND BACKGROUND

1.1 The Beginning, Silicon and Germanium

Every age of human civilization has been defined by a material, and the knowledge and skills needed to fashion it to our uses. First was the Stone Age, which saw obsidian used for arrowheads and knives. Then came the Bronze Age where the smelting of copper allowed the creation of bronze weapons, armor, and other tools and artifacts. Then came the Iron Age, which saw the appearance of more durable iron tools and weapons. The mass production of high quality steel was the breakthrough that allowed the industrial revolution, while the economic production and working of aluminum allowed the development of modern flight. Today we live in what future historians may term the silicon age, although very few today realize it. Electronic devices have become so prevalent that high quality camera phones have even made it to the poorest third world countries.

These devices all contain numerous chips made primarily of silicon, with some dopants and other elements added. Silicon-germanium alloys are the most commonly used materials in the semiconductor industry, which has revolutionized the way we live, work, play, and communicate. The Internet has arguably done more for the widespread dissemination and reproduction of information than any invention since the Gutenberg printing press. It has shaken up politics and democracy itself the world over by giving people an alternative to state-run media. Nearly every human today carries billions of silicon transistors in their pocket daily that grant them instant access to nearly the entire sum of human knowledge, and hardly consider this modern marvel as anything other than routine.

From a production point of view, silicon has the chief advantages of being enormously abundant, easy to purify to extreme purities, the ability to be grown into large single crystal boules and wafers, and a suitable bandgap (1.12eV at 300K) for operation at most commonly encountered temperatures. In addition to these advantages, it provides a strong mechanical substrate compared to other semiconducting materials for handling during processing. However silicon's most important property, which drove it to prominence over other semiconductor materials, was the ability to readily grow a stable native oxide with properties that made it ideal to serve as the gate dielectric on MOSFET transistors. It has been the workhorse of the semiconductor revolution which has changed the way we work, play, and generally live our lives for the last 5 decades.

However, the semiconductor revolution goes all the way back to the early 20th century, with mineralogical cat's-whisker detectors acting as rectifiers in radio sets [1]. The commercialization of semiconductor devices really began to pick up speed after the war in the early 50s with the commercialization of the first germanium diodes, used in consumer radio sets. Germanium was also the basis of the first transistor produced by William Shockley in 1947 that changed the world [2].

Germanium was an ideal material for these early diodes and transistors because it could be readily obtained in high enough purity and was less sensitive to impurities than silicon. It was quickly supplanted by silicon for the reasons stated above.

From there, transistors were used as discreet components in circuits and computers for some years until Kilby and Noice and others invented the integrated circuit. This allowed multiple devices to be produced on the same piece of material,

known as a wafer, thus producing a lighter, more efficient, and more reliable product [3]. The first integrated circuits were more expensive than their discreet component counterparts, but the work received heavy funding from the space and defense programs where light weight, reliability, and efficiency were paramount and cost was no object [4]. Around that time Gordon Moore observed that the number of devices on a circuit was doubling roughly every 1.5 years. Thus was born Moore's law which has become a self-fulfilling prophecy to this day [5, 6].

Integrated Circuits making use of CMOS required a different set of properties than germanium could provide. Despite germanium's higher carrier mobility, silicon could be grown in larger wafers with very few defects and provided a native oxide that served as an excellent gate dielectric, whereas the oxide of germanium is soluble in water and thus sensitive to moisture, making it a poor material for reliability [7];[8];[9];[10];[11].

In recent years, silicon native oxide has been replaced with hafnium based high-k dielectrics in the highest performance chips, but the stability of silicon oxides to moisture relative to germanium oxides remains one of its chief advantages, and silicon dioxide still has a role to play in electronic devices where lower cost and higher throughput is more important than higher performance and older technology nodes are still in use [12].

Germanium is currently heavily used in device design for both bandgap and strain engineering [13]. In strain engineering a material (usually SiGe) applies strain to the gate of a transistor. This alters the band structure and improves carrier mobilities. Germanium can be readily used to apply a compressive strain to silicon, thus improving

hole mobilities for PMOS in the [110] direction. It does this by lowering the energy of the light hole band over the heavy hole band and providing a new pathway that reduces effective carrier mass, thus increasing mobility. Similarly, a buffer layer of relaxed germanium can biaxially strain silicon and improve electron mobility by up to 70% [14].

Although these materials have been studied for decades, research into SiGe oxidation and particularly response to thermal treatments is an ongoing area of research, with a focus on integration and post-processing thermal treatments on chips that may contain multiple types of devices, all with separate thermal budget requirements. [15]-[16]-[17]-[18]-[19]-[20]

1.2 Silicon Oxidation

The oxidation of silicon has been one of the most studied topics in the world due to its importance to industry and chip production. The most basic understanding of silicon oxidation is the reaction: Si(solid) + $O_2(gas) \Rightarrow SiO_2$ (Solid). However, in practice it is much more complicated. The Deal-Grove equation is considered the standard benchmark by which silicon dioxide thickness as a function of time and temperature can be predicted [21]. This equation is shown in Equation 1-1 [21, 22]:

$$T^{2}_{ox} + At_{ox} = B(t + \tau)$$
(1-1)

Where T represents time of oxidation, A and B are both constants derived from differential equations, A/B represents the linear rate constant, and t_{ox} is the starting thickness of the oxide. The equation works on the assumption that the rate-limiting step is the oxidant diffusion through the pre-existing oxide, rather than silicon diffusing up through the oxide. This equation takes into account the possible presence of a pre-

existing oxide of arbitrary thickness. The equation has two limiting forms, wherein for short oxidation times the thickness may be simplified to:

$$t_{ox} \approx B/A (t + \tau) \tag{1-2}$$

In this form B/A is known as the linear rate coefficient, although one must be careful when applying this equation for very thin oxides as there is an enhancement for very short thicknesses, believed to arise from space-charge driven enhancement of oxidant diffusion [23].

For thicker oxides the governing equation is:

$$T^{2}_{ox} \approx B(t + \tau) \tag{1-3}$$

In this case B is known as the parabolic rate coefficient. It is important to note that the equations above are valid for dry oxidations. They will also model a wet oxidation, but with altered rate constants to account for the more rapid speed of a wet oxidation. [22]·[24] It is also important to note that these equations are only accurate for thicker oxides. [23] For thin oxides <200Å-300Å these equations are not as accurate, and the oxidation rate can increase by a factor of up to 4 [22]. Explanations have been proposed suggesting that charged states of the oxidizing species generate a field that accelerates diffusion and is responsible for enhanced oxidant concentration and faster reaction [25-29].

Wet oxidations proceed at a much faster rate and are not the focus of this work, wherein all oxidations take place in a dry ambient. They generally follow the same model, but with faster constants. Interestingly, the presence of germanium at the oxidizing interface acts as a catalyst for oxide growth during wet oxidations, but not for

dry oxidations where the oxide growth rates remain the same

 $[30]^{1}[31]^{1}[32]^{1}[33]^{1}[34]^{1}[35]^{1}[21].$

1.3 Point defects

In the earliest days of the semiconductor industry, dopant atoms in a glassy phase would be spun on the surface and then the dopant atoms driven in using solidstate diffusion to drive in the dopant atoms to form a deep junction that was compatible with the larger nodes at that time [3]. It was soon discovered that oxidation greatly enhanced diffusion of common dopant atoms. The reason the dopants (primarily boron and phosphorus) were being driven in at an accelerated rate was the injection of silicon self-interstitial point defects by the silicon oxidation reaction. It was soon made clear that it did not matter whether these point defects came from an oxidation or an ion implantation [36] [37] [38]. In the former case, Oxidation Enhanced Diffusion was known as OED, whereas enhanced diffusion following an ion implant came to be called Transient Enhanced Diffusion (TED) [38]. It was also noticed that since stacking faults accompanied oxidation and enhanced diffusion, and that stacking faults are made up of interstitials, that the point defect responsible must be the interstitial, not the vacancy [39] [40] [41] [28, 40, 42]. Since then it has been studied with a combination of experimental and computational methods [29].

One of the simplest and most effective methods to study point defect-diffusion interactions is a marker layer study wherein a thin layer with a known concentration of dopant is grown into the silicon and the point defects introduced before (ion implantation) or during (ambient annealing) [41]. Depending on the movement of the marker layer relative to a control sample, it is easy to determine the type of defect being injected, as long as the dominant diffusion mechanism of the dopant in the marker layer

is known. Phosphorus and Boron for example are almost pure interstitial diffusers, whereas antimony and tin diffuse purely by a vacancy mechanism [43]. This is generally referred to by f₁ number where f₁ represents the interstitial fraction or contribution to overall diffusion. For example, phosphorus has an f₁ number roughly equal to 1, making it a pure interstitial diffuser, whereas the f₁ number for Boron is 0.9 See Table 1-2 [44]. When considering the f₁ values presented in Table 1-2 it is important to remember that the diffusion mechanism, and thus the f₁ values can vary with temperature and experimental technique used. In compiling the table, values were chosen from experiments that most closely matched the temperatures used in this work whenever possible.

OSF and OED have even been used in conjunction to demonstrate point defect injection and the resultant retardation or enhancement of stacking fault growth and diffusion [39]. S.M. Hu put together an excellent review paper on the state of knowledge of point defects in silicon and the role they play in diffusion and defects [45]. Pichler offers a more up to date and thorough review on the topic [43]. Modeling and experimental work continues on how exactly the point defects develop from points to clusters into extended structures and how these structures evolve with response to time and temperature. [46]

1.4 Generation of Silicon Interstitials During Oxidation

The importance of these defects naturally raises the question of what is it about oxidation of silicon that causes the injection of silicon interstitials into the substrate? The most obvious cause is that a unit volume of SiO₂ has a larger volume than the silicon it came from. This means that less than a monolayer of silicon is required to form one monolayer of SiO₂. One unit volume of silicon will produce 2.24 unit volumes of SiO₂.

This will generate intense tensile stress at the interface. Germanium is more closely lattice matched to SiO₂ than Si is, but it does not make up for the full difference. One way of relieving the built up stress is injection of excess silicon atoms into the bulk as interstitials [45]. These can then form OSF as seen in Figure 1-1. Each white loop represents an extra plane of captured interstitial atoms, with flat surfaces only because of the wafer surface and sample bottom. Only half of the defects are in contrast due to the g[220] imaging condition used in imaging. If an orthogonal g<220> condition had been used, such as [2-20] or [-220] the other set would become illuminated and the ones currently visible would be out of contrast.

Further, as diffusion of oxidant through the oxide layer is the rate-limiting step, this leaves a lot of free silicon atoms with only three places to go. They can travel into the oxide where they are oxidized and consumed. This is the predominant view of where the bulk of them go [45, 47]. They can also recombine at the surface, or travel into the bulk and diffuse away, see Figure 1-2, where J1 represents the flux of silicon atoms into the oxide, J2 represents re-growth, and J3 represents injection. In this case J1>>J2>>J3. We know this because when one considers the number of excess silicon atoms being consumed vs the number injected, only a few per thousand actually contribute to J3. In fact, all three are known to happen [48]. Silicon interstitials have been observed using STM studies to show island re-growth at the surface during an oxidation, and silicon interstitials flowing in to the oxide from the substrate have been shown to reduce mixed oxides into germanium nanocrystals [49] [50]. There is still controversy over the exact mechanism by which a Si interstitial is freed from the lattice, but there is general agreement that the driving force for whatever mechanism produces

them is the volume mismatch between the oxide and the substrate and the resulting excess of silicon atoms [45, 48, 51-54].

1.5 Silicon-Germanium Alloy Oxidation

When silicon and germanium alloys of any composition <50%Ge are oxidized above 800°C [55]. The silicon oxidizes preferentially, leaving behind an enriched layer of germanium capable of travelling through the substrate as shown in Figure 1-3 [56]. Silicon (134 kJ/mol) has a higher electron affinity than germanium (119 kJ/mol) and is therefore more readily oxidized than germanium. The energies of formation of SiO₂ and GeO₂ are $E_{SiO2} = -8.2eV$ and $E_{GeO2} = -4.7eV$ thus creating a strong preferential thermodynamic driving force for silicon oxidation over that of germanium and leading to a pileup of reduced germanium as the silicon oxidizes and creates the underlying layer enriched in germanium [57] [58]. Thus, even if a germanium atom were to be transiently or partially oxidized, it would be reduced by the first silicon atom it encountered. Rabie et. al. propose this as an important step in the overall oxidation process of germanium containing layers [59]. This may be one possible mechanism for the consumption of silicon interstitials before they can penetrate into the bulk. It is also worth noting here that the $E_{SiO2} = -8.2eV$ is more than sufficient to generate silicon interstitials, as the formation energy of these in silicon is roughly 4eV.

This brings us to the main point of this dissertation: Layers containing germanium do not inject interstitials the way silicon does. It is worth noting that the equilibrium diffusion of germanium in silicon is much slower than the oxidation rate, with a diffusivity of $\sim 1 \times 10^{-18}$ cm²/s at 900°C, although the diffusivity of germanium does increase as the germanium concentration increases during the condensation and rejection phase [43]. In fact, even at 750°C, the diffusion coefficient of Ge in Si_{0.5}Ge_{0.5} is reported to be 5

orders of magnitude higher than that of Ge in Si_{0.8}Ge_{0.2} [58]. This presents one possible mechanism for why germanium piles up to an equilibrium concentration dependent on temperature with no concentration gradient, then stops abruptly at the silicon interface. If the germanium atoms are free to move rapidly within the pileup layer but slow down by several orders of magnitude once encountering the silicon substrate, it could lead to the abrupt box-like profiles observed.

