AMORPHIZATION AND SOLID PHASE EPITAXIAL GROWTH OF GERMANIUM

By

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To my family and friends who have made this dissertation possible
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<tr>
<td>α-Ge</td>
<td>amorphous germanium</td>
</tr>
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<td>α/c</td>
<td>amorphous crystalline interface</td>
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<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>BF</td>
<td>brightfield</td>
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<tr>
<td>c-Ge</td>
<td>crystalline germanium</td>
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<tr>
<td>CMOS</td>
<td>complimentary metal oxide semiconductor</td>
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<td>DF</td>
<td>darkfield</td>
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<td>E-beam</td>
<td>electron beam</td>
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<td>EOR</td>
<td>end of range</td>
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<tr>
<td>FFT</td>
<td>fast fourier transform</td>
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<tr>
<td>FLOOPS</td>
<td>florida level-set object oriented process simulator</td>
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<tr>
<td>PTEM</td>
<td>plan view transmission electron microscopy</td>
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<td>RIE</td>
<td>reactive ion etching</td>
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<tr>
<td>SAD</td>
<td>selected area diffraction</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SPEG</td>
<td>solid phase epitaxial growth.</td>
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<tr>
<td>SRIM</td>
<td>the stopping and range of ions in matter</td>
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<td>TDD</td>
<td>threshold damage density</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>WBDF</td>
<td>weak beam dark field</td>
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<td>XTEM</td>
<td>cross sectional transmission electron microscopy</td>
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AMORPHIZATION AND SOLID PHASE EPITAXIAL GROWTH OF GERMANIUM

By

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Chair: Kevin Jones
Major: Materials Science and Engineering

The substrate orientation dependence on SPEG was studied for the first time in Ge. The velocity showed a strong dependence on substrate orientation and the [001] direction displayed a velocity 16 times greater than the [111] direction. Cross sectional (XTEM) and plan view transmission electron microscopy (PTEM) revealed stacking fault and twin defect formation in the [111] orientation with densities ~1×10⁸ cm⁻², where all other orientations showed only hairpin dislocations with densities of ~3×10⁸ cm⁻². Unlike Si, Ge had considerably less {111} defects upon SPEG, which contributed to higher normalized velocities as a function of orientation.

Multidimensional (2D) SPEG was studied for the first time in Ge. Pattern induced stress was found to promote mask edge defect formation, which became more pronounced with decreasing pattern width. The 1D substrate orientation dependence on SPEG was then used to construct a model for 2D SPEG using the Florida Level-set Object Oriented Process Simulator (FLOOPS). Mask edge defect formation was accurately simulated in FLOOPS by using a curvature factor of 8×10⁻⁸ cm. The evolution of the α/c interface matched well with simulations for both convex and concave interfaces.
2D SPEG was also studied for non-planar Ge substrates. The effect of a free surface was studied for trench structures by passivating the surface with an oxide. The presence of an oxide hindered the SPEG process by forcing the Ge to template off the SiO$_2$. These defects were effectively eliminated by creating a free surface via an HF etch. Ge was found to be less defective than its Si counterpart and the results show promise for using Ge in non-planar finFET structures.

Overall, the SPEG process in Ge was shown to be less defective than Si in terms of mask edge defects, \{111\} defects, trench corner stacking faults, and EOR; however, a high dose regime exists where a porous layer forms within the amorphous Ge. This suggested that implant conditions should be chosen to avoid this high dose regime. All of these studies lead to a much better understanding of ion implantation and SPEG in Ge.
CHAPTER 1
INTRODUCTION

1.1 Motivation and Technological Relevance of Ge SPEG

The semiconductor industry has made enormous strides in order to keep pace with Moore’s Law, which states that the number of transistors on a chip doubles roughly every 2 years [1]. In order to achieve this goal, companies like Intel have scaled down device lengths, changed device geometries, and implemented stress to achieve the desired electronic properties. The predominant substrate material, Si, is currently reaching its fundamental limits and researchers are turning to new materials, like Ge for higher performance. Ge has superior electronic properties, such as higher electron and hole mobilities, and also allows for less aggressive annealing due to its lower recrystallization temperature. With this new interest in Ge for CMOS devices, it is important to understand the defects that form from ion implantation and the solid phase epitaxial growth (SPEG) process.

Although the first transistor was made from Ge in 1954, researchers quickly abandoned the material and started using Si due to its beneficial oxide properties and low cost. Recently, there has been a push to return to Ge as an alternative source drain material in CMOS devices. Ge has many beneficial properties such as higher electron and hole mobilities than Si. Ge also has a lower melting temperature, which would allow for less aggressive annealing steps. Moreover, the low diffusivity of B in Ge makes the creation of ultra-shallow junctions in Ge realizable [2]. It has also been shown that high electrical activation of B can be achieved with Ge substrates that have been pre amorphized [3]. The need for a pre amorphization step warrants research on
the SPEG process for Ge. The SPEG process has been studied in great detail for Si substrates, but basic knowledge of the SPEG process for Ge remains unknown.

1.2 Objective and Statement of Research

The goal of this work is to explore SPEG and defect formation for ion implantation in Ge. More specifically, the following aspects have been studied.

• The substrate orientation dependence on Ge SPEG and subsequent defect formation
• Multidimensional SPEG around patterned structures and the effect of silicon nitride induced stress on defect formation
• FLOOPS modeling of concave and convex α/c interfaces for patterned Ge structures
• Multidimensional SPEG around non-planar surfaces and the effect of a free surface during SPEG on the formation of defects in trench structures
• The effect of implant energy and dose on Ge SPEG
• The effect of high dose implantation in Ge and proposed theory and models

1.3 Ion Induced Amorphization

Ion implantation is one of the most common methods for introducing dopant atoms into semiconductor materials. It is a process by which ions are accelerated at a semiconductor target and come to rest in interstitial sites within the lattice of the material. The main advantages include precise control over the depth and amount of dopants, uniformity, and reproducibility. The depth is controlled through implant energy, whereas the amount of dopant ions is controlled through the dose.