Enhanced diffusion of germanium in an oxygen containing ambient was also observed by Oingo et. al [60]. It is also important to note that as the fraction of germanium in the layer increases, the melting point decreases according to the phase diagram, and therefore at a given temperature a more highly concentrated layer will be closer to its absolute melting point and more mobile. Other work postulates that it is the strain-energy enhancing the diffusion of the germanium layer into the substrate by reducing the strain energy in the system [58]. Brewer et. al. have also recently demonstrated the ultra-rapid diffusion of germanium along the Si/SiO₂ interface in what may be a redox driven reaction, or an attempt to relieve interfacial strain energy [18]. This previously unseen diffusion demonstrates the rapidity with which germanium can diffuse under the right conditions near the oxidizing interface, and may in time offer up further explanations for the pileup phenomenon and interstitial shutoff effects. The concentration of the germanium pileup layer is a competition between the speed of oxidation and diffusion of germanium. This concentration varies with temperature as shown in Figure 1-4. These equilibrium pileup values may have some deeper significance concerning the shutoff of silicon interstitial injection, as at least one author has observed transient interstitial injection from lower concentration SiGe alloys during

the very early stages of oxidation before the thermal equilibrium pileup concentration could be reached, then total shutoff following that. [61]

Much of the current implant work with SiGe oxidation focuses on creation of SiGe on insulator substrates. An excellent paper by David et. al. shows that pileups well in excess of the thermal equilibrium can be achieved once the travelling germanium front starts to encounter the buried oxide and run out of silicon. However, at this point mixed oxides of the form SiGeOx will begin to form and germanium loss ensues [58]·[62]. It is unknown what effects this consumption of germanium into a mixed oxide has on the point defect population, as the SiGe on insulator substrates are fabricated before doping and device creation. It is also important to note that in these SiGeOI processes, the oxide is periodically stripped off to enhance the rate of subsequent oxidations and produce a product in a reasonable time. This could lead to further germanium loss and is quite different from this work. Nevertheless, concentrations nearing 100% germanium are possible under the right set of conditions, regardless of whether the germanium was introduced via an implant or epitaxial growth [58]·[62]·[57].

Until now most literature has postulated that whatever the mechanism, only the single monolayer of germanium enriched material at the surface is sufficient to prevent oxidation induced injection of interstitials [31, 47, 64, 65]. However, nobody has performed experiments to see if this is in fact the case or explored the monolayer to sub-monolayer surface regime. In addition, it is unknown if there exists an intermediate range where interstitials are still injected, but at a lower rate than that for pure silicon. This is what these experiments will seek to find out.

1.6 Strain and Pseudomorphic Thickness

Germanium, being a larger atom than silicon, has a larger lattice constant by about 4%. The misfit strain can be given by Equation 1-4

$$\mathcal{E}_{xx} = \mathcal{E}_{yy} = a_s - a_s/a_f = \mathcal{E}_{mf} \tag{1-4}$$

Where a_s and a_f are the lattice constants of the substrate and film respectively. ($a_{Si} = 5.431$ Åand $a_{Ge} = 5.658$ Å From this, the misfit stress can be calculated using

Equation 1-5 below.

$$\sigma_{\rm mf} = [C_{11} + C_{12} - 2C_{12}^2 / C_{11}] \mathcal{E}_{\rm mf}$$
(1-5)

With the relevant values for silicon and germanium given in Table 1-1.

The addition of germanium in both concentration and thickness gradually builds up 2D compressive stress in the SiGe layer and causes a vertical tetragonal distortion in the unit cell [66]. Once this strain reaches a critical level, misfit dislocations will form at the interface to relieve strain [67]. The depth of the layer one can grow of SiGe before these defects start to form depends heavily on germanium content and growth conditions, although research is ongoing to understand and prevent misfit nucleation and propagation, thus attempting to extend the metastable zone, and make higher concentration devices possible [68, 69]. See Figures 1-5 and 1-6 for examples of these misfit dislocations. Note that they propagate orthogonally on the <110> set of directions. There is a fully stable zone, a metastable zone, and a misfit zone as shown in Figure 1-7. This property of controllable strain has been taken advantage of in industry to enhance mobility of silicon by straining it by growing on top of relaxed germanium, but this is beyond the scope of this work [70]. At higher temperature anneals, the strain energy favors homogenization of the SiGe layer [58].

	Silicon	Germanium
<u>C11</u>	166	126
C ₁₂	64	44
	70.6	67 7
C 44	79.0	67.7

Table 1-1. Summary of the values for the independent components of the stiffness
tensor for silicon and germanium. All units are in Gigapascal (GPA) [71]

Table 1-2. F₁ numbers for common dopant atoms in silicon

Dopant	Fi
Aluminum	0.92-1.00 [72]
Antimony	≤ 0.0035 [73]
Arsenic	0.09 [74]
Boron	0.8-0.99 [75]
Gallium	0.65 [76]
Germanium	0.3-0.4 [77]
Indium	0.3-0.38 [78]
Phosphorus	≥ 0.96 [79]
Silicon	0.7273 [80]
Tin	≤ 0.0035 [81]



Figure 1-1. An example of the sorts of stacking faults that can form under long-time high-temperature oxidations.



Figure 1-2. Possible pathways for excess silicon atoms at an oxidizing interface. [48].



Figure 1-3. Example of SiGe condensation. The starting layer of Si0.7Ge0.3 has become more concentrated and traveled below its original location with no loss of germanium



Figure 1-4. Germanium pileup concentration as a function of temperature. The red box denotes the range of conditions investigated throughout this work [61].



Figure 1-5. Example of misfit dislocations taken on mostly relaxed germanium on silicon using the g400 two-beam condition in dark field



Figure 1-6. Schematic of a misfit dislocation and how it allows the overlying layer with a larger lattice constant to relax.



Figure 1-7. The ranges at which SiGe layers are stable on a silicon substrate. The X markers denote concentration-thickness points that will be discussed in later experiments [68].

CHAPTER 2 ANALYTICAL METHODS AND TECHNIQUES

A wide range of techniques was used to characterize our samples and it is important that the reader gets at least a cursory understanding of each. How it works, its limitations, and why we chose to utilize it.

2.1 The Buried Loop Detector Method

In order to study the flux of the injected interstitials we need a method for doing so. The method used throughout this work is the buried loop detector method wherein Type II dislocation loops are deliberately introduced from a prior ion implantation and anneal are used to quantify interstitials [82]. This method has been shown to be viable as long as the loop density remains above 1×10^{10} cm⁻², which all samples studied do See Figure 2-1 for an example where a buried loop layer is used to trap all the interstitials from an overlying boron implant. [83]. The loops themselves are essentially an extra plane of atoms lying on the {111} planes of the crystal. They tend to be circular in shape, but do not always appear so due to the fact that in PTEM you are looking at a projection. Therefore the although the loops may appear elongated or distorted, this is merely an artifact from the projection and loops are always assumed to be circular and measured along the longest axis. When an interstitial reaches the edge of a loop it can become trapped, and the loop grows through the process of climb. Loops are generally detrimental to the functioning of electronic devices due to the dangling bonds at the edges serving as efficient deep level traps. Nevertheless, loops have been used in engineering applications to trap charge carriers in silicon [84].

The samples were prepared using a polish and etch method described extensively below, and then imaged in WBDF TEM. This allows for images with good
contrast that can be easily counted and quantified. The open-source OsiriX medical imaging software package was used for this purpose, with some plug-ins added to allow for the exportation of the raw length in pixels of each loop into a spreadsheet format where trapped interstitials could be determined using basic math. [19]-[85]-[86].

Once the length of the scale bar and image size in pixels is known, it is then simple to convert the pixel measurements of the loop diameters to a length in nm, then a circular area. Converting the picture area into cm² and adding the total bound interstitials measured within the sample area then gives us a number of total bound interstitials per cm². Because the measurement of counted interstitials has an r² dependence on the measurement of the loops, typically the images with a high density of loops, or large loops that take on imperfect shapes tended to have larger error. This is why it is essential to count multiple images per sample, as even though implanters are fairly uniform, the loop evolution may not be perfectly so, or perfectly countable within the area visible in one TEM image.

By comparing different samples, it is possible to see the net change in bound interstitial population. By subtracting out the bound interstitials from control samples given the same original detector loops and same thermal treatment under an inert argon atmosphere, a net of injected interstitials can be obtained. An example is given in Figure 2-2 where A) Is a control sample that has not been subjected to an interstitial flux whereas Figure B) has been oxidized, and trapped the injected interstitials through loop climb. Both images are from the same original wafer. The bound interstitial values of B)-A) will give a value for the number of interstitials injected during processing. Since loop density can vary slightly across the imaged areas of a sample it is important to count

multiple images in order to obtain adequate error bars. In this work four images per sample were quantified, and the 95% confidence interval calculated to give the error bounds.

2.1.1 WBDF TEM

Dislocations in silicon were first observed via TEM in 1956, and since then techniques have been refined to achieve better contrast and quantification [87]. In 1969 the WBDF technique was developed by Cockayne, Ray, and Whelan, and remains today one of the primary techniques in the study of dislocations. Properly performing WBDF is a difficult task that requires a sample holder that can tilt in both the x and yaxis. It requires tilting both the sample and the electron beam to get the precise condition that will cause strong diffraction from only the defect cores. Even so, it is called "weak beam" for a reason and a good detector and strong electron source is needed since the images produced are often guite dim. It is also often necessary to converge the beam to get higher intensities. A dislocation is visible when $q \cdot b \neq 0$ where g is the reciprocal space lattice vector and b is the burgers vector for the given dislocation [88]. By first tilting the sample to achieve a two-beam condition, and then tilting the electron beam to achieve a g3g condition we enable strong diffraction from the dislocation core. The actual ideal condition was calculated by Cockayne et. al. to be 3.1g [89]. The type II dislocations studied in this work have burgers vectors of a/2 < 110 > 100or a/3 < 111 > making the g220 spot ideal for imaging [83].

In practice this involves using the kikuchui lines from a thicker region of the sample as a guide to bring your sample to zone axis (typically (100) for a (100) wafer) and then mechanically tilting along a <220> band so that s>0 and one of the g220 spots is strongly illuminated. Next, the dark coil deflectors tilt the beam so that the excited

spot is moved to the original location of the direct spot on the viewing screen in diffraction mode. It will become very dim and the 3g spot will become illuminated relative to the spots around it. Using the appropriately sized objective aperture, the dim g220 spot is selected and the condition is ready [88]. For examples, see Figures (2-3, 2-4, and 2-5). In Figure 2-5 The blue arrow denotes the direction of **g** tilt of the electron beam using the dark field deflector coils and the small circle represents the imaging aperture. The (660) spot (3**g**) is illuminated relative to those around it. The (220) spot being imaged through the aperture has now become very dim. In practice, any of the {220} set of reflections may be used. When imaging loops for the purpose of quantifying bound interstitials, it is important to use a magnification sufficient to get a statistically significant population, which will vary by sample.

2.1.2 PTEM Sample Prep

Sample preparation for getting good WBDF PTEM images is a long and involved process that takes several hours depending on the number of samples being fabricated and involves multiple steps. First the piece of silicon wafer to be imaged must be secured to a glass slide using crystal bond. For this the slide is heated, coated with crystal bond, the sample placed side-of-interest down, then the slide removed and allowed to cool. A coring tool is then used to make a 3mm diameter disk from the silicon sample. Since silicon is a brittle material, rather than trying to cut through it with a sharp bit, the coring tool uses a metallic bit with a dull edge and relies upon wetted silicon carbide cutting grit to wear away at the surface, thus preventing chipping and fracture. This silicon carbide paste must be applied before drilling commences. We used a VCR group Model no. V7100 coring drill. Since this machine was made in 1995 and the manufacturer appears to be defunct, new drill bits were impossible to obtain as they

slowly wear with each sample and need occasional replacement. To solve this problem, new bits were manufactured by the author using stainless steel tubing with an inner diameter of 3mm and thickness of 1mm. One end of this was then bonded to 1mm outer diameter Stainless steel tubing using JB weld so that it would fit in the drill chuck. Finally, two to four flutes were cut into the cutting end of the bit using a dremel tool and the rough edges cleaned up with a file. These in-house manufactured bits were found to last far longer and produce superior and more consistent samples than the brass-based bits that originally came with the tool.

Following coring, the slide is again heated to liquefy the crystal bond and allow the cores to be removed via tweezers. The cores are then placed in a bath of acetone to dissolve away extra crystal bond and any cutting grit that may have contaminated it.

After this cleaning step, the sample(s) are mounted face down on an aluminum polishing puck using crystal bond and hand polished on 400 grit polishing paper using 15µm alumina powder mixed into a slurry with water to provide lubrication. The samples are polished down to a thickness of roughly 100µm and are kept as uniform in thickness as possible using hand-polishing. Subsequently, the polishing puck is placed back on the hotplate to liquefy the crystal bond and the thinned samples carefully removed. The thinned samples are subjected to a double wash in acetone to remove all traces of crystal bond and any residual polishing grit before being mounted to a PTFE (Teflon) stub face down. Sample stubs were also custom manufactured by the author using a drill press, hacksaw, and PTFE bar-stock. The stub consists of a block of PTFE with a large drill hole centered in the bottom to accommodate the light pipe, and a smaller hole going through the top to allow the light to pass. A small cup is cut in the very top to

support the sample using a scalpel. Liquid paraffin is first applied to the sample and serves to hold the sample in place on the stub, and mask off and protect the portions not to be etched. It is critical that the paraffin cover the side of interest to prevent underetching and destruction of the sample. Once mounted, a small hole in scratched in the top of the paraffin to allow a hole for the acid to etch through to the backside of the sample.

The samples are then placed in the drip etcher and a mixture of 25% Hydrofluoric acid and 75% Nitric acid (both undiluted and at full bottle strength) dripped over the sample. The Hydrofluoric acid serves to strip away the SiO₂ that forms while the nitric acid prevents hydrogen passivation normally associated with Hydrofluoric acid and oxidizes the next layer of silicon. Only with these two acids working in tandem can a hole be formed in the sample. As soon as a hole is observed by the passage of light through the sample, the sample is removed from the etch system and the reaction stopped by dunking it in a plastic beaker filled with water. The sample is removed from the stub, and the paraffin is cleaned off using two baths of heptane before the sample is ready for imaging. The thin regions around the hole thus formed are where the PTEM imaging takes place. For samples with thick oxides on the side of interest it may also be necessary to dip the samples in HF to remove the oxide that would otherwise only add amorphous signal and noise to your image.

2.1.3 The Etch System

The etch system described above is not available commercially and had to be constructed in-house using original techniques. A simplified schematic of this system is given in Figure 2-6 and will be explained in this section. The acid cycles continuously through the system and etches away from the backside of the sample until a hole is

formed. This is detected when the user observes light from the light system. A monochromatic light source was chosen when constructing the system to prevent room light reflections from confusing the user. A green diode laser was selected for this purpose because red light has too much penetration depth into silicon, so may become visible before a hole has formed. Blue was rejected as being harmful to the human eye. It is also the case that the human eye is most sensitive to green light, allowing for the earliest possible detection of a hole.

The construction of the light system first entailed the production of a light-pipe to transmit the light from the source to the sample. For this we used 0.25 inch diameter acrylic rod cut to a one foot length. The cutting must be performed using the hot-wire technique so as to leave a glassy rather than rough surface. One end of this is then heated with a heat gun and an inch of material slowly bent to 90° and allowed to cool. The rod is then covered in black heat-shrink tubing to prevent scattered light from becoming a distraction. The light source was a generic 5mW green laser diode module that was first encapsulated in non-conductive epoxy, and then placed inside a specially designed 3D printed ABS shell that can connect and disconnect from the light-pipe while sealing out all corrosive vapors. A set of four pieces of silicon wafer bonded together with JB weld were used as a heat-sink extending out of this shell to prevent overheating of the laser diode. A 3V transformer provided power, as the laser was originally designed to run on two AA batteries in series. It was found that this light source proved extremely reliable over a period of years even in the harsh conditions of the acid fumes, however the acrylic light pipe over time suffers from swelling and embrittlement and must periodically be replaced. This is not the only consumable part.

Tygon MasterFlex tubing is used to move the acid throughout the system, but must often be replaced as it hardens with extended use. The peristaltic pumps from Colepalmer also suffer from parts needing replacement, specifically small plastic clips that hold the tubing in place and prevent it from getting wound into the rotor. This is part of the pump head unit, and as such cole-palmer will not sell these small plastic pieces separately. Therefore it was necessary for the author to design and 3D print a more economical consumable part that would perform the same function. ABS plastic was selected for this role due to its standard in the 3d printing industry, as well as its ability to resist acid degradation better than the clips that came with the pump head. The actual system can be seen in Figure 2-7

2.2 Ellipsometry

Ellipsometry is a technique that uses the polarization of different wavelengths of light to determine the thickness of a layer non-destructively and at low cost. Like so many other measurement techniques, Ellipsometry really took off in the 1960s with the growing semiconductor industry and the need to measure films on the order of angstroms [90]. The technique uses mutually perpendicular polarized light waves reflected off the surface of the sample and into a detector. It takes its name from the fact that when these perpendicular waves are out of phase they are said to be "Elliptically Polarized". Two arms rest on opposite sides of the sample. One contains a light source that is passed through a polarizer, and a secondary compensator. This polarized light then strikes the sample at a precise angle and an analyzer and detector on the other arm then detect the phase changes in the polarization of the reflected light. The method takes advantage of the differences in indices of refraction of materials and is excellently suited for measuring thin films, and especially SiO₂ on Si due to the large difference in

index of refraction. Modern systems can also simultaneously measure multiple layers of different materials. The end result will be a measured signal derived from the change in polarization of the light. This signal alone does not give a thickness, but rather a precomputed model must be used to fit to the output signal. Although this curve fitting is a trial and error process, modern computing has made it fast, easy, and reliable. For well known materials such as SiO₂, Si, and Ge these models are readily available and highly accurate [91]. A thorough discussion of the quantum mechanics behind the development of these models is beyond the scope of this work. Ellipsometry was primarily used as a more rapid and less expensive method for rapidly determining how much oxide had been grown during our anneals compared to XTEM which is time consuming and expensive.

2.3 XTEM

XTEM or Cross Sectional TEM uses a transmission electron microscope to image a sample from the side. This is useful for measurements of layer thicknesses, detection of defects, surface uniformity, and other information that might not be obtainable from PTEM. Samples are generally prepared in a FIB, to be described in detail in chapter 3.4.

Once sample preparation is complete, the grid can then be loaded into the TEM. The electron wave functions interact with the atoms, producing a characteristic diffraction pattern. It is important to note that this only occurs in crystalline samples. Amorphous layers such as SiO₂ will give a diffuse halo on the viewing screen in diffraction mode. Spots are selected using the Selected Area Diffraction aperture on the TEM. Typically the center spot and the closest surrounding spots are chosen if a highresolution image is desired. However, other imaging techniques using other diffracted

spots such as center dark field, HAADF, and WBDF can also be performed on XTEM samples. For an example of a high resolution image see Figure 2-8. The sample in Figure 2-8 was prepared using a FIB. It is important to note that in this image although it may appear as though we are directly observing atoms, we are actually seeing fringes caused by their interaction with the electron wave function.

2.4 HAADF

High angular annular dark field is a technique used because of its' excellent sensitivity to Z-number (elemental composition). Elements with higher Z numbers have increased scattering similar to Rutherford backscattering with a dependence on Z^2 [88]. This enables us to observe Z contrast by collecting only high angle scattered electrons. The technique is performed in an aberration corrected TEM with the beam focused down to a sub-angstrom (0.78Å probe which rasters across the sample in scanning

mode. Instead of a detector being directly below the sample as normal, the detector is an annular shape. This detector is designed to only collect electrons with deflection angles of greater than about 50mrad, or ~3°. In order to acquire atomic resolution images, a probe-aberration corrected TEM is needed, and the HAADF images in this work were performed at the FSU High Magnetic Field Laboratory by Dr. Yan Xin using their JEM-ARM 200cF TEM. See Figure 2-9 for a crude schematic of the technique, and Figure 5-4, and Figures in chapter 6 for actual HAADF images.

2.5 EDS

EDS or Energy Dispersive X-ray Spectrometry is a technique that can be used to characterize the elemental composition of a TEM sample via the characteristic energies of the X-rays given off when a core-shell electron is displaced by the TEM electron

beam. When this happens an electron from an outer shell falls into the newly vacated lower energy level, emitting the excess energy as X-rays that can than be detected and counted to determine the elements present and their abundance [92]. In this work, all EDS spectra were collected on the JEM-ARM 200cF TEM at FSU by Dr. Yan Xin in conjunction with the HAADF analysis. Unless otherwise stated, all scans were box-type scans with an area of 0.6nm by 7nm. Line-scans were attempted but proved to be too damaging to the sample. The elements analyzed were oxygen, silicon, and germanium using the silicon k α line at 1.739keV, the oxygen K α line at 0.525keV, and the germanium L α line at 1.188keV [93]. See Figure 2-10 for an example spectra. EDS can also be performed using Scanning Electron Microscopy, but was this was not performed in this work [94].

2.6 XRD

XRD uses the diffraction of x-ray photons within the crystal lattice. The condition for constructive interference occurs when Bragg's law is satisfied:

 $n\lambda = 2dsin\theta$

(2-1)

In this equation the variable d represents the lattice spacing. Since the fully strained SiGe is tetragonally distorted in the (100) direction, its peak will shift relative to that of silicon. A partially strained (relaxed) layer will show an intermediate value. For silicon and germanium, both diamond cubic structures, the (400) reflection is used [95]. This plane represents atoms orthogonal to the surface that have undergone tetragonal distortion and is the first allowed reflection for a diamond cubic structure. The sample is rotated relative to the x-ray beam to generate an $\omega/2\theta$ rocking curve scan which produces a 2-dimensional representation of reciprocal space [96, 97]. XRD was only used once to look for SiGe relaxation upon annealing, however the 5nm silicon-capping

layer complicated the results. This data was considered of insufficient quality to publish and the technique is only mentioned because it showed us what wouldn't work and sent our research in a different direction. In Figure 2-11 an example of a high quality SiGe on silicon XRD spectra can be observed. Note the sharp silicon peak at 69 and the broader SiGe peak at 67.5 (in units of 20). Note also that there are repeat satellite peaks arising from higher order reflections [98]. This is only observed in high quality samples.



Figure 2-1. An example of the buried loop detector method. The interstitials introduced were mostly trapped by the loops with the blue line denoting good correlation between implanted dose and bound defect growth [83].



Figure 2-2. An example of the buried loop detector technique in practice. A) was annealed under inert ambient, while B) was oxidized. Loop growth is clearly observed in B) but not A)



Figure 2-3. (100) Diffraction pattern with kikuchi bands visible when on zone axis.



Figure 2-4. Excited two beam condition created by tilting sample mechanically with stage in the X and Y directions.



Figure 2-5. Final WBDF imaging conditions. The (3g) is illuminated relative to those around it. The (220) spot being imaged through the aperture has now become very dim.



Figure 2-6. Schematic of the etch system and how it works. Acid is pumped from the reservoir and dripped over the sample. When a hole has formed light from the light pipe becomes visible to the user and the sample is removed.



Figure 2-7. Actual system prepped for operation. Acid reservoir was left sealed for safety reasons. The appropriate personal protective equipment must always be worn when working on, using, or approaching the system. Photo credits courtesy of the author.



Figure 2-8. Example of a XTEM image taken in the [110] direction showing silicon dioxide over silicon. Lattice fringes are readily visible and show no discontinuities or defects.



Figure 2-9. Extremely simplified schematic of how HAADF works. The electron beam rasters across the sample in scanning mode, and over time more signal is collected from the elements with higher Z number due to stronger scattering to the annular detector.



Figure 2-10. Representative EDS spectra showing a relatively even mixture of silicon, germanium, and oxygen by their characteristic x-rays.



Figure 2-11. Representative XRD spectra of a SiGe on silicon sample of high quality.

CHAPTER 3 PROCESSING TECHNIQUES

In order to collect useful data, before they can be analyzed samples must first be created and processed. This can be quite involved, with multiple steps needed to achieve the needed sample. This chapter explains the techniques used to create and process the samples used in this work.

3.1 Ion Implantation

Ion implantation provides superior dose and depth control compared to solidstate diffusion. It has been the primary doping technique in industry for several decades now [68]. It is used to introduce a precisely controlled dose of dopant atoms into a substrate at the desired depth. First the desired species is ionized, then accelerated through an electric field to the desired energy. This energy controls the depth of the implant. Along the way, the beam is curved using a magnetic field, taking advantage of the fact that the beam will separate according to mass/charge ratio and only the beam of the desired species will pass through the small aperture used so as to block out any unwanted species or impurities[68]. See Figure 3-1 for an example of how this works. Ion implanters are large and expensive, and the phosphorus ion implantation in this work was performed by IBM/Global Foundries to create the buried loop layer. A 50keV 2 x10¹⁴cm⁻² phosphorus implant was used to create these detector loops. In Figure 3-2 it is shown that the choice of ion implanter and subtle variations in implant conditions can have a dramatic effect on defects observed after annealing. The red numbers at the top of each sub-Figure denote the implanter number (no further information on these implanters was provided by IBM). Samples A) - E) show remarkable differences in defect morphology, despite seeing nominally identical implant and anneal conditions.

After this trend was noticed, IBM was asked to use the same implanter (number 22) on all subsequent wafers, as this provided the highest density of useable loops. The sample designated "No-LTE" in Figure F) is from a later sample matrix received from them and matches closely with Figure B), showing that we could eliminate implanter effect as a complication in our later experiments by ensuring that the same implanter was used in all subsequent samples. Applied materials performed low-energy germanium implants that will be the focus of this work.

3.1.1 Extended Defects

The impact of a single ion creates a cascade of thousands of frenkel pairs. These rapidly recombine at relatively low annealing temperatures (~500°C). However, there remain excess interstitials in accordance with the implantation dose according to the "+1 model" [99]. Provided the implant is non-amorphizing, these extra interstitials can get bound up in extended defects that dissolve under continued annealing and contribute to an excess of interstitials that leads to TED. Defects can also impede electrical performance by acting as carrier traps. The evolution of these defects depends on dose and anneal time and temperature as shown in Figure 3-3. Defect evolution can also depend on the local strain state of the material[100]. A review of extended defects in silicon can be found in the work of Jones et. al. [101]. This work focuses primarily on the dose and anneal temperature regime where dislocation loops remain stable over long time periods. This is necessary for us to be able to use them to act as detectors.

3.1.2 SRIM

SRIM or Stopping Range of Ions In Matter is a computational tool that can be used to predict the projected range of one species implanted into another. It allows for

the implant parameters to be designed prior to implantation. The software models collisions and cascades between atoms and can predict other phenomena such as sputtering[102]. This software was used to design and predict the depths of the implants in this work. An example of a SRIM output for several implant energies (not used in this work, merely given as examples) can be seen in Figure 3-4. For this work SRIM was run on a MacBook pro using a virtual machine running Microsoft XP.