Once the ions enter the lattice, they are slowed by both electronic and nuclear stopping mechanisms. Electronic stopping refers to the interaction of the incoming ion
with the electron cloud of the target material and can be modeled with the following equation:

\[ S_e(E) = kE^{1/2} \]  

(1-1)

where \( S_e(E) \) is the electronic stopping power as a function of energy, \( k \) is a variable associated with the ion and target materials, and \( E \) is the energy of the incoming ion. The nuclear stopping mechanism refers to the interaction of the incoming ion with the atomic nucleus of the target material and can be modeled with the following equation:

\[ S_n(E) = 2.8 \times 10^{15} \cdot \frac{Z_1Z_2}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}} \cdot \frac{m_1}{m_1 + m_2} \]  

(1-2)

where \( S_n(E) \) is the nuclear stopping power as a function of energy, \( Z_1 \) is the ion atomic number, \( Z_2 \) is the target material atomic number, \( m_1 \) is the ion mass, and \( m_2 \) is the target material mass. The nuclear stopping mechanism dominates for low energy implants and implants with high ion masses, while the electronic stopping mechanism dominates for high energy (MeV) implants and implants with low ion masses. Both electronic and nuclear stopping mechanisms need to be accounted for when determining the total energy loss as a function of depth into the sample. This can be modeled in the following equation:

\[ \frac{dE}{dx} = -N[S_n(E) + S_e(E)] \]  

(1-3)

where \( N \) is the atomic density of the target material. This combination of nuclear and electronic stopping is what determines the range or depth that the ions travel into the material. The ion projected range is often referred to as \( R_p \), which follows a Gaussian distribution. As the ion loses energy through nuclear and electronic stopping, it
transfers some of this energy to the lattice of the target material causing Frenkel pair defects. A Frenkel pair refers to a pair of interstitial and vacancy point defects and is created when a crystalline atom is displaced off its lattice site. For this work, it is assumed that 15 eV of energy is required to displace a Ge atom off its lattice site. The distribution of vacancies created also follows a Gaussian type and is referred to as \( R_d \).

Once a critical concentration of point defects is created, the semiconductor material turns amorphous during a first order phase transformation. This critical density is dependent on the ion mass, dose, implant energy, and temperature of the substrate. In this work, the critical density is referred to as the threshold damage density. Oftentimes, the target material is pre-amorphized with a heavy ion species prior to implanting with dopant ions. This effectively reduces channeling and has been shown to increase electrical activation upon SPEG.

### 1.4 Introduction to the SPEG Process

Once a critical amount of damage is created through ion implantation, an amorphous layer is created through a first order phase transformation. The damage can be recovered through a process called solid phase epitaxial growth (SPEG), where the amorphous material adopts the crystalline structure of the underlying seed crystal [4]. This occurs on the atomistic level through the nucleation of an atomic ledge, followed by the lateral propagation of this ledge [5]. On a local scale, this growth interface is expected to be atomically sharp.

SPEG is different than vapor or liquid phase epitaxy in that solid phase epitaxy involves a solid-solid growth interface. This means that SPEG is not concerned with the flux of atoms to the \( a/c \) interface and surface diffusion does not play a role in the growth process [6]. SPEG is also quite different that other solid-solid crystallization models,
such as grain growth, in that SPEG is limited in one dimension. In classical nucleation and growth, grains take on preferred shapes due to differences in surface energy. This brings multiple grains and crystallographic orientations into play. 1D SPEG is limited to only one crystallographic orientation, so the growth is limited only by the geometry of the sample and not surface energy.

SPEG is a thermally activated process in which the amorphous layer recrystallizes from the \( a/c \) interface up to the surface as seen in Figure 1-2. SPEG for Si has an activation energy of 2.7 eV, which is significantly higher than the 2.17 eV reported for Ge [7-11]. Consequently, the recrystallization temperatures for Si are typically much higher than Ge.

SPEG is technologically important in that it is one of the most common methods to achieve electrical activation of dopant atoms in semiconductors. In this process, a pre-amorphization implant is typically used to create a continuous amorphous layer. This is achieved through heavy ion implantation, such as Ge\(^+\). This allows for reduced channeling during the dopant implant, which is advantageous for the realization of ultra shallow junctions. It is also well understood that dopant atoms transition from interstitial to substitutional sites during the SPEG process, resulting in electrical activation. SPEG effectively increases the activation percentage for Si and Ge, which further increases the value of this process.

Many factors can influence the SPEG rate, such as stress, temperature, crystallographic orientation, electrically active impurities, and electrically inactive impurities. The following sections will discuss the dependencies most important for this body of work.
1.5 Temperature Dependence of SPEG

The SPEG velocity increases with temperature through the following Arrhenius relationship:

\[ v = v_0 \exp \left( \frac{-\Delta G}{kT} \right) \]  \hspace{1cm} (1-4)

where \( v_0 \) is a temperature independent prefactor on the order of \( 1 \times 10^7 \text{ m/s} \), \( \Delta G = 2.17 \text{ eV} \) is the activation energy for Ge, \( k=8.62 \times 10^{-5} \text{ eV/K} \) is Boltzmann’s constant, and \( T \) is the absolute temperature [11-15]. The activation energy and velocity prefactor can be found from the slope and y intercept of the Arrhenius line.

1.6 Dopant and Composition Dependence on SPEG

1.6.1 Electrically Active Impurities

The effect of dopant atoms on SPEG velocity depends on whether the impurity is electrically active or inactive. Electrically active dopants like B, Al, As, and P tend to increase SPEG velocity in Si and Ge, which has been explained by a Fermi-level shifting model [11, 16-22]. This model relates structural changes at the interface to the Fermi level. It follows the assumption that the ratio of charged to uncharged kink sites present at the \( \alpha/c \) interface is Fermi level dependent. If we consider a doped semiconductor, then we can express the enhancement in velocity, \( v \) as:

\[ v = v_i \left[ 1 + \frac{C_B}{n_i} g \exp \left( -\frac{E^I_F - E^P_{\alpha/c}}{kT} \right) \right] \]  \hspace{1cm} (1-5)

where \( v_i \) is the intrinsic velocity, \( C_B \) is the concentration of dopant, \( n_i \) is the intrinsic carrier concentration at \( T \), \( g \) is a degeneracy factor, \( E^I_F \) is the Fermi level of the intrinsic material, while \( E^P_{\alpha/c} \) is the energy level at the \( \alpha/c \) interface from the charged site. One can see that a greater shift away from the intrinsic Fermi level results in a larger increase in SPEG velocity.
SPEG rate enhancement in Ge does not occur until $5 \times 10^{19} \text{ cm}^{-3}$ for As, $1 \times 10^{19} \text{ cm}^{-3}$ for Al, and $2 \times 10^{19} \text{ cm}^{-3}$ where typical enhancements are on the order of 1.5-5x [11, 17]. A compensating effect was found for α-Ge regions which contained equal concentrations of n and p-type dopants. Ge SPEG was enhanced for P concentrations between $1 \times 10^{18}$ - $5 \times 10^{19} \text{ cm}^{-3}$, while a SPEG reduction occurred above $4 \times 10^{20} \text{ cm}^{-3}$ due to supersaturation and P precipitation [23].