3.2 MOCVD

MOCVD or Metallorganic Chemical Vapor Deposition is a technique for growing epitaxial layers on a substrate. It involves flowing gaseous precursors over the substrate while heating it to a temperature where the gaseous precursors break down and the desired atom adheres to the substrate. The temperature must also be high enough that the deposited atoms can move around on the surface until they can find an available lattice site. Through this technique, layers of different thicknesses and compositions can be grown. The epitaxial layers used in this work were 30nm thick and were grown by IBM/Global foundries using their low-temperature epitaxy techniques at ~600°C[20, 103, 104] [105]. Since this temperature is lower than the previous anneal temperature postimplant, minimal effect on the defect evolution is expected.

3.3 Furnace Annealing

The tube furnace is just what it sounds like. At its' most basic it is a quartz tube contained in a box made of refractory materials and containing heating elements. After the furnace temperature has stabilized and been measured by thermocouple and the ambient gas flow rate stabilized, the samples are inserted for a set period of time before being removed. Although more rarely used in industry today, the tube furnace provides

an ideal platform for carrying out the long-time high-temperature anneals needed to observe loop evolution and cause substantial dry thermal oxide growth.

The anneals in this study were performed in a Lindberg model 54233 tube furnace calibrated by a Digi-sense Scanning Thermometer made by Cole-Palmer and using a K-type thermocouple. This thermocouple was tested against other thermocouples, as well as ice baths and boiling water and found to be accurate to within +/- 2°C. Importance was placed on making sure the thermocouple was placed at the location where the samples would rest. As can be seen in Figure 3-6, the furnace has a very narrow hot-zone and stable area, therefore great care was taken to place the samples in the same region consistently and verify via thermocouple that it was the correct region for the desired temperature.

While one might expect a tube furnace to act as a nearly perfect black-box radiator, in point of fact ours has a very narrow hot zone and great care must be taken to ensure the samples are loaded consistently to receive the proper temperature. Contrary to industry where wafers are loaded vertically, the small square samples were laid flat on a quartz boat with a buffer of silicon to prevent contamination. Different source gasses including Ar and O₂ were flowed in from the back end with flow rate measured using a flow meter. Typically a flow rate of 5 Liters per minute was used. An end-cap with a small outlet hole was used to retain heat and prevent contamination of the source gas within the tube.

Challenges along the way included making sure the tube did not shift within the furnace, and making sure that all source gasses were totally dry. The furnace was found to have a very narrow zone at the desired temperature, and so only two samples could

be annealed at once after this was discovered. See Figure 3-6. Samples were inserted and removed by means of a quartz rod that would hook to the quartz boat. See Figure 3-5 for an image of this setup. The only exception to this annealing technique are the samples annealed by IBM/Global foundries at 750°C for 30 minutes under inert ambient in their tube furnace prior to delivery.

3.4 Focused Ion Beam

A FIB or Focused Ion Beam is an instrument that uses a beam of gallium atoms to produce XTEM samples for imaging. It sputters away material on the micron scale by rastering the Gallium ion beam away at both sides of the piece to be imaged. The surface is protected by first a carbon-based layer, then a deposited platinum layer [106]. When the sample is suitably thin, the stage is tilted and the sample undercut, leaving only one small piece to hold it in place. A thin tungsten wire known as an omniprobe is then carefully positioned and platinum welded to the sample. The sample can then be freed from the substrate and lifted out. After the sample has been welded to a grid using the same platinum source, the omniprobe is cut loose by the ion beam and the sample further thinned. A good PTEM sample should be 100nm or less. If WBDF imaging is to be performed on the sample it should be left 200nm-300nm thick so that Kikuchi lines can be seen. After final thinning, the sample is showered with lower energy ions to reduce the thickness of the damaged layer. One key downside to this technique that a thin amorphous region will always be produced by the gallium ions. The following references describe in detail the techniques used in preparation of XTEM samples in this work [106-109]. The one exception to this are the last three samples fabricated using a FEI Helios NanoLab 600 dual beam FIB/SEM, and the referenced procedures [110-112].



Figure 3-1. Simplified example of an ion implanter.



Figure 3-2. Example of samples implanted to an identical dose of 2 x10¹⁴cm⁻² and annealed under identical conditions of a 750°C 30m inert anneal followed by an 850°C 10m inert anneal.



Figure 3-3. Defect evolution over time as a function of dose and anneal time. All Loopforming implants used a 2×10^{14} cm⁻² implant. [38].



Figure 3-4. Example of projected ranges for different energies of germanium implanted in silicon produced using the SRIM software package.

Boat Positioning Rod



Figure 3-5. Tube furnace setup used for the vast majority of thermal processing in this work.



Cm From Front of Quartz Boat

Figure 3-6. Measured temperatures from front of quartz boat The nominal temperature the furnace was set to was 900°C for these measurements.

CHAPTER 4 TRANSPARENCY OF A BURIED SIGE LAYER TO A FLUX OF INTERSTITIALS

Before we can explore the effects of low-dose germanium we must first know if the germanium itself acts as a barrier to interstitial flux as this is one of the leading theories as to why it blocks interstitial injection.

4.1 Background

One of the leading theories behind why germanium has the effect of preventing interstitial injection is that it simply acts as a transport barrier. It is known that the formation energy of a silicon interstitial in SiGe is much higher than in pure silicon, with ab-initio calculations putting the silicon interstitial formation barrier at 0.3eV in intrinsic material for Si_{0.5}Ge_{0.5} [61, 113]. This would result in a 20-fold reduction in interstitial migration into the bulk, and likely drop the injected interstitials below most technique's detection limits. If germanium is acting as a barrier or reflector to interstitials, then it should have an effect even when not in direct contact with the oxidizing interface.

4.2 Experimental Methods

To probe the transparency of SiGe to interstitial fluxes, a heterostructure was created with a 5nm silicon capping-layer overlying a 20nm Si_{0.7}Ge_{0.3} layer with the buried loop detectors underneath. Processing was begun with Czrochalski wafers implanted with a 50keV 2 x10¹⁴ cm⁻² phosphorus implant. Although this dose is on the verge of the amorphization threshold, samples were verified to not contain any amorphous regions via XTEM, see figure 4-1 where damage at the expected range is apparent, but non-amorphous. Subsequently, the wafers were subjected to a 30 minute 750°C furnace anneal under inert ambient. This served to form a buried defect layer with an R_P of

~70nm with the defects well into the loop stage of evolution. This anneal step also repaired implantation damage for subsequent epitaxial growth.

Following this anneal, a low-temperature epitaxial growth was performed. Starting from the surface a 5nm Si buffer layer was grown, followed by a 20nm layer of Si0.7Ge0.3 and finally a 5nm Si capping layer. A set of control samples were also grown which consisted of a uniform Si layer 30nm thick grown on top of the implanted layers so that the detector loops would all be at the same final depth of ~100nm. The implant, anneal, and epitaxial growth were all performed by IBM/Global Foundries. The epitaxial layers used in this work were grown using their low-temperature epitaxy techniques at ~600°C [20, 103, 104] [105]. Since this temperature is lower than the previous 750°C furnace anneal performed post-implant, minimal effect on the defect evolution occurred. See Figure 4-2 for an example of the starting structure. Further annealing took place in the lindberg tube furnace for times ranging from 15 minutes to 2 hours at 900°C, under an ambient of argon (for control samples) or pure dry oxygen. Following these anneals, PTEM samples were prepared using the polish and etch method described in Chapter 3 and imaged in WBDF on a JEOL 200cx TEM. XTEM samples were prepared via FIB and imaged on a JEOL 2010F S/TEM. The bound interstitials and loop density were then quantified using the OsiriX software package [85, 86].

4.3 Results and Discussion

Figure 4-4 shows that the buried Ge layer had no effect within margin of error on the transport of the interstitials to the loops. The consumption of 5nm of silicon at 900°C under dry oxidizing ambient occurs in roughly 20min according to the modified Deal-Grove model utilized in the Florida Object Oriented Project Simulator (FLOOPS) software[114]. This is in good agreement with our results where the samples containing
a buried SiGe layer behave like normal silicon until the SiGe layer is reached. This layer then rapidly condenses and shuts off all further injection. One potential downside of using loops as a detector is that they undergo slow thermal evolution (coarsening) during annealing. The observed loop morphologies after the longest time anneal of 2 hours can be seen in Figure 4-3 parts B) and D). Planar loop densities can be seen in 4-4 part B). This problem can be overcome by comparing oxidized samples to samples annealed under inert ambient to account for any interstitials lost during thermal coarsening. It is also important to note that in Figure 4-3 both the silicon control sample and the germanium sample grew the exact same amount of thermal oxide, indicating that they saw the same thermal budget and that they were in a totally dry ambient, as any moisture would have caused the germanium containing sample to oxidize at a faster rate [35] [32].

However, once formed these loops are extremely stable even at very long times and high temperatures and as such the total loop area is a better indicator of bound interstitials than total loop density provided that the loop density remains above 1 x10¹⁰cm⁻² and can thus serve as an efficient trap for any passing flux of point defects [115]. It is important to note the absence of misfit dislocations in Figure 4-2 parts C) and D), which implies that the germanium layer remained pseudomorphic despite the flux of interstitials travelling through it, and despite the increase in concentration, contrary to previous work [116, 117]. This is also important to note because it shows there are no other defects that could be slowing or trapping the interstitial flux. It can be observed in Figure 4-4 B) that the samples containing a buried germanium layer underwent far more loop coarsening than the pure silicon sample, presumably due to the higher

concentration of interstitials in the silicon sample. The loop density was also in good agreement with our control samples where only mild coarsening was observed.

This set of experiments showed that the germanium must be present at the active oxidizing interface to have any affect whatsoever on interstitial movement. It also presents a technique for measuring the consumption of a heterostructure by the time of interstitial injection shutoff. Referring back to Figure 4-4 A) it is clearly easy to see when the capping layer has oxidized. Referring to Figure 4-2 parts A) and C), one can see that more oxide was grown than expected. This did not significantly impact the experiment since the thicknesses were identical. Some literature states that a strained layer of SiGe should oxidize more rapidly than silicon even in a dry ambient, but this was not observed [118]. One possible reason for the anomalously thick oxides is water contamination, although this seems highly unlikely given that the germanium sample would have grown more oxide than the silicon sample under those conditions [35]. It is far more likely that the oxides grown were thin enough to fall under the initial rapid oxidation regime that does not yet fit into the linear portion of the deal-grove model [22]. If this is the case, then the bound interstitial peak seen in Figure 4-4 A) for the SiGe sample may have been already beginning to drop off if the SiGe layer was reached earlier than expected. From a practical industrial standpoint it also shows that the epitaxial interfaces grown by IBM/Global foundries are completely transparent to interstitial fluxes.

4.4 Conclusion

This work shows that a buried germanium containing layer is fully transparent to a flux of interstitials, despite the higher energy costs of forming a Si interstitial in SiGe [53]. This work also shows that vertical SiGe heterostructures can be monitored in

PTEM and the onset of shutoff of injection predicted and validated, as shown in Figure 4-4. Figure 4-4 A) shows that while the 5nm Si cap is being consumed, the injected interstitials pass directly through to be captured by the bound loop layer in a manner almost identical to the Si control. However as soon as this 5nm Si capping layer is consumed (as predicted from time and temperature) interstitial shutoff occurs and the bound interstitials in the Si_{0.7}Ge_{0.3} samples dissipate to an equilibrium level no different from control samples annealed under argon, which is an interesting finding in and of itself. Figure 4-4 B) shows the total number of counted loops and that the presence of germanium during oxidation allows the loop density to gradually coarsen and return to values almost identical to those seen under the inert ambient. It shows that the buried implants have no effect on SiGe relaxation in the regime studied and the condensation process does not induce defects in the condensed layers that could lead to relaxation of pseudomorphic strain, at least in the concentration and thickness regime studied. Thicker or more heavily concentrated layers would likely relax at some point during condensation as they come to exceeded the metastable strain region shown in Figure 1-7.

It may be possible that the interstitials are slowed by the SiGe layer but not enough to be detected with our methodology. In this case we have two competing phenomena. One is that the SiGe alloy has a lower melting point, is closer to its melting point, and thus the silicon interstitials should be more mobile. However formation energy would tend to act against them entering the SiGe layer at all. At this point the exact reason that germanium must be at the oxidizing interface and condensed to an equilibrium concentration to have a shutoff effect is still a matter of debate. It is possible

that the buried germanium layer would have acted as a reflector, or at least had some effect, if it were at the equilibrium pileup concentration of Si_{0.5}Ge_{0.5} instead of the Si_{0.7}Ge_{0.3} actually used. In fact, samples with a buried layer of Si_{0.5}Ge_{0.5} were originally intended to be part of the experiment, but arrived too defective to be of any use. See Appendix A for Figures and discussion on this. In fact, at least one author has seen brief transient injection of interstitials from a Si_{0.89}Ge_{0.11} layer and a Si_{0.85}Ge_{0.15} layer until pileup to roughly Si_{0.53}Ge_{0.47} after which interstitial injection shut off completely [61]. Therefore the prospect of a sub-surface layer with a higher germanium content acting as a partial or total barrier is not entirely out of the question and should be considered as a possibility in future work.



Figure 4-1. XTEM showing damage layer from implant prior to anneal or epitaxy



Figure 4-2. Starting structure of samples in A) XTEM and B) PTEM. Silicon control samples were identical except without the SiGe layer. Defect morphology was identical for both sets of samples [19].