Ho et al. studied the effect of dopant enhanced regrowth for different crystallographic orientations and observed a constant enhancement factor among the [100], [110], and [111] directions for both B and P type dopants [24]. While a tenfold enhancement was observed, no TEM analysis was performed to confirm whether crystalline quality was improved from the dopants. The effect of electrically active dopants was also studied for patterned Si SPEG. It was determined that dopants enhanced SPEG velocity in an isotropic fashion, which confirms that the interface curvature effect is independent of the electronic effect that controls the enhancement in SPEG velocity [25].

1.6.2 Electrically Inactive Impurities

Some common electrically inactive impurities that affect SPEG include H, O and C. Atomic H can be introduced at the surface from the oxidation reaction or from water vapor in the ambient [11, 26]. Once introduced, H can quickly diffuse through the amorphous layer to the α/c interface. It is believed that H segregates on the amorphous side of the α/c interface during SPEG, causing a reduction in velocity by passivating crystallization sites [10, 11, 27]. However, the presence of H is believed to be less pronounced in Ge relative to Si since H diffuses much slower in Ge and Ge does not
form a stable oxide. Nonetheless, a concentration of $6 \times 10^{18}$ H/cm$^3$ has been observed to cause a 3.7 fold reduction in SPEG velocity in Ge [11].

The presence of O and C impurities can retard SPEG velocities in Si and Ge [28]. Since the Fermi level shifting model does not apply to electrically inactive impurities, it is assumed that these impurities negatively affect the migration kinetics since additional energy is needed to incorporate an impurity atom in non-substitutional sites within the lattice [29, 30]. C and O impurities in Si have shown to promote the formation of twins on {111} planes, and was found to be highly dependent on solute concentration. Impurities were found to affect the interface stability, leading to non-planar a/c interfaces and twin formation [31].

1.6.3 Composition Dependence

SPEG rate measurements have been conducted using time resolved reflectivity (TRR) of SiGe alloys of varying composition. Arrhenius plots showed a decrease in activation energy from 2.64-2.19 eV for increasing Ge content [14]. Interestingly, a linear relationship was not observed between the activation energy and composition [32, 33]. This was explained in terms of 2 components which affect activation energy: a bond breaking energy and a bond reorientation energy. It was concluded that variations in the reorientation energy was non-linear with composition due to varying amounts of strain in the lattice. The activation energy reached a maximum for alloys near Si$_{0.8}$Ge$_{0.2}$ compositions before decreasing down to 2.17 eV for increasing Ge content.

Other impurities such as Ni or In have shown to increase SPEG in Si by more than a factor of 300 [34-36]. This was attributed to metal diffusion to the a/c interface forming nuclei for SPEG to take place.
1.7 Stress Dependence of SPEG

1.7.1 Hydrostatic Stress Dependence

The effect of hydrostatic stress on SPEG velocity has been studied by several authors using a high pressure diamond anvil cell [15, 37-43]. For both Si and Ge, the application of hydrostatic stress in the GPa range increases the velocity of SPEG. This enhancement can be explained thermodynamically since the SPEG process is characterized by a negative activation volume. This means that the transition from the amorphous state to the activated state is characterized by a negative volume change. This volume change is independent of dopant concentration and dopant type. The negative sign implies that the velocity is enhanced by the application of pressure, which can be up to 2 orders of magnitude for ~5 GPa of stress. The stress dependence on SPEG velocity can be expressed through the following equation:

\[ v = v_0 \exp \left( \frac{-\Delta G + P\Delta V}{kT} \right) \]  \hspace{1cm} (1-6)

where \( v_0 \) is the pre-exponential, \( \Delta G \) is the activation energy, \( P \) is pressure, and \( \Delta V \) is the activation volume [15]. From this equation, one can mathematically see how a negative activation volume would be enhanced by pressure. Aziz et al. have measured the activation volume for Si and Ge to be -0.28\( \Omega \) and -0.45\( \Omega \), respectively, where \( \Omega \) is the crystalline atomic volume. The fact that Ge has a more negative activation volume than Si implies that the application of pressure has a larger effect on SPEG kinetics for Ge.

1.7.2 Uniaxial Stress Dependence

In contrast to hydrostatic stress, it is well known that the application of uniaxial stress can cause drastically different changes in the SPEG velocity. Carter and Aziz conducted 3 point bending experiments to study the effect of non-hydrostatic stress.
(\sigma_{ij}) on Si SPEG [44-46]. The experiments were done by elastically bending Si with an amorphous layer present, while annealing the sample to measure SPEG rates. The conclusion from the experiments was that in plane tension enhanced SPEG kinetics, while in plane compression slowed SPEG kinetics. Aziz was able to describe stressed SPEG using the following equation:

\[ v = v_0 e^{\frac{\Delta V_{ij} \sigma_{ij}}{kT}} \]  

(1-7)

where \( \Delta V_{ij} \) is the activation volume tensor and \( \sigma_{ij} \) is an arbitrary stress. The expression is similar to the expression for hydrostatic pressure, except the numerator of the exponent is replaced with an activation strain tensor (\( \Delta V_{ij} \sigma_{ij} \)). The activation volume \( \Delta (V_{ij}) \) is given by:

\[ \Delta V_{ij} = kT \frac{\partial \ln(v)}{\partial \sigma_{ij}} \]

The activated state for stressed SPEG was described as expansion in the two in-plane directions and a contraction in the direction normal to the surface large enough to make the overall volume change negative.

This model was expanded upon by Rudawski, who showed finite limits to the velocity under compressive stress [47]. Wafer bending experiments for ultra thin Si have shown that compression retards SPEG up to values of -0.5 GPa at which point the velocity plateaus. Interestingly, the application of tensile stress did not appreciably affect SPEG velocities, even up to 1.5 GPa of applied stress. The relative decrease in SPEG velocity with compression was shown to be independent of annealing temperature. A dual timescale model was proposed for SPEG, which consisted of nucleation of an atomic ledge and propagation of the ledge along the interface.
Considering this atomistic model, it was proposed that in-plane compression retards the velocity by increasing the time required for a crystalline island to propagate along that ledge.

Uniaxial stressed SPEG for Ge substrates remains widely unstudied. The application of in-plane tensile stress has shown to reduce threading dislocations in SiGe alloys layers grown in Si by means of a strain stabilization technique [48]. Another study showed that high in-plane stresses can be generated in Ge arising from the incorporation of dopant atoms that differ in size from the host lattice[9]; however, the calculated stresses from this experiment were low compared with uniaxially stressed samples. Another study showed that in-plane compressive stresses were generated during Kr$^+$ implantation into Ge, where the generated stresses increased with dose at a fixed implant energy [49]. The generated stresses led to dramatic swelling of the Ge surface, but this study lacked a SPEG correlation.