Figure 4-3. Comparison Ge epi-layer and silicon control in both XTEM A), C) and PTEM B), D). Both samples were annealed under oxygen at the same time for 2h at 900°C.



Figure 4-4. Experimental results from time dependent anneals. A) Shows the bound interstitials as a function of time, while figure B) shows loop density as a function of time. It also shows that throughout this work all samples retained a loop density greater than 1 x10¹⁰cm⁻², which is the threshold for total trapping of interstitials[83].

CHAPTER 5 EFFECTS OF MONOLAYER TO SUB-MONOLAYER GERMANIUM ON INTERSTITIAL INJECTION DURING OXIDATION.

5.1 Background

Although silicon and germanium have been oxidized in countless different conditions and ambients and been found to suppress interstitial injection, many authors have speculated that it is only the first monolayer of germanium that is responsible for the interstitial suppression effect [31]·[64]. To the best of the author's knowledge, nobody has put this to the test by introducing single monolayers or sub-monolayers and then measuring the interstitial injection. It is currently unknown what effects ultra-low dose germanium at the oxidizing interface has. This work will seek to answer this question.

5.2 Experimental Methods

One of the reasons it is so difficult to study sub-monolayer concentrations of germanium is that at room temperature it will form a mixed native oxide that is vulnerable to attack by moisture, therefore losing (a difficult to quantify) dose in the process. In order to overcome this problem a low energy implant of 3keV was performed by Applied Materials on the silicon control wafers containing buried detector loops described in Chapter 4 provided by IBM/Global foundries. These wafers were subjected to a 50keV 2 x10¹⁴ cm⁻² Phosphorus implant followed by a 750°C anneal to repair the implant damage and nucleate the detector loops. The implant had an R_P of ~70nm. 30nm of silicon was then grown using IBM/Global foundries methods temperature epitaxy techniques at ~600°C [20, 103, 104] [105]. This gives the detector loops a range of ~100nm. Although originally intended as control samples for a separate experiment, these samples were readily repurposed for this experiment. Applied

Materials implanted the germanium at 3keV and room temperature in doses that can be seen in Table 5-1. Referring back to Figure 1-3 it is noted that as long as the germanium is being oxidized above around ~700°C none of it is consumed or lost to mixed oxide formation and it will form a travelling front.

This allows for the entire dose of germanium to be piled up at the active interface without risking any loss of dose. Previous authors had solved this problem by capping the germanium layer with a layer of silicon as in chapter 4, but this would have complicated the experiment by adding excess interstitial injection[56]. In order to ensure the entire implanted dose was present at the oxidizing interface, a preliminary condensation step had to be performed. This step was designed to oxidize through the range of the implant, thus confining the entire implanted germanium dose at the silicon/SiO₂ interface. Because the interstitial injection shutoff effect will begin to assert itself as the germanium dose condenses, and there were different doses, control samples for each implant condition also had to undergo the same condensation step so that later only the net interstitials injected during subsequent anneals would be measured. Separate sets of samples were annealed at 850°C and 900°C respectively under a pure O_2 ambient to oxidize through the range of the implant and trap the germanium at the Si-SiO₂ interface. For the samples annealed at 850°C this pileup time was 3 hours and for the 900°C samples it was 70 minutes. These times were chosen according to the modified Deal-Grove model utilized in the Florida Object Oriented Project Simulator (FLOOPS) software[114]. Calculations of time and temperature required to oxidize through >99% of the ranges of the implants were chosen.

Since any interstitial shutoff effects would increase during the condensation step as the germanium dose piles up, control samples for each dose were also subjected to the same condensation anneal, then later an inert anneal at identical time and temperatures to their oxidized counterparts so that the interstitials from condensation and initial implant could be separated from those injected during subsequent oxidations, and to account for coarsening effects. The oxidized samples were then subjected to a further oxidizing anneal, all bound interstitials counted, and the difference between the inert and oxidized samples giving the count of net injected interstitials during the second oxidation step. Since loop density can vary slightly over the areas imaged, a total of 4 images per sample were quantified and error bars generated from the 95% confidence interval. A schematic of the experimental processing steps can be seen in Figure 5-1. Loop morphologies after these anneals at 850°C can be seen in Figure 5-2 while loop morphologies after the 900°C anneals can be seen in Figure 5-3.

Before these structures and results could be trusted however, it was essential to verify that the germanium was piling up as expected. Although germanium is widely recognized not to be lost to mixed oxide formation or volatilization of GeO during oxidation in the temperature ranges used, to the knowledge of the author nobody has probed such minute quantities of near-surface germanium before, and therefore the loss or partial loss of such sub-monolayer quantities would not have been detected by their techniques. Therefore HAADF imaging was performed at the High Magnetic Field lab at FSU by Dr. Yan Xin to verify that the germanium layer morphology was as expected. HAADF was chosen because of its excellent Z-contrast and ability to pick up minute levels of the heavier germanium in silicon. For HAADF only the 850°C samples were

imaged due to time and financial constraints, however the 900°C samples would appear very similar. The results can be seen in Figure 5-4 with part A) Showing the sample after the condensation anneal, and part B) showing the same sample after the subsequent oxidation. HAADF-STEM images were acquired on a JEM-ARM200cF at 200kV with a 0.078 nm resolution, a beam semi-convergence angle of 22 mrad, and a 78 mrad collection angle. This sample had been implanted with 2 monolayer equivalents (1.4 x10¹⁵ cm⁻²) of Ge. Thus due to thermal pileup and as shown in Figure 1-4, and the implanted dose, 4 layers of ~Si0.5Ge 0.5 was expected to form at the Si-SiO₂ interface. This is exactly what was observed, implying that there was no detectible loss of germanium during the condensation step. Lower dose samples could not be reliably imaged in this fashion due to the sensitivity of the instrument, but since no germanium was lost in the highest dose implanted sample, it is a reasonable assumption that no germanium would have been lost in the lower dose samples. In Figure 5-4 part C) a MATLAB script was used to average the intensity along the rows while normalizing for background intensity and layer position within the image. This showed that there was no change in the germanium profile between the 3 hour and 9 hour anneals.

5.3 Results and Discussion

Contrary to the assumptions of previous literature, it was found that even the lowest dose germanium implant of 0.25 monolayers $(3.4 \times 10^{14} \text{ cm}^{-2})$ produced a dramatic and measureable suppression in the injection of interstitials, while even two monolayer equivalents of implanted germanium $(1.4 \times 10^{15} \text{ cm}^{-2})$ were insufficient to completely suppress injection [31]·[64]. Raw bound loop counts for the 850°C anneals can be seen in Figure 5-5 as a function of both implanted dose and monolayer, while

raw bound loop counts for the 900°C anneals can be seen in Figure 5-6 as a function of both implanted dose and monolayer. In both cases it is very clear that germanium has an effect well below the monolayer level, and does not shut off interstitial injection entirely even at the highest doses of 2 monolayer equivalents. Figure 5-7 Shows the net number of interstitials injected into silicon upon oxidation for the 850°C samples. The implanted dose is represented as a function of germanium monolayer-equivalent. There is a lower detection limit of roughly 5 x 10^{13} cm⁻² below which the interstitial trapping by the loops is below a reasonable noise floor. It is apparent there is a clear decrease in interstitial injection with increasing germanium dose that appears exponential in nature and the injection falls below the noise limit for doses >2.5 monolayers. In Figure 5-8 The trend of interstitial injection being exponentially dependent on implanted germanium dose was found to be similar for the 900°C samples as well, albeit shifted towards higher injection at 900°C. For any given germanium dose, it is more effective at shutting down interstitial suppression at lower temperatures even though the exponential fits to the data are almost identical, with an R² fitting value of .98 for the 900°C samples and an R² fitting value of .97 for the 850°C samples as can be seen in Figure 5-9. Extrapolation of the exponential curves to the detection limit shows that it would take roughly 5 monolayers of Si0.5Ge0.5 at 850°C and 9 monolayers of Si0.5Ge0.5 at 900°C to shutoff injection below our anticipated detection limit of 5 x10¹³cm⁻².

Dose Ge+	Monolayer Equivalent (100)	
3.4x10 ¹⁴ cm ⁻²	0.25	
3.4 x10 ¹⁴ cm ⁻²	0.5	
5.1 x10 ¹⁴ cm ⁻²	0.75	
6.8 x10 ¹⁴ cm ⁻²	1	
1.4 x10 ¹⁵ cm ⁻²	2	

Table 5-1. Doses implanted into the wafer pieces and their monolayer equivalent along the (100) plane where the oxidation occurs



Figure 5-1. Schematic of experimental process flow. Part A) shows the samples after the Ge⁺ implant. In part B) an oxidation has been performed to condense the entire dose. In part C) the oxidation has been continued.



Figure 5-2. Loop morphologies for 850°C annealed samples. A) and B) were implanted with the highest dose of Ge⁺, while C) and D) were un-implanted control samples



Figure 5-3. Loop morphologies for 900°C annealed samples. A) and B) were implanted with the highest dose of Ge⁺, while C) and D) were un-implanted control samples



Figure 5-4. HAADF-STEM images of oxidized samples A) HAADF-STEM image of a sample with 3 keV, 1.4 x10¹⁵ cm⁻² Ge⁺ implant followed by a 3 hour 850°C furnace annealing under dry O₂. B) HAADF-STEM image of the same sample followed by an additional 6 hour anneal for a total of 9 hours. C) Comparison of image intensity when normalized for background and intensity.



Figure 5-5. Raw density of bound interstitials as a function of A) implanted dose and B) monolayer equivalent for the set of 850°C anneals.



Figure 5-6. Raw density of bound interstitials as a function of A) implanted dose and B) monolayer equivalent for the set of 900°C anneals.



Figure 5-7. Net bound interstitials following the 3 hour condensation and subsequent 6 hour Oxidizing anneal minus the interstitials bound in the control samples subjected to a 3 hour condensation and 6 hour inert anneal. All anneals were performed at 850°C.



Figure 5-8. Net injected interstitials from 900°C anneals compared with those from the 850°C anneals.



Figure 5-9. Net injection of interstitials extrapolated out to beyond their theoretical detection limits for both 850°C and 900°C annealed samples.



Figure 5-10. Possible mechanism for interstitial shutoff. In part A) Pure silicon is shown along with volume mismatch between the silicon lattice and SiO2 and subsequent injection of interstitials. In part B) the SiGe layer has reduced the volumetric mismatch, thus greatly reducing the injection.



Figure 5-11. Possible mechanism for shutoff involving the SiGe acting as a transport barrier preventing the silicon interstitial from reaching the bulk.



Figure 5-12. Dose re-plotted as a thickness of Si_{0.5}Ge_{0.5} vs net injected interstitials. This shows a possible transport barrier with an exponential decay post-generation for silicon interstitials.

CHAPTER 6 INTERSTITIAL SUPPRESSION VIA LOW ENERGY IMPLANTATION OF GERMANIUM

In order for the variable suppression effect observed in Chapter 5 to have practical uses, it is desirable to avoid the preliminary condensation step by directly implanting the germanium at a low enough energy that it is at the surface and active immediately. Furthermore, the lack of need for a pileup step would be necessary to more precisely control the total interstitials injected, and increase throughput while minimizing thermal budget.

6.1 Background

The challenge with implanting germanium directly at the surface is the instability of germanium native oxides towards water, as well as the potential for the volatilization of any GeO formed during the early stages of oxidation. There is also the risk of forming a mixed oxide as the sample heats through the 500°C -700°C range [119] [30]. All of these factors would contribute to effective dose loss such that the implanted dose may not be the dose actually present and active during the subsequent oxidation. Furthermore, the dose loss and subsequent effects would be highly dependent on the equipment used and the rate of heating. Most previous work studying the direct oxidation of SiGe and its interstitial injection properties use much thicker SiGe layers, to the point where the loss of a few monolayer equivalents to the heating phenomenon, either through a few monolayers of mixed oxide or volatilization of GeO would not be noticed or important.

However, our technique requires precise control of the active germanium at the surface to the sub-monolayer level, and as such any losses would have a much more dramatic and unpredictable effect. It is noted from attempts to form SiGe on insulator

that once the grown oxide is stripped away (i.e. the germanium is exposed) that a mixed SiGeO_x phase can form upon subsequent thermal cycles, however it is important to consider that in SiGeOI works the germanium concentrations were much higher [63].

In our previous work the germanium was implanted deeply enough into the substrate that by the time the oxidizing front reached it, temperatures >800°C had already been achieved, and there was a substantial SiO₂ layer already grown. However for the germanium implanted at and near the surface, extra steps may be needed to avoid germanium dose loss. To avoid this problem it was proposed that the samples be pre-heated above 800°C under an inert argon environment before exposure to any oxidizing species. These could then be compared with directly oxidized samples to determine the necessity or lack thereof of an inert pre-heat.

6.2 Experimental Methods

A Czochralski 200mm wafer was implanted with 50keV 2 x10¹⁴cm⁻² Phosphorus, then subjected to a 30 minute 750°C anneal in a tube furnace under an inert ambient. This combination of implant and anneal served to nucleate a buried layer of dislocation loops at a depth of ~70nm to serve as detectors for the later study. IBM performed this part of the work at their Essex Junction facility in Vermont, now a part of global foundries. Once we received this wafer, a portion was sent off to applied materials and implanted at room temperature with 200eV 3 x10¹⁵cm⁻² germanium, forming a thin amorphous region at the surface. See Figure 6-2 for an example of the as-implanted morphology. A single germanium implanted sample was annealed for five minutes at 600°C under an inert argon ambient and imaged in XTEM to ensure clean defect-free solid phase epitaxial re-growth was occurring. See Figure 6-3 for the XTEM image of the re-crystallized layer.

Subsequently, three anneals were performed in the same tube furnace used in our previous work at 900°C. Each anneal consisted of a germanium-implanted sample placed directly besides a non-implanted control sample from the same wafer. A general overview of these anneals can be seen in figure 6-1.

Great effort was put into ensuring that all anneals occurred at the same location within the hot-zone of the tube furnace since this hot zone had been found to be highly non-uniform during previous calibrations, and the furnace was allowed to stabilize overnight to ensure no drift during anneals. All anneals were for two hours, except for the samples that received an additional 5 minute pre-heat under argon. An implanted sample and an un-implanted sample were annealed for 2 hours under pure dry argon to serve as controls for background bound interstitials and loop coarsening. Another set of two samples, one implanted and one un-implanted, were directly inserted into the furnace under an ambient of pure dry O₂. The last set of samples consisted of an implanted and un-implanted sample and were inserted into the furnace under a flow of pure dry argon, then the end of the furnace sealed so that gas could only escape and no contamination from outside air could get into the furnace. After five minutes the gas flow was switched from argon to oxygen and the samples annealed for a subsequent two hours. Although these last two samples received a slightly longer anneal, the added thermal budget was considered negligible when compared to the total.

PTEM samples were made from all annealed samples using the procedure described in chapter 2.1.3. In addition, these PTEM samples underwent a final cleaning step in Hydrofluoric acid to remove the grown silicon oxide so as to reduce the amorphous signal, which would only add noise to later TEM imaging. These samples

were then imaged under WBDF conditions at UCF using their FEI Technai F30 TEM operating at a beam energy of 300keV.

Subsequently, four images from each sample were quantified using the Osirix software package and the number of bound interstitials and error determined for each sample [19, 85, 86]. See Figure 6-5 for examples of the images obtained. XTEM samples of the as-implanted, inert pre-heated, and direct oxidized samples were made using a FEI Helios NanoLab 600 dual beam FIB/SEM. All samples were sub 100nm in thickness and low keV cleaned down to at least 3keV to minimize interference from amorphization caused by the ion beam. These samples were then imaged at FSU by Dr. Yan Xin at the FSU High Magnetic Field Laboratory by Dr. Yan Xin using their JEM-ARM 200cF TEM. Both HAADF images and XPS data were obtained for all three samples.

6.3 Results and Discussion

While ion implantation is generally associated with an increase in the interstitials in the material, and thus upon annealing a growth in the loop detectors, figure 6-4 shows that any implant effect was minimal due to the extremely low implant energy and shallow re-growth. The 3×10^{15} /cm² Ge⁺ implanted sample showed a net increase of only 3.7×10^{13} /cm² bound interstitials, which is below our confident detection limit of 5×10^{13} /cm² as discussed in previous work.

Our results as visualized in Figures 6-6, 6-7, and 6-8 demonstrate that an inert pre-heat does have an effect on the amount of interstitial suppression subsequently observed upon oxidation. Interstitial injection as compared to inert conditions still takes place in the pre-heated germanium implanted sample, but at a lower rate than the implanted sample exposed directly to oxygen. Although this effect has been seen before

during wet oxidations, to our knowledge this is the first time it has been quantified for dry oxidations. [119]

When analyzing this data, it is important to compare to our previous results and the equations obtained from that work. Remember that when fitting an equation to the 900°C 2h anneals an exponential equation was obtained of the form:

$$y = 4.1355 \times 10^{14} * e^{(-6.4166 \times 10^{-16} * x)}$$
(6-1)

Where y represents the net injected bound interstitials, and x represents the active germanium dose. For 900°C 2 hour net anneals. When referring to Figure 5-10, total shutoff was expected to occur at a dose just slightly above 3 x10¹⁵cm⁻², which is the dose used in this study. When using the numbers presented in Table 6-1, it is important to remember to subtract the inert samples as background from the original detector loops so as to get a net number of interstitials injected from the oxidation as opposed to residual from the 50keV 2 x10¹⁴cm⁻² phosphorus implant needed to form the detector loops. This can be seen in Figure 6-8, whereas Figure 6-7 shows the raw values without the inert control subtracted. It is interesting to note that the directly oxidized sample comes closer to the predicted value from the exponential fit, however the pre-heated sample is more efficient at shutting down interstitial injection, and in fact shuts it down to the point where it can be considered negligible, or at least barely above the detection threshold for the buried loop technique. This suggests that the trailing end of the exponential function may behave slightly differently than what was fit from lower dose implants. Even so, it lies very close to within the margin of error.

When we apply Equation 6-1 for the germanium sample subjected to an inert pre-heat the result is 1.920×10^{13} cm⁻², which would be below the limit of our detection

threshold without the residual interstitials from the loop-forming implant, suggesting that near-total shutoff has occurred. However, when we apply the same subtraction to the germanium-implanted sample exposed directly to oxygen we get a value of 5.173 x10¹³cm⁻², which is substantially higher. Plugging in our implant dose of 3 x¹⁵cm⁻² to equation 6.1, the ideal value would be 6.371 $\times 10^{13}$ cm⁻², so although the directly oxidized sample more closely matches the exponential fit in equation 6.1, more complete shutoff is achieved with the inert pre-heat. This is possibly due to the fitted exponential function being less accurate for higher doses, as only lower doses were used in deriving the exponential fit. It is also likely that some germanium loss or oxidation may have occurred to achieve the higher net injections observed when the samples are not pre-heated. Although the interstitials injected by the samples directly oxidized in this experiment fell within the margin of error of the exponential curve, had they been substantially higher, the easiest way to measure lost dose would be to assume that the exponential fits are essentially correct and measure the dosage lost during the direct oxidation. In this case, one would simply need to draw a tie-line from the higher than expected value to where it intersects the curve, then down to the dose that matches that point on the exponential.

In order to quantify the effect of the pre-heat and prove statistical difference, a ttest was performed on both the germanium implanted samples and the silicon control samples, separately. Because each data point was comprised of the average of four quantified images, each implementation of the t-test compared two data sets of four values. This test takes the postulate that the two sample sets are statistically identical to within 95% confidence and returns an h value determining whether or not the postulate

is true. If it is true the t-test returns a value of 0, and if the postulate is not true it returns a value of 1. The t-tests were implemented in MATLAB for both the germanium and silicon datasets shown in Figure 6-6 and Table 6-1. The value returned from the t-test on the germanium implanted samples was h=1 (failed), implying that they show a statistical difference. The un-implanted silicon samples were subjected to the same test, which returned a value of h=0, implying that to within a 95% confidence interval, they passed the test and are statistically equal. Thus the inert pre-heat had a statistically significant effect on the germanium-implanted samples, but not on the silicon control samples. This was as expected, but a statistical test still needed to be performed to confirm these results due to overlap in the error bars in both sets of pre-heated and directly oxidized samples.

It is also a possible source of error that germanium loss could have occurred across all implanted samples simply due to the instability of a germanium surface to native oxidation at room temperature and humidity, and the dose implanted may have deviated slightly from the nominal value of 3×10^{15} cm⁻².

However, if we look at Figure 6-9 we see that contrary to the SRIM calculations which had predicted a R_p of 2.5nm, or right at the interface between the silicon and the native oxide, instead it was found that much of the germanium dose simply deposited on the surface, with relatively little of it making it to the projected range. When considering this result, it is important to remember that the SRIM software package was developed in the 90s and optimized for much higher energy implants, thus some error for ultra-low energy implants could be expected.

Nevertheless, such bimodal concentrations were unexpected and for now unexplained. Surprisingly, the surface layer of germanium was found to be in mostly reduced form, as the XPS results in Figure 6-10 show a very strong germanium signal and only very weak oxygen and silicon signals. Germanium is known to form a native oxide at room temperature in air, so the reason for it remaining in largely reduced form is currently unknown, however some literature points to it being nonreactive during initial stages of oxidation, and every effort was taken to keep the samples sealed and shielded from humidity after receiving them [120]. Upon thermal annealing, it was clearly able to re-crystallize and become active at the Si/SiO₂ interface. In Figure 6-11 XPS results show that some of the germanium did indeed make it much deeper and directly to the crystalline silicon beneath. The visible oxygen signal is likely due to oxygen atoms from the silicon native oxide being knocked further into the material by collisions during the implant.

The images obtained through HAADF in Figures 6-12, 6-13, and 6-14 give some of the most surprising results, and suggest another possible mechanism for the reason germanium layers shut off silicon interstitial injection in general. These Figures show upside-down pyramidal structures that are enriched in silicon relative to the surrounding material, with boundaries along the {111} habit planes. It is also interesting to note that these structures penetrate roughly 8-9 monolayers into the material, or the amount predicted and observed for total shutoff of interstitial injection. Since the {111} plane has the second lowest cleavage energy in silicon, the exposure of such a plane by the rejected germanium would make a good low-energy site for free silicon interstitials to attach and undergo epitaxial re-growth [121]·[122].

Since germanium is known to adopt {111} faceted pyramids when grown on silicon under the proper conditions, it is not inconceivable that a similar phenomenon could be happening here, with the germanium adopting {111} faceted structures upon rejection from the oxide and re-growth at the surface. These features could allow extra lower energy sites for silicon interstitial re-crystallization, thus forming the silicon-rich pyramidal structures within the SiGe that consume the excess interstitial silicon that would otherwise become free to enter the bulk [123, 124]. Although these structures were not observed in our earlier experiments (see Figure 5-4) the samples where they were observed were prepared on a superior FIB, and were thinner with a lower keV clean and overall of higher quality. The ability to see the structures at all is extremely challenging as they measure only roughly 1nm on a side. Assuming they are pyramidal in shape, that means they would be only 1nm in the other direction, and so seeing them in a sample with a thickness of >80nm or a thick amorphous layer would be highly unlikely. It is also important to remember that these structures are merely enriched in silicon relative to the surrounding material, and are not pure, thus making them even harder to detect. It is also possible that these pyramidal structures are in fact pits rather than a silicon-enriched crystalline solid, with material in front and behind the pit giving the illusion of material within them. If so, further surface studies would be required to determine this.

Table 6-1. Bound interstitials for all samples studied.

Sample	Bound Interstitials (cm ⁻²)	Error (cm ⁻²)
Germanium in Argon	6.371 x10 ¹³	1.531 x10 ¹³
Silicon in Argon	7.125 x10 ¹³	7.313 x10 ¹²
Germanium in Oxygen	1.149 x10 ¹⁴	2.150 x10 ¹³
Silicon in Oxygen	2.047 x10 ¹⁴	2.281 x10 ¹³
Germanium Pre-heat	8.292 x10 ¹³	1.323 x10 ¹³
Silicon Pre-heat	2.269 x10 ¹⁴	1.979 x10 ¹³



Figure 6-1. Simplified schematic of experimental plan showing germanium-implanted samples and un-implanted control samples with their annealing conditions. All germanium implants were 3 x10¹⁵cm⁻².



Figure 6-2. XTEM image of as implanted structure. The red arrow denotes the thin amorphous region of ~2.5nm while the material underneath remains single crystal.


Figure 6-3. XTEM of 200eV Ge⁺ 3 x10¹⁵cm⁻² after undergoing a 600°C 5 minute anneal under argon ambient to re-crystallize the amorphous layer from the implant.



Si control with no Ge+ implant

3keV Ge+ 1.4 x 1015/cm2





Figure 6-5. Examples of images obtained post-anneal at UCF. A) shows the effect of the 2 hour oxidizing anneal post pre-heat. B) shows the same anneal without the pre-heat. C) and D) show silicon controls for comparison.



Sample

Figure 6-6. Bound interstitials for all samples studied. In the legend, "Ge" denotes implanted samples, while "N" denotes non-implanted Si control samples.



Figure 6-7. Raw values of pre-heated germanium implanted sample plotted against previous exponential fit. Within margin of error it comes very close to the predicted value.



Figure 6-8. Pre-heated and directly oxidized germanium implanted samples once the background inert values have been subtracted.



Figure 6-9. HAADF image of as-implanted structure. It is important to note that the Zcontrast is consistent with an amorphous region and the lower crystalline structure simply appears brighter due to greater dynamical scattering.



Figure 6-10. XPS area-scan showing a high concentration of reduced germanium at the top of the as-implanted sample. Surprisingly little oxygen was observed. This is contrary to what was predicted by SRIM, which calculated the germanium penetrating to an R_p of 2.5nm.



Figure 6-11. XPS area scan showing that the germanium was able to penetrate the amorphous layer and make it through to the crystalline silicon underneath.



Figure 6-12. HAADF image of sample after 5min argon pre-anneal followed by 2h oxygen anneal. Regions enriched in silicon along the {111} planes are observed.



Figure 6-13. Lower magnification HAADF image of sample after 5min argon pre-anneal followed by 2h oxygen anneal. Regions depleted in germanium along the {111} planes are observed to repeat throughout the structure.



Figure 6-14. Sample directly oxidized without argon pre-heat. Similar structures along the {111} planes are observed. It is important to note that a larger probe size was used, so the image is a convolution of Z-contrast and strain contrast.

CHAPTER 7 CONCLUSIONS

These experiments prove the viability of ultra-low energy surface implantation in suppressing and controlling interstitial injection without the need for a condensation step as was used in chapter 5. It also shows that pre-heating has a slight but measureable effect on the germanium available to act as a catalyst in reduction of interstitial injection.

7.1 Possible Mechanisms

There exist competing models and theories as to the mechanism responsible for the shutoff phenomenon and why it should follow the exponential and temperature trends that it does. The following sections will try to cover some of the most prominent ones.