1.8 The Effect of α/c Interface Roughness

While planar unstressed SPEG is known to occur with root mean square (rms) roughness of less than 2 nm, stressed SPEG can result in increased interface roughness [50]. SPEG was studied in strained SiGe layers and it was determined that rms roughness of the α/c interface can increase up to 80 nm as the interface proceeds up to the surface[50]. The SPEG velocity was reduced in areas of increased roughness, which also led to defective growth. It was also demonstrated that B doping can minimize the interface roughness by increasing the number of kink sites available for nucleation.

The influence of stress on interface roughness and SPEG was further studied in Si, where it was shown that compressive stress increased α/c interface roughness. The
application of tensile stress was similar to the unstressed case, where no interface roughening occurred [51]. When interface roughness did exist, it was found to increase over time [45, 52-54]. This was linked to an local concentration of stress near the trough of the α/c interface, which is less than that of the apex. This gives rise to a reduction in local interfacial mobility when under compressive stress. A kinetic model showed that the rate of roughening increased for smaller wavelengths of roughness[52].

Several researchers have theorized that even [100] SPEG is dominated by nanofaceting and regrowth along [111] terraces [12, 55, 56]. Molecular dynamic simulations at different temperatures have shown that the propensity to facet changes with temperature and could affect interface roughness[12]. While this effect has not been directly correlated with SPEG velocity, it may be responsible for changes in {111} defect formation. Rechtin et al. studied the effect of temperature on defect formation in (111) oriented Si. At low temperatures, a slower regrowth velocity and reduced nucleation rate yielded lower number densities of {111} defects. At higher temperatures, the size of the defects parallel to the (111) surface was observed to increase [57].

1.9 Orientation Dependence of SPEG

The orientation dependence on SPEG refers to the effect of crystallographic orientation of the substrate on the velocity. The substrate orientation dependence on Si SPEG was measured by Csepregi annealing implanted wafers cut at different angles away from the (001)[58]. The Rutherford Backscattering (RBS) technique was then used to measure the SPEG velocities at 550°C. The highest SPEG velocity was found to exist for the [001] direction, which was nearly 25 times greater than the [111] and 3
times greater than the [110]. All orientations had the same activation energy, so the variation in velocity derives from the pre-exponential factor ($v_0$).

A bond rearrangement model was used to explain the orientation dependence [16, 59]. An amorphous atom can recrystallize only if it is attached to 2 undistorted crystalline atoms. For diamond cubic crystal structures, there are different numbers of amorphous atoms at the amorphous crystalline (α-c) interface that are needed to attach to a crystalline atom with 2 undistorted bonds depending on the orientation. This number is 1, 2, and 3 for [001], [011], and [111], respectively as seen in Figure 1-3 [60]. This gives rise to a minimum velocity at the [111] orientation and a maximum velocity at the [001] orientation. The entire orientation dependence for Si can be seen in Figure 1-4.

Linear velocities exist for the [100] and [110] directions, but the [111] direction displayed bimodal growth for Si. The slow regime in the first 100 nm was attributed to a higher density of twin defects, as observed in angled XTEM experiments [57]. The fast regime of the bimodal growth for [111] Si was marked by a lower density of larger twins, but a highly non-uniform α/c interface. The amount of dechanneling observed in RBS for [111] was much greater than in [100] and [110] oriented samples. The higher amount of dechanneling was believed to be related to the amount of residual defects in the regrown layer. This high concentration of defects was also observed within 16° of the 111 axis, through RBS measurements. These defects were characterized as large twins using electron diffraction in TEM [57].

It has been hypothesized that the presence of defects retard the SPEG velocity near the [111] orientation[61], and recent kinetic lattice Monte Carlo simulations have
addressed the influence of defects on velocity [60, 62-65]. Substrate orientation models that neglect the influence of defects tend to overestimate experimental velocities [61], while models that do take into account defect formation match better with experimental velocities [60, 65].

Thus far, there are only velocities for 3 different substrate orientations for Ge in the literature [59, 66]. Of these velocities, the normalized [111] velocity matches closely with that of Si, but the normalized [110] velocity is nearly double compared with Si. Investigation of the entire orientation dependence is warranted in this area if Ge will be incorporated into next generation devices. Knowledge of the substrate orientation dependence on SPEG is essential for understanding multidirectional growth and subsequent defect formation [25, 47, 67].

1.10 Effect of Implant Conditions

The most common implant variables include ion type, dose, dose rate (flux), implant temperature, and implant energy. Ion irradiation usually induces amorphization of the target material, but can also induce recrystallization of the amorphous layer depending on sample temperature and ion beam parameters [68-70]. Ion beam induced crystallization is a process by which the amorphous layer can recrystallize upon implantation due to the production of point defects at the $\alpha/c$ interface, typically from a high energy implant [71]. This promotes a dynamic rearrangement of dangling bonds at the interface, contributing to SPEG. It was shown that regrowth rate decreases with increasing dose rate and increases with increasing ion mass [71]. This implies that ion induced recrystallization occurs by mobile point defects created at the $\alpha/c$ interface [69, 72-75]. Ion induced recrystallization only occurs in a temperature range where the thermal process is inhibited and follows an Arrhenius temperature dependence with an
activation energy of \( \sim 0.3 \) eV for Si. The critical temperature is referred to as the reversal temperature \( (T_R) \) since amorphization is reversed and crystallization begins. This critical temperature is near 200°C for Si[76]. Thus far, there is limited knowledge as to how implant conditions affect SPEG in Ge [77-79]. Ion induced recrystallization is less apparent in Ge, possibly due to its low threshold for amorphization.

1.11 SPEG Mechanisms

Several theories have been proposed for what governs the SPEG process. Suni \textit{et al.} has proposed a model based on the number of mobile point defects at the \( \alpha/c \) interface[17]. Based on this correlation, a higher number of vacancies at the \( \alpha/c \) interface would enhance the bond breaking process, which precedes atomic rearrangement during recrystallization. This argument is substantiated by the fact that the activation energy for epitaxial growth matches well with the energy of vacancy formation for Si and Ge [6, 17, 61, 80, 81]. In this case, the rate of defects diffusing to the interface should change with time or thickness of the amorphous layer, but we know this is not observed experimentally[6]. Presumably, the rate of defect diffusion should be isotropic in amorphous materials and cubic crystals, yet a substrate orientation dependence is observed with SPEG [59, 66, 81, 82]. In addition, it was later calculated that the self diffusion coefficient of Ge is too low to account for the growth rate [15]. Other theories have proposed that kink sites or dangling bonds at the interface control the SPEG process. In this theory, dangling bonds help reconstruct the random network of the amorphous solid into a crystalline network [83]. This theory seems plausible since the number of charged kink sites increases with doping, as does the SPEG rate. The mobility of dangling bonds is also increased with pressure since the transition state
has a lower local volume (negative activation volume). The most commonly accepted theory of SPEG is a bond rearrangement at the α/c interface since the Si-Si bond strength (2.5 eV) corresponds well to the activation energy of SPEG\cite{83, 84}. The amorphous phase is composed of a combination of fivefold and sevenfold rings, which need to conform to a sixfold ring of the diamond crystal substrate. In this theory, bond breaking and bond forming is the process by which sixfold rings are achieved \cite{5}.

### 1.12 SPEG for Patterned Si Substrates

Although 1D SPEG is often studied in the literature, 2D SPEG is much more applicable to device processing since patterned wafers are often used. A 2D interface involves regrowth in multiple directions and is therefore more complicated than 1D SPEG. The substrate orientation dependence on SPEG gives rise to an overlap of regrowth fronts, creating what is known as a mask edge defect. The following sections will highlight some of the relevant work done for Si substrates so that it can be compared with Ge in the research chapters.

#### 1.12.1 Pinned Interface

A pinned α/c interface is defined as one which has only convex curvature and intersects the surface. Cerva and Kusters were the first to report mask edge defects in pinned interface structures in Si\cite{85}. The origin of the defect was linked with the anisotropy of the substrate orientation dependence, which caused the evolving [001] and [110] fronts to overlap. The defect was noticed to form within the regrown layer and proceed up the surface. Saenger \textit{et al.} studied a similar structure in (001) and (011) Si substrates and presented a nanofacet model of SPEG \cite{55, 86}. In this model, crystallization proceeds quickly, until the growth is faceted on slow \{111\} planes. Eventually, mask edge defects form on these \{111\} planes, which are 54.7° away from
the (001) surface and 35.3° away from the (011) surface [87]. This facet model was later supported by lattice kinetic Monte Carlo simulations showing similar evolution [63, 64].

The effect of pattern induced stress was studied in (001) Si by Rudawski et. al and was created through successive implants of $1 \times 10^{15}$ Si$^+$/cm$^2$ at 20 and 60 keV into a silicon nitride patterned sample [47]. It was determined that the presence of the nitride mask significantly affected the mask edge defect formation. When the nitride was removed prior to annealing, mask edge defects formed within the regrown layers. However, the presence of the nitride significantly reduced the defect formation. This was attributed to a tensile stress created by the nitride. In all cases, a band of EOR defects formed near the original α/c interface.

Further investigations of this stress effect revealed that compressive stresses enhanced mask edge defect formation, while unstressed samples reduced defect formation. Stress was applied to patterned samples by wafer bending during the anneal [47]. Defect formation for the compressed samples implies that ratio of the [100] to [110] was altered due to the stress. Interestingly, applied tension was found to result in defect suppression, similar to the unstressed case.

The influence of dopant enhanced SPEG on mask edge defect formation was studied at a range of energies for As$^+$ implants in Si [88]. In theory, one could tailor a dopant implant such that the projected range of the dopant ion is near the nucleation site of the mask edge defect, thus suppressing defect formation. However, it was concluded that such doping effects did not significantly influence mask edge defect formation.
1.12.2 Unpinned Interface

An unpinned \(\alpha/c\) interface is defined as one that does not intersect the surface at any point and is therefore no subjected to surface pinning effects. Planar 1D SPEG was studied with patterned SiN overlayers in Si substrates and a reduction in SPEG velocity was found to occur in areas under the pattern[89]. A “body effect” was invoked to account for the reduction in velocity, where the rigidity of the SiN could reduce the mobility of Si atoms in the underlying \(\alpha/c\) interface. The presence of H released from the SiN pattern during the anneal could have also played a role in the reduction of SPEG velocity [26, 27, 61].

The recrystallization of unpinned interfaces which have both convex and concave curvature (2D) was recently investigated in Si substrates [25, 47, 67]. This type of interface was created in Si using successive implants of 20, 60 and 160 keV with doses of \(1 \times 10^{15} \text{ Si}^+/\text{cm}^2\), \(1 \times 10^{15} \text{ Si}^+/\text{cm}^2\), and \(3 \times 10^{15} \text{ Si}^+/\text{cm}^2\). Upon annealing, mask edge defects began to form and two triangular \(\alpha\)-Si regions remained at the surface due to the slow moving [111] and [110] fronts. This caused the a/c interface to facet on \{111\} planes during SPEG, causing triangular amorphous regions to remain near the mask edge. In all cases, the evolution of the \(\alpha/c\) interface was found to be independent of annealing temperature.

1.12.3 SPEG for Non-planar Surfaces in Si

Non-planar surfaces are particularly of interest recently since the advent of the FinFET device. These devices allow for increased scalability since they are designed vertically from the surface. They are often referred to as “tri-gate” transistors since the gate covers three sides of the device, which allows for reduced threshold voltage and steeper sub-threshold slopes[90, 91]. One of the central challenges in designing a
FinFET device is reducing parasitic resistance, which can stem from the extension and source/drain regions [92]. One of the ways to reduce this resistance is with angled ion implantation and SPEG[93]. This technology has been explored for Si and is known to cause \{111\} stacking fault formation in the middle of the fin and polycrystalline growth in the upper regions of the fin [94, 95]. Similar fin structures have also been studied in Ge and are observed to be far less defective than Si, but stacking fault defects become more prominent as the fin width decreases and devices are scaled down [96, 97]. Thus far, no research has explored ways to reduce the stacking fault formation in non-planar Ge structures.

Several researchers have studied the effect of a free surface on stacking fault formation [98-100]. SPEG was studied for non-planar trench structures in Si surrounded by SiO$_2$. The trenches were implanted with $1 \times 10^{15}$ Si$^+/cm^2$ at 40 keV, which created an $\alpha$-Si layer pinned by SiO$_2$. Upon annealing, triangular $\alpha$-Si regions pinned against the corner of the trench due to the slow velocity of the [111] front. The fully recrystallized structure resulted in a region of defective Si in the corner. When the SiO$_2$ was removed prior to annealing, the amount of corner defects was reduced. The results indicated that the presence of the SiO$_2$ hindered growth at the point of attachment, forcing the Si to break the Si/SiO$_2$ bond to complete the SPEG process. Saenger et al. studied rectilinear patterned structures in Si and found that trench structures aligned in the [100] direction resulted in less stacking faults in the corner regions than trenches aligned in the [110] directions [55, 98]. In addition, a 5 hour anneal at 1325°C further reduced defect formation for the [100] aligned samples. If Ge is to be incorporated in
future FinFET devices, ways to control defect formation is essential in order to optimize the performance.