7.1.1 Formation Elimination

One possible explanation is that excess silicon interstitials simply aren't formed when sufficient germanium is present. It is noted that the lattice constant of a SiGe alloy more closely matches the volume mismatch of the SiO₂, however this alone is insufficient to account for all the mismatch strain energy. For a Si_{0.5}Ge_{0.5} alloy the mismatch is still 1.13 as opposed to 2.25 for pure Si, therefore it seems unlikely that this phenomenon can totally explain the interstitial shutoff. A schematic of this can be seen in Figure 5-10. The formation energy of a silicon interstitial in intrinsic Si_{0.5}Ge_{0.5} is 0.3eV [113]. If you plug this into a standard Boltzmann equation

exp(-0.3 eV /*k*_BT)

7-1

Where $k_{\rm B}$ is Boltzmann's constant and T is absolute temperature. Using this equation for a temperature of 850°C gives a 20 fold reduction in silicon interstitial injection, which is well below our detection limit [61].

The problem with this model is that our results show that it takes more than 2 monolayer equivalents to shut down injection, and the lowest dose implants still have a dramatic effect despite being unable to even come close to achieving full coverage of the surface. When dose is converted in to a thickness of Si_{0.5}Ge_{0.5} there is an exponential decay, suggesting some sort of transport effects in addition to formation energy. See Figure 5-12.

7.1.2 Migration Barrier

It has been suggested by some authors that the SiGe layer presents a migration barrier to silicon interstitials, see Figure 5-11, favoring the other two possible pathways for them (injection into the oxide or re-growth at the surface) [61]. See Figure 1-2 for the possible pathways. If it becomes more energetically favorable to flow into the oxide or re-grow rather than migrate into the interior, then that would account for the shutoff effects. Although our previous work has shown that a buried Si0.7Ge0.3 layer presents no barrier to interstitial migration, this has not been shown for a buried Si_{0.5}Ge_{0.5} layer, which is the pileup concentration seen during the actual oxidation reaction. Since transient injection has been shown for lower concentration layers that shuts off once the equilibrium condensation has been reached [61], it is possible that the germanium must reach a certain concentration before it becomes a migration barrier sufficient to shut off injection. The experiment of a buried Si_{0.5}Ge_{0.5} layer with a silicon capping-layer to inject interstitials was attempted, but the samples proved too defective upon arrival. See Figures A-1 and A-2 for examples. Since evidence exists for multiple mechanisms of silicon interstitial formation and migration, it could likely be the case that the presence of germanium simply favors one pathway over the other, or suppresses the previously

dominant mechanism in favor of one that does not inject interstitials [125][,][53][,][126][,][40][,][54].

7.1.2 Nanoscale Segregation

Although silicon and germanium are fully miscible in their phase diagram, a compressive strain destabilizes this and favors phase separation. The driving force for this is release of strain energy and minimization of chemical potential [127]. The SiGe layers were too thin to observe in PTEM, and even when using HAADF the technique is looking through 100nm or so of material, so any nanoscale islands of phase separation would likely be missed. The results observed in Figure 5-12 may simply be the critical thickness required to suppress this phenomenon, or to ensure that any generated interstitials encounter a germanium phase before they can penetrate beyond the SiGe layer into the bulk. At the very least, the lowest dose implants below one monolayer equivalent of germanium would have been unable to provide total coverage, making some injection of silicon interstitials almost a certainty. Germanium tends to favor selfsegregation at the Si_{0.5}Ge_{0.5} composition, making this a potential mechanism for silicon islands to inject interstitials until a critical thickness is reached [128]. In fact, it has been demonstrated during SiGe on insulator experiments that the Si_{0.5}Ge_{0.5} composition is only metastable, and a local minima that is controlled by a kinetic barrier [58]. The formation of germanium rich islands upon rejection from the oxide may also give the silicon interstitials fresh sites to re-crystallize on [59]. None of our analytical methods would have detected this, and certainly for the sub-monolayer implants complete coverage would have been impossible, although isolated islands of rejected and reduced germanium on the surface could have provided convenient nucleation sites for silicon interstitial re-growth, thus explaining why such low doses of germanium can have

such a dramatic effect in partially shutting down silicon interstitial injection. Silicongermanium phase separation has been observed in literature, with thin films less stable than thicker ones, making it a possible explanation for our observed results [129].

7.1.3 Reaction Zone

Although silicon oxidation is generally thought of as being a simple process with all the reactions taking place at a smooth Si/SiO₂ interface, this may in fact not be the case. Kageshima et. al. used a combination of experiments and equations to show that there is a zone with a finite thickness that arises at the interface during silicon oxidation, driven mostly by the effects of the emission of massive amounts of silicon interstitials at this interface [52]. Esteve et. al. used Monte Carlo simulations to show much the same thing, that there is a zone of reaction extending somewhat beneath the surface, or rather a reaction zone separating the bulk silicon from the overlying fully formed SiO₂ [29]. Earlier, Tiller et. al had proposed that the alpha-christobalite form of SiO₂ formed at the interface, pinned by the Si-O bonds that would later gradually break up into the amorphous phase of SiO₂ [54]. This work observed that interstitial injection decays not only as a function of germanium dose, but also as a function of the thickness of the surface SiGe layer (see figure 5-12). This may have some deeper meaning to silicon oxidation in general if the reaction zone model is correct. It may be the case that only by filling the entire thickness of the reaction zone with germanium can total shutoff be achieved. If this is the case, then this work provides a possible method for quantifying the thickness of this reaction zone under different conditions.

7.2 Summary and Final Thoughts

An important aspect of this whole study is that the results were relatively repeatable within reasonable error with the results from chapter 6 closely matching the

previous work in Chapter 5, despite using wildly different doses and energies, and despite the absence of a condensation step. The exponential fitting applied to the lower dose implants seems to hold reasonably accurate regardless of the manner in which the germanium is introduced onto the surface prior to oxidation. Remember that in chapter 5 the post-condensation anneal during which interstitial injection was measured was at 900°C for two hours, which is the same time used in the experiments performed in Chapter 6 without the condensation step. Despite the different manner of germanium introduction and dose, and the different manner with wich it was concentrated at the active surface, it was possible to achieve the same results within a reasonable margin of error.

This shows that the technique has promise in future applications where the modulation and control of interstitial injection during an oxidative step is desired so as to control diffusion or other phenomena. The germanium layers used are so thin that it would be trivial to strip them with a selective etch once they had served their purpose if the germanium was not desired in the final product. The fact that this technique can be used to predict injection based upon the equations derived from variable dose implants speaks to some underlying fundamental phenomenon as not yet fully understood, however the results in chapter 6 offer up a whole new potential mechanism for why germanium suppresses and eventually shuts down silicon interstitial injection, that is in agreement with previous literature. It is already known that epitaxial re-growth accounts for some fraction of the interstitials produced even in the absence of germanium, and it is known that it is far less energetically favorable to form a silicon interstitial in a

Si_{0.5}Ge_{0.5} alloy, however the presence of a buried SiGe layer away from the oxidizing interface poses no barrier to their passage [19, 48, 53].

One possible theory, based on the available evidence, is that as the germanium gets rejected from the growing oxide, it forms {111} faceted ledges that present lower energy sites for silicon interstitials to attach and re-crystallize, thus favoring lowered energy re-growth over the much higher energy silicon interstitial formation in Si_{0.5}Ge_{0.5} [49]. Although the {111} surface shows the slowest growth rates in bulk studies. In fact certain silicon re-growth studies show the {111} family of planes as being the most favorable for growth until a critical size is reached [130, 131] [132] [133]. However, it is also true that in germanium the {100} planes re-grows 15 times faster than the {111} planes, at least in the bulk 2-dimensional phase [134]. Nevertheless, this would still be lower in energy than the barrier to form silicon interstitials in Si_{0.5}Ge_{0.5}. Also, the diameter at which the {111} growth for nanostructures becomes unfavorable exceeds the feature sizes observed in this work of ~1nm. Furthermore, although these feature sizes might seem quite small, they may provide enough volume to soak up the interstitial numbers observed even for the highest values, depending on their silicon concentration.

If we assume the average features to be pyramidal and measure the width and depth from the HAADF image in Figure 6-11 we get a volume of 0.68nm³ whereas the volume of a silicon atom can be expressed as 0.0068nm³. This would provide enough volume for 100 or so silicon atoms, although because it is merely enriched in silicon as opposed to being pure silicon the number would likely be quite lower. Nevertheless, the features seem to have a high areal density, and as only a few silicon atoms per

thousand oxidized make it into the bulk even without germanium present, this mechanism could be capable of soaking them up. As the second most close-packed plane after {110} ($9.59 \times 10^{14} \operatorname{atoms/cm}^{-2}$), {111} ($7.83 \times 10^{14} \operatorname{atoms/cm}^{-2}$), planes would offer a larger number of sites for silicon interstitials to undergo re-growth than the (100) plane with only 6.78 $\times 10^{14} \operatorname{atoms/cm}^{-2}$.

The critical thickness of germanium needed to form enough such sites to completely shut down injection appears temperature dependent and is at around the 8-9 monolayers of Si_{0.5}Ge_{0.5} alloy at 900°C, with less being needed at lower temperatures, presumably due to the higher SiGe pileup concentration at the interface [55]. This mechanism would also explain why the germanium must be at the interface to have any effect. A buried layer of single crystal material would have no new ledges forming, thus precluding the silicon interstitials from having a site to re-crystallize. Because the concentration gradients are so minor and the structures so small, it is likely that they would have gone un-noticed until now with the availability of superior equipment, and highly unlikely that they would have any effect on experiments, device function, or manufacturing besides trapping the silicon self-interstitials that would otherwise travel into the bulk. Furthermore, this theory is in agreement with available literature. The only literature it contradicts is that which speculates that only the first monolayer of germanium participates in the reaction and is sufficient to shut down silicon interstitial injection.

7.3 Future work

At this point in time the only real evidence for the above-proposed mechanism is the observation of repeating contrast changes in HAADF images correlating with interstitial injection shutdown. This could be due to relative enrichment of silicon in these

faceted regions, or it could be due to some sort of pitting or other surface phenomenon. The easiest way to distinguish between these two possibilities would be to do a surface study using STM (Scanning Tunneling Microscopy) capable of resolution on the atomic scale. The oxide would first need to be stripped in a manner non-disruptive to the SiGe layer underneath, then before a native oxide can re-grow, the surface imaged with STM. STM can provide not only atomic level resolution that would detect any nanometer-scale pitting, but would also be able to use differences in tunneling potential to determine if these structures are indeed enriched in silicon, or whether this is just an artifact from looking through a comparatively thick XTEM sample. STM would also give an accurate areal density that could then be correlated back to numbers of interstitials injected in the absence of germanium to see if the density is high enough to provide sufficient regrowth volume for them all.

APPENDIX A EFFECTS OF A BURIED IMPLANT ON RELAXATION OF A SILICON-GERMANIUM LAYER

The origins of this project and the original experimental matrix centered around the effect of defect evolution from a buried implant, and the interstitials they released on the relaxation of an overlying SiGe layer during subsequent thermal processing.

A.1 Background

The Heterojunction Bipolar Transistors or HBT is simply an extension of the preexisting Bipolar Junction Transistor (BJT), which actually pre-dated the MOSFET as there were problems growing suitable gate dielectrics, with the first of these being constructed purely from germanium1951[135] [136]. In its simplest form, a BJT can simply be thought of as two diodes, one in the forward biased position (base-collector junction), and one in the reverse biased position (emitter-collector junction). In practice, this is accomplished via a thin layer of material of one doping type (p or n) sandwiched between two much thicker layers doped oppositely. When a small current is applied from the base to the emitter, this allows a much larger current to flow from the collector to the emitter, with the base acting as a valve, thus allowing for signal amplification. Remember that current direction is opposite to charge carrier direction, thus the terminology wherein the emitter is actually emitting the charge carriers, and the collector collecting them. The collector itself is usually more heavily doped towards the bottom (sub-collector) than near the base. This is to minimize the depletion region critical for device function, as well as to eliminate parasitic capacitances. Since the electrons will be minority carriers in the p-doped base region, it is a critical device performance metric that they diffuse across this layer as rapidly as possible before recombining with holes,

and to improve device speed in general, hence the drive towards thinner and more steeply graded base regions with a higher germanium content.

BJTs and HBTs are normally grown as vertical devices with the base wafer having an n-doped collector region atop which is grown the p-type base, followed by the deposition of a heavily n-type doped poly-silicon emitter. As vertical devices, their scaling relies more upon epitaxial growth limits than lithographic ones. An HBT operates essentially the same as a BJT, but with the base layer making use of stoichiometrically graded germanium to modulate the base's bandgap in a process known as bandgap engineering to effectively create an electric field that can accelerate the minority carriers through the base region, minimizing recombination and dramatically improving speed [20]. This speed is necessary for high frequency communications and sensor technologies, and such devices were often made using III-V materials that were far more costly and difficult to integrate than their silicon counterparts [137]. Germanium however is fully compatible with standard silicon processing and the massive infrastructure built up around it, and as such SiGe based HBTs have been an active field of development to lower costs and produce hybrid chips with multiple device types on them, each requiring separate thermal budgets [136] [104] [20]. Although both n-p-n and p-n-p device types exist, this experiment was centered on the far more common np-n device structure. In these devices, the germanium is normally graded from around 20% germanium at the collector interface to nearly pure silicon at the emitter interface. Because the bandgap of germanium is only 0.7eV as compared to 1.12eV for silicon, this creates a built in gradient to help accelerate the charge carriers through the base region and improve device speeds. In the next generation of devices, collector current

will need to increase dramatically, thus necessitating increased doping [20]. In addition, there is a driving force to make the base region thinner and more highly graded (higher germanium concentration at the collector-emitter interface) [20]. This presents challenges as higher collector doping via ion implantation is beginning to enter the regime where extended defects will form. See Figure A-1 for a simplified example of an HBT structure. Furthermore, to achieve integrated chips that have multiple device types on them, each requiring a different thermal budget, it is important to understand how the thermal evolution of these buried collector defects will interact with the more highly strained germanium layer above it. When constructing such a hybrid chip with multiple device types, the completed HBT would likely be required to survive subsequent high-temperature anneal steps to create the other devices on the same chip. Since the base is normally grown using LTE, their subsequent response to higher thermal budgets subsequent to growth is a major area of concern in developing hybrid chips.