1.13 Defect Formation Upon SPEG

Ion implantation introduces an excess population of point defects in the target material. Several different types of defects can form during the SPEG process. These defects are categorized based on the type of damage created in the crystal.

1.13.1 End of Range Defects

For amorphizing implants, end of range (EOR) defects form near or just beyond the original α/c interface upon annealing [101, 102]. The source of this type of defect is believed to be excess interstitials that come to rest just beyond the α/c interface. In Si, it is well known that these extrinsic defects can cause device leakage. In addition, transient enhanced diffusion (TED) has been linked to EOR dissolution during annealing [103-107]. TED is the anomalous diffusivity enhancement from dopant atoms interacting with defects. TED is well known to cause electrical deactivation in Si, where boron interstitial clusters are formed from excess interstitials diffusing from the EOR to the doped region [108, 109]. Recently, this same phenomenon was observed for B dopants in Ge[110].

The nature of the defects differs greatly between Si and Ge. EOR damage in Ge is characterized by small 5-10 nm interstitial clusters and dislocation loops, while these defects can be orders of magnitude greater in size in Si, and can also take the form of \{311\} defects [103, 111, 112]. The nature of the defects depends greatly on the implant and annealing conditions used. EOR density decreases with decreasing implant temperature since less interstitials are able to contribute to EOR formation [113, 114]. Likewise, increasing the implant temperature has the opposite effect. It has also been
demonstrated that increasing the implant dose and energy can increase the number of interstitials bound in the EOR region by several orders of magnitude [115]. EOR defects undergo a process called Ostwald ripening, which causes the defects to decrease in density and increase in size throughout the anneal. An example of EOR damage in Ge after a 1MeV, $2 \times 10^{15}$ Ge$^+/\text{cm}^2$ self implant and 11 minute anneal at 330°C is shown in Figure 1-5. The small size of EOR damage in Ge has been linked in part to the limited transport of self interstitials in Ge [116]. Self diffusion in Ge is largely driven by vacancies, which makes the formation of large dislocation loops more difficult in Ge. In addition, Ge has a lower threshold for amorphization [117], which limits the population of interstitials that are able to contribute to EOR. Unlike Si, EOR damage is highly unstable in Ge and can dissolve out at temperatures as low as 400°C [110].

### 1.13.2 Regrowth Related Defects

Regrowth related defects consist of regrowth related defects which form within the amorphous region. One of the most common type of regrowth related defects are hairpin or spanner dislocations. Hairpin defects nucleate when the advancing $\alpha/c$ interface encounters microcrystalline pockets at a slightly different orientation than the bulk substrate [102]. Hairpin dislocations are more prominent with a rough $\alpha/c$ interface, as this increases the number of pockets which serve as nucleation sites (Figure 1-6(a)). Results have shown that low temperature (liquid nitrogen) implantation can reduce hairpin formation by creating a smoother $\alpha/c$ interface[118]. It has also been theorized that hairpins nucleate from dislocation loops near the $\alpha/c$ interface, where the two ends of the truncated loops act as nucleation sites [119]. An example of a hairpin dislocation in Ge is shown in Figure 1-6(b). This type of defect nucleates at the $\alpha/c$ interface and
propagates up towards the surface in a characteristic “V” shape. In Si, hairpins were determined to be perfect dislocations with Burger’s vector of \(a/2[110]\) determined by diffraction contrast analysis [120].

Stacking fault defects are another type of regrowth related defect observed for Si and Ge. Stacking faults are 2D defects that are characterized by faulty stacking sequences. An intrinsic stacking fault has a stacking sequence of ABCBCABC, and is formed by an agglomeration of vacancies. An extrinsic stacking fault has a stacking sequence of ABCAABCA, and is formed by an agglomeration of interstitials. At the boundary of the stacking fault is a Shockley partial dislocation, which has a Burger’s vector equal to \(a/6[112]\) for FCC crystals. Although the perfect dislocation for FCC is of the [110] type, it is more energetically favorable for this dislocation to split into partials of the [112] type as seen in the following equation.

\[
a/2 [110] \rightarrow a/6 [121] + a/6 [21\overline{1}] \tag{1-5}
\]

Stacking faults are best imaged in a dynamical 2 beam condition in TEM. This results in a 2 fringe system, known as stacking fault fringes. The nature of stacking faults can be determined from the outer thickness fringes following the two-beam bright field/displaced aperture dark field imaging procedure of Williams and Carter [121], where intrinsic stacking faults start with a white fringe and extrinsic stacking faults start with a dark fringe for a 220 type \(g\) vector. In Si and Ge, these defects appear on the close packed (111) planes. An example of an intrinsic stacking fault in (111) Ge is shown in Figure 1-7.

Twin defects are another type of regrowth related defect observed in TEM for Si and Ge [60, 82, 94, 96, 97, 120, 122]. Twin defects can be thought of as a single
crystal region within another single crystal, where the two crystals share common lattice points. The stacking sequence for a twin is AB(C)BACB, where (C) represents the twin boundary between the two regions. In Si and Ge, twinning occurs on (111) planes during SPEG since there is a high probability that one of the three amorphous atoms will crystallize along the ledge in a defective manner [57, 59]. Occasionally, twin planes are repeated in a periodic fashion, known as microtwins. Twins and microtwins are typically observed through HRTEM, but can also be characterized through electron diffraction. Twinning causes the appearance of satellite spots occurring 1/3 the distance between adjacent (111) spots. In Si, it is well known that the presence of stacking faults and microtwins can cause device leakage[123] and high sheet resistance in spreading resistance profiling[124-126]. TEM evidence suggests that these defects are stable even after 20 minutes at 1000°C. In this regard it is valuable to understand the formation of these defects in Ge. Thus far, there is no documentation of SPEG for [111] Ge and subsequent stacking fault and microtwin defect formation.
Figure 1-1. Schematic of an ion implanter.

Figure 1-2. A schematic of the a/c interface evolving over time in the SPEG process.
Figure 1-3. Schematic showing the number of amorphous atoms needed to attach to 2 crystalline atoms at different orientations.

Figure 1-4. Plot of regrowth vs. substrate orientation for Si measured at 550°C [59].
Figure 1-5. A WBDF XTEM image of EOR defects in Ge. The sample was implanted at 1 MeV with $2 \times 10^{15}$ Ge$^+/\text{cm}^2$ and annealed at 330$^\circ$C for 11 minutes.

Figure 1-6. XTEM images of hairpin dislocation formation in Ge. Amorphous and microcrystalline pockets at the α/c interface produced by a 1MeV, $2 \times 10^{15}$ Ge$^+/\text{cm}^2$ implant (a) and an XTEM image of (110) Ge implanted at 1MeV, $1 \times 10^{15}$ Ge$^+/\text{cm}^2$ annealed at 330$^\circ$C for 885 min showing hairpin dislocations nucleating at the a/c interface (b).
Figure 1-7, PTEM images of stacking fault defects in (111) Ge implanted with $1 \times 10^{15}$ Ge$^+$/cm$^2$ at 1MeV and annealed at 330°C for 7.5 days. A 2 beam BF image of an intrinsic stacking fault (a) and an axial DF image of the same stacking fault in (b). “b” and “t” indicate the bottom and top of the sample, respectively.
CHAPTER 2
EXPERIMENTAL AND SIMULATION TECHNIQUES

The following sections will give background information to some of the most important material processing and characterization techniques used in this body of work. The exact recipes and procedures of these techniques will be elucidated in the experimental sections of subsequent chapters.

2.1 Material Processing

2.1.1 Electron Beam Lithography

Electron beam (E-beam) lithography is a process that uses a focused beam of electrons to form patterns in a resist material. Unlike traditional photolithography, which is limited by the wavelength of light, E-beam lithography is limited only by the forward scattering of electrons. This allows for the creation of much finer patterns with higher precision, but E-beam lithography requires a vacuum and more time for processing [127].

The system typically consists of an electron gun which generates the electron beam and an optical column which focuses the beam with a system of lenses. The sample surface is the target of the electron beam which contains either positive or negative resist. Positive resist softens upon exposure, while negative resist hardens upon exposure. After exposure, the sample is then immersed in a developer solution of MIBK (methyl isobutyl ketone), which exposes the pattern.

Despite the high precision of E-beam lithography, there are some disadvantages to the technique. Since an electron beam is required, the system must be held in a vacuum and is expensive. This scanning of the E-beam also takes longer than traditional photolithography, making it impractical for high volume production. Another disadvantage of E-beam lithography is electron scattering. When electrons enter the
resist, the backscattered electrons spread out and cover a much larger volume than the initial focused beam. When the beam scans 2 areas that are close to one another, the overlap of scattered electrons causes unwanted etching, known as the proximity effect. The line widths in this work were spaced several hundred nanometers apart to minimize this effect.

2.1.2 Reactive Ion Etching

Reactive ion etching (RIE) is a dry etch technique which results in anisotropic etching of the surface. The system consists of a cylindrical vacuum chamber with a sample platform in the middle. Gases such as SF$_6$, CH$_3$F, and C$_4$F$_8$ are fed in through the top of the chamber, where a plasma is created by a radiofrequency (RF) electromagnetic field. The chemically active plasma is then directed at the sample due to charge build up on the platen and then pumped out through the chamber bottom. As the ions reach the surface of the wafer, they not only get directed by an electric field, but also chemically react with the surface. This leads to an anisotropic etch of patterned wafers and is advantageous over wet etches, which typically result in isotropic etches. Parameters such as gas flow, power, pressure, and time can be adjusted to control the etch. A schematic of a typical RIE chamber can be seen in Figure 2-1.

2.1.3 Temperature Calibration and Annealing

To activate the SPEG process, the samples in this study were annealed in a quartz sample boat within a tube furnace. The tube furnace consisted of a 3 foot glass tube with a gas inlet on one end and an end cap on the other. All anneals were done with the sample boat positioned in the center of the furnace as seen in Figure 2-2. The temperature was calibrated before each anneal using a thermocouple, which rested on top of the sample boat. To avoid measurement errors, samples within each experiment
were annealed together. Temperatures ranging from 330-400°C were explored in this study and the error in all thermocouple readings was estimated to be ±1°C.

2.1.4 XTEM Sample Preparation

A focused ion beam (FIB) was used to prepare site specific samples for cross sectional transmission electron microscopy in this work. The FIB works by a focused beam of Ga⁺ ions accelerated at 30 keV towards the area of interest. A carbon rod evaporator system was used to deposit ~200 nm of C on the sample to protect the surface from Ga⁺ damage. In addition, a ~8×2×1.5μm layer of Pt was deposited in situ to further protect the sample during preparation as seen in Figure 2-3(a). Trenches were milled using the 5000 pA aperture as seen in Figure 2-3(b), and then progressively thinned with smaller currents until the sample was ~500 nm thick. At this point, the stage was rotated to 0° and undercut using the 300 pA aperture as seen in Figure 2-3(c). Further sample thinning with the 100 pA and 50 pA apertures were used until the sample thickness reached ~100nm as seen in Figure 2-3(d). During the final mills, the stage was rotated to 51° and 53° to preserve Pt at the surface. At this point, the samples were cut out placed onto a copper grid for imaging.

2.1.5 PTEM Sample Preparation

Traditionally, plan view samples are made by a standard polish and etch process, but this method consumes several mm² of implanted material. Since Ge material was in short supply for this research, plan view transmission electron microscopy samples were prepared using the FIB technique, which only consumes several μm² of material. In this technique, the bulk Ge sample was mounted edge-on so that the implanted surface was facing away from the ion beam. Then, Pt was deposited
near the edge of the implanted surface. Care was taken to deposit the Pt at 51° instead of 52° to avoid Pt damage on the implanted surface. Then, a trench was milled on one side of the sample as seen in Figure 2-4(a). Once the sample was thinned to ~1μm of thickness, the stage was rotated to 0° where the undercut and one sidecut were made, as seen in Figure 2-4(b). The sample was then welded to an Omniprobe needle using Pt and transferred to a Cu Omniprobe grid as seen in Figure 2-4(c)-(d), respectively. At this point, the samples were continually thinned from the bulk side down to ~100 nm thickness.

2.2 Material Characterization

2.2.1 Transmission Electron Microscopy

TEM is the most frequently used technique for microstructural characterization in this work. TEM uses a focused beam of electrons generated by a thermionic or field emission source and accelerated with 200 keV at the sample of interest. Considering that electrons contain a wave-particle duality, the wavelength (λ) of such electrons can be calculated from the following equation:

$$\lambda = \frac{\hbar}{\sqrt{2m_e e V_e}}$$

(2-1)

where $\hbar = 6.626 \times 10^{-34}$ Js is Planck’s constant, $m_e = 9.109 \times 10^{-31}$ kg is the mass of an electron, $e = 1.602 \times 10^{-19}$ C is the electric charge of an electron, and $V_e$ is the accelerating voltage. Under 200 keV, $\lambda = 2.5 \times 10^{-12}$ m, which gives rise to the ability to obtain nanometer scale features in the TEM.