Here one might ask why the n-type dopant isn't simply grown into the subcollector regions [138]. This would eliminate the implantation-induced defects and provide a high level of doping. However, epitaxial growth is more expensive than ion implantation as a method of dopant introduction, and since one of the main drivers for SiGe HBT development in the immediate future is as a replacement for III-IV based HBT amplifiers in the cellphone and mobile consumer market, price is paramount. Many manufacturers maintain two lines of HBT development. One a higher performance, higher cost, lower volume device that is primarily used in defense contracts and other high performance applications where price is less of a concern. The other, a device that needs to be competitive both in terms of speed, but also in volume and price so that it

can become incorporated into consumer electronics. It is these later devices which rely upon ion implantation to achieve the doping of the collector region [20].

There is some evidence that interstitials from defects formed by a buried implant and anneal could cause relaxation and defects in the SiGe, and changes in the defects themselves as they undergo thermal evolution, and there is great interest in the effects of post-implant and post-growth thermal processing for integration of SiGe technologies on to other chips [139]-[20, 136]. Specifically IBM was worried about increasing the phosphorus dose in the sub-collector region of their Heterojunction Bipolar Transistors to the point where extended defects would form upon activation annealing, and the effects that defect evolution during subsequent thermal processing releasing interstitials in a phenomenon similar to TED may have on performance and quality of the SiGe base layer.

A.2 Experimental Methods

Three implant conditions were chosen to mimic the collector doping. One set of samples was left un-implanted as a control, another set of samples received a 1 x10¹⁴cm⁻² P⁺ implant, while another set of samples received a 2 x10¹⁴cm⁻² P⁺ implant. Both implants were 50keV. These implant doses were chosen due to threshold for loop formation as shown in Figure 3-3. This dose and energy placed them well into the loop-forming regime, but below the amorphization threshold. The orange arrow is placed to help denote our region of interest Subsequent to implantation, all wafers underwent a 750°C furnace anneal under an inert ambient, placing them into the regime where {311} defects and loops are both present. This was to repair implantation damage and nucleate defects, while ensuring that subsequent LTE at around 600°C would have minimal effect on defect evolution [103]·[104]. Two SiGe Compositions were chosen:

Si_{0.7}Ge_{0.3} and Si_{0.5}Ge_{0.5} along with silicon control samples. All followed the same basic structure illustrated in Figure 4-1 A) where 5nm of silicon was coated with 20nm of either Si_{0.7}Ge_{0.3}, Si_{0.5}Ge_{0.5} or Pure Si followed by a 5nm Si capping layer using LTE.

Upon receiving the samples they were analyzed in both XTEM and PTEM. It was quickly discovered that while the Si_{0.7}Ge_{0.3} samples appeared as expected, the Si_{0.5}Ge_{0.5} samples were highly defective. Figure A-2 shows an example in XTEM where defects and non-homogeneity are clearly present both laterally and vertically. This same phenomenon was observed in all Si_{0.5}Ge_{0.5} samples received and made these sets of samples nearly worthless for our studies. Figure A-3 shows the same sample in PTEM. Height, compositional, and strain variations can all be readily seen, as well as a misfit dislocation, indicating partial relaxation of the SiGe even prior to any annealing. Nevertheless, samples were annealed at 850°C for times of 10 minutes. Rocking curve XRD measurements were performed on these samples as well as un-annealed control samples to look for any signs of relaxation.

A.3 Results and Discussion

It was first important to analyze the as-received samples to ensure they were as specified by IBM. It was found through XRD that the $Si_{0.7}Ge_{0.3}$ samples were compositionally correct to within +/-1% and the layer was nearly fully strained. The as-received spectra can be seen in Figure A-4. Figure A-5 shows that even after an 850°C 10m furnace anneal, the highest dose buried implant of 2 x10¹⁴cm⁻² had no discernable effect, and neither the implanted nor un-implanted layer relaxed appreciably. Given these results it was decided to forgo the analysis on the lower dose (1 x10¹⁴cm⁻²) implants because the lower dose would have even less of an effect, and XRD is an expensive and time-consuming process.

The nominally Si_{0.5}Ge_{0.5} samples were found via XRD to have only ~43% germanium and to be of relatively low epitaxial quality. This becomes readily apparent upon comparing the spectra in Figures A-4 and A-6 where the Si_{0.7}Ge_{0.3} samples show prominent satellite fringes and the Si_{0.5}Ge_{0.5} samples do not. This result was unsurprising given the defects and non-homogeneity evident in Figures A-2 and A-3. The Si_{0.5}Ge_{0.5} samples started off nearly fully strained, but upon annealing at 850°C for 10m in an inert ambient the un-implanted samples underwent a relaxation of ~17%, whereas the highest dose implanted samples (2 x10¹⁴cm⁻²) relaxed ~21% under the same conditions. This appears to show a very slight, albeit measureable, effect from the implant. However, due to the highly defective starting structure of these samples there is no way of knowing if the buried implant would have had different effects on non-defective starting samples. The bulk of the relaxation seemed to be thermal in nature, with the implant only contributing 4% or so to an already occurring process.

It had been postulated that the tensile strain applied to the silicon by the SiGe layers might affect defect evolution by stabilizing interstitials and structures comprised of them. For example it might apply a driving force to cause the loops to climb towards the more heavily tensile strained silicon layer. In Figure A-8 the evolution of these buried defects from the implant were studied via PTEM for both SiGe concentrations and were compared to silicon control samples subjected to the same annealing conditions. The defect evolution was found to be totally unaffected by an overlying SiGe layer.

A.4 Conclusion

The results unequivocally show that at least for the doses and temperatures studied, a buried implant has no effect on the Si_{0.7}Ge_{0.3} layer. This could be attributed to

the fact that in referring back to Figure 1-7 the blue X denotes the Si_{0.7}Ge_{0.3} samples, which lie solidly in the metastable strain region. If insufficient driving force is available to cause relaxation, then the relatively small number of interstitials released during defect evolution would have no effect, as a Si_{0.7}Ge_{0.3} layer was previously shown to be fully transparent to interstitials in chapter 4 without undergoing relaxation.

As for the Si_{0.5}Ge_{0.5} samples, although an implant related effect was observed, this was likely just aiding the already occurring relaxation process as the Si_{0.5}Ge_{0.5} samples are shown to lie outside the metastable region as denoted by the red X in Figure 1-7. Unfortunately, the samples arrived in such an already defective state that it is impossible to determine whether this buried implant effect, or relaxation at the temperatures and times studied would occur in a higher quality sample. In our Si_{0.5}Ge_{0.5} samples, pre-existing defects in the SiGe layer likely played a large role in the relaxation process, for both implanted and un-implanted samples. Therefore, it is impossible to draw general conclusions from this data, as the defective samples were a one-off glitch that would be very unlikely to be repeatable, especially since the exact recipe and growth conditions were not made available to us by IBM as they wished to keep them proprietary.

Just looking at the phase diagram, silicon and germanium are fully miscible, and the phase separations observed in Figures A-2 and A-3 should not happen. However, similar structures have been predicted and observed in III-IV materials, with strain providing the driving force for phase separation, with the maximum value for separation occurring at the 50% composition [127, 129]. This is one possible reason our Si_{0.5}Ge_{0.5} samples came out of the growth process so defective and phase-separated. More

research and possibly different growth conditions may be able to stop these phenomena in the future, as pseudomorphic Si_{0.5}Ge_{0.5} structures have been successfully grown by other groups [140]. Regardless, this phase separation effect presents a challenge to future HBT designers who wish to increase the germanium fraction in their base layers while thinning them. One possible solution based on our previous experiments would be to grow a thicker and less concentrated layer, then oxidize it until it reaches the proper composition and thickness since none of the oxidization condensed SiGe layers studied in this work showed the bulk phase separation phenomenon present in the epitaxially grown Si_{0.5}Ge_{0.5} layer. The challenge to this approach however would be achieving the germanium gradient necessary for bandgap engineering. Most likely the samples simply proved defective because the recipe used during their growth would not have been a standard well-developed one currently used by any of IBM's technology nodes yet.



Figure A-1. Simplified schematic of a basic HBT structure with higher dose sub-collector implants forming defects.



Figure A-2. XTEM of the Si_{0.5}Ge_{0.5} samples as received from IBM.



Figure A-3. PTEM bright field image of Si_{0.5}Ge_{0.5} sample as received.



Figure A-4. XRD of $Si_{0.7}Ge_{0.3}$ sample as received from IBM



Figure A-5. XRD of Si_{0.7}Ge_{0.3} sample before and after 850°C 10m anneal. The peak position of the SiGe layer is consistent with a fully strained layer presence of superlattice fringes suggests high quality epitaxy. No relaxation was observed upon annealing.



Figure A-6. XRD of Si_{0.5}Ge_{0.5} sample as grown. Layer appears fully strained but lack of superlattice fringes suggests rough surface consistent with TEM.



Figure A-7. XRD of Si_{0.5}Ge_{0.5} samples annealed at 850°C for 10m under inert ambient. A slight shift in the germanium peak is visible, indicating a minor effect from the implant.







Figure A-8. Defect morphologies for all samples studied. Buried defects were unaffected by strain from overlying SiGe layers.

APPENDIX B LIST OF WORKS BY THE AUTHOR

Publications

Martin, T. P., Jones, K. S., Camillo-Castillo, R. A., Hatem, C., Xin, Y., & Elliman, R. G. (2017). Quantification of germanium-induced suppression of interstitial injection during oxidation of silicon Thomas P. Martin, K. S. Jones, Renata A. Camillo-Castillo, Christopher Hatem, Yan Xin & Robert G. Elliman. *Journal of Materials Science*, 52(17), 10387-10392. http://doi.org/10.1007/s10853-017-1196-1

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Presentations

T.P. Martin, E.L. Kennon, H. Aldridge Jr, K.s. Jones, R.A. Camillo-Castillo "Elimination and Quantification of Oxidation Induced Interstitial Injection via Ge Implants" Presented at the 231st ECS Meeting June 1 2017 in New Orleans.

T.P. Martin, E.L. Kennon, H.L. Aldridge jr., K.S. Jones, C. Hatem, R.A. Camillo-

Castillo "Elimination of Oxidation Induced Interstitial Injection via Ge Implants"

Presented at the Ion Implantation Technology (IIT), 2016 21st international Conference

in Taiwan

Patents Pending

METHODS FOR MODULATION OF INTERSTITIAL INJECTION DURING OXIDATION OF SILICON USING LOW ENERGY GERMANIUM IMPLANTATION Docket #: 222109-8550-1

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BIOGRAPHICAL SKETCH

The author was born in Boston in 1988 to two loving parents who were themselves finishing graduate school and medical school at the time. After a brief 6 months in Boston, the author spent his childhood growing up in Albuquerque New Mexico. As he grew older his parents gave him a great deal of latitude in performing (often dangerous) experiments in the backyard that developed into an interest in chemistry and materials. He attended Albuquergue Academy from 6th through 12th grades and spent his teenage years overworked, but with close friends and enough spare time to experiment with blowing things up out in the desert. He was also captain of a Science Bowl team that won the state competition every year from grade 7 on except once, and got third and second at nationals. He also captained the swim team his senior year and participated in other activities like speech and debate. After graduating high school he spent his undergraduate years at the University of Washington in Seattle where he switched majors from Chemistry to Materials Science and Engineering after being introduced to the department. Over the summers he worked in Professor John Grey's lab at University of New Mexico on Raman imaging of organic solar cells, and contributed to building the experimental setup, writing code to process spectra into images, and was listed as an author on several papers. These were the happiest days of his undergraduate career. He hand-built a 3D printer back when they were considered cutting edge, and designed an improved part for it, which was picked up on and currently sold by Gallium Source LLC. This printer has served him well in research ever since where custom parts for experimental setups could be rapidly and cheaply produced. It also allowed for interesting hobby projects. He disliked the weather and culture in Seattle, but survived the four and a half years to get his BS in

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Materials Science and Engineering 2012 and move on to graduate school in Florida where the climate and culture were far more agreeable. Despite arriving with no funding and no contacts, Professor Kevin Jones generously offered to take him into the group at the end of his first semester. During his time as a graduate student he worked on many different projects including atom probe tomography, and Heterojunction Bipolar Transistor work for IBM. He eventually spent 5 months working at their Essex Junction facility in Vermont where he enjoyed the coldest February on record and designed and built a drip-etch system for them to fabricate plan-view samples, while also training their staff on WBDF TEM. When not working he enjoyed spending time with family in the area, and driving his truck out across the frozen lake Champlain to go ice-skating. Upon returning to Florida, he had to completely re-think his project after half his samples arrived too defective to use. His best work came in his last year, as it so often does. He finished up his experimental work and received his PhD in Materials Science and Engineering in 2017 from University of Florida. He also enjoys skiing, hiking, scuba diving, and pretty much anything to do with the outdoors.