Following electron generation, the electrons are guided by electromagnets through the TEM column which consists of various lens systems that focus the electron beam onto the sample. The condenser lens system serves to control the formation of
the initial beam, the objective lens system then focuses the beam onto the sample itself, and then the projector lens system expands the beam onto a phosphor screen for viewing. An illustration of a TEM column and its components is shown in Figure 2-5.

The most common method to image amorphous layers is on-axis brightfield mode, where the objective aperture is aligned around the zone axis of the bulk crystal. Due to the difference in electron scattering from crystalline Ge and α-Ge, a phase contrast occurs. This allows for the measurement and characterization of amorphous layers.

The weak-beam dark field technique is another common technique for imaging defects in crystals. The sample is typically tilted away from the [110] zone axis along a kikuchi band. In the SAD pattern, the diffracted and transmitted spots will overlap the kikuchi band, creating a 2 beam condition. The vector from the transmitted to diffracted spot is referred to as the g-vector. Once the 2 beam condition is aligned in both brightfield and dark field mode, the incident beam is tilted in dark field mode such that the transmitted beam is translated in the –g direction and becomes “weak”. Then, an objective aperture is placed over this weak beam.

When imaging dislocations and stacking faults under 2 beam conditions, the defect will only be visible if the following equation is satisfied:

\[ g \cdot (b \times \lambda) \neq 0 \]  

(2-2)

where \( b \) is the Burger’s vector of the defect. By tilting to different g vectors, a Burger’s vector analysis can be done to determine \( b \) for different defects.
2.2.2 Amorphous Layer Measurements and Velocity Calculations

In order to measure SPEG velocities, the amorphous layer must be quantified. This was done by taking XTEM images at various annealing times and importing the image into ImageJ © analysis software. For each sample, the amorphous layer thickness was measured from the surface to the beginning of the α/c interface. By plotting amorphous layer thickness as a function of annealing time, a linear fit could be used to determine the rate (slope) of SPEG. Since SPEG velocity is essentially a slope, the following equation was used to determine the standard deviation ($\sigma$) of the velocities.

$$\sigma = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2} \sqrt{\sum_{i=1}^{n} (x_i - \bar{x}_i)^2}$$

(2-3)

where $y_i$ is the value of the amorphous layer thickness, $\hat{y}_i$ is the calculated value for the amorphous layer thickness based on the slope, $x_i$ is the annealing time, and $\bar{x}_i$ is the mean annealing time. The standard deviation is expressed as positive and negative error bars throughout this work.

2.2.3 Scanning Electron Microscopy

Scanning electron microscopy is a common technique for imaging sample surfaces. Similar to TEM, an electron beam is generated by thermionic or field emission means and then directed at the area of interest. Unlike TEM, electrons in an SEM system are directed to different detectors which give rise to different methods of contrast. Secondary electrons are formed from inelastic collisions between electrons and atoms in the sample. This method of imaging is typically used for resolving small features on the sample surface. Alternatively, a backscattered detector can be used to provide information on the atomic number ($Z$) of the sample. Backscattered electrons
are formed from elastic collisions with atoms in the specimen, thus samples with higher (lower) Z number will produce more (less) elastic collisions and form a brighter (darker) contrast. The accelerating voltage for SEM is typically much less than 40 keV and the majority of samples in this work were imaged using 5 keV. Usually a conductive coating is deposited on the surface of the sample to prevent charging, but this was not necessary for this work due to the high conductivity of Ge.

2.2.4 Atomic Force Microscopy

AFM is a technique where a Si cantilever is scanned across the surface of the sample to measure the height and roughness of surface features. When the cantilever tip is brought in close proximity of the surface, forces such as Van der Waals, chemical bonding, electrostatic forces, and magnetic forces result in the deflection of the cantilever. By focusing a laser on the top surface of the cantilever, the deflection of the cantilever can be used to determine a force \( F \) through Hook's law:

\[
F = -kz
\]

where \( k \) is the stiffness of the cantilever and \( z \) is the distance the cantilever is bent.

There are 2 basic modes of AFM: contact and tapping mode. Contact mode involves a cantilever that is constantly in contact with the sample surface. The contact force is set by a piezoelectric positioning element. As the tip scans back and forth across the sample, the height is constantly adjusted to maintain a constant deflection. In this fashion, the height of the surface features can be inferred from the movement of the tip. Tapping mode is another AFM technique which uses an oscillating cantilever, vibrating at its resonant frequency. As the tip is scanned across the sample surface, it lightly taps the surface. The changes in height result in changes in the vibrating
frequency. Tapping mode results in high resolution images since the tapping action imparts a vertical force and minimizes shear forces. The AFM for this work was done in tapping mode with Si cantilevers that had a 2nm tip radius and a resonant frequency of 320 kHz.

2.2.5 Tencor Stress Measurement Technique

The Tencor stress measurement technique is a highly accurate way to measure the radius of curvature of a wafer caused by the stress of a thin film. The system measures the radius of curvature through a laser, which maps the height of the sample at various points (Figure 2-6). By measuring the sample before and after the deposition of a thin film, the residual stress ($\sigma_T$) can be calculated by the change in curvature.

$$\sigma_T = \left[ \frac{E}{(1-\nu)} \cdot \frac{h^2}{6Rt} \right]$$ (2-5)

where $E$ is the elastic modulus (1.03×10^{11} Pa for Ge), $\nu$ is Poisson’s ratio (0.26 for Ge), $h$ is the substrate thickness (3.5×10^{-4} m for this work), $R$ is the substrate radius of curvature (m), and $t$ is the film thickness (m).

Residual stress is a function of intrinsic stress $\sigma_i$ and thermal stress $\sigma_{th}$ as denoted in the following equation:

$$\sigma_T = \sigma_i + \sigma_{th}$$ (2-6)

The thermal component can be expressed as:

$$\sigma_{th} = \left( \frac{E_f}{1-\nu_f} \right) \Delta a \Delta T$$ (2-7)

where $E_f$ and $\nu_f$ are Young’s modulus and poisson’s ratio for the film, respectively and $\Delta a$ and $\Delta T$ are the differences in thermal expansion coefficients and difference between the deposition and measurement temperatures, respectively [128].
2.2.6 Raman Spectroscopy

Raman spectroscopy is a technique for studying the vibrational and electronic properties of semiconductors using the inelastic scattering of light. In this technique, a focused laser is used to illuminate the sample. The light that is scattered from the sample can either occur without a change in energy from the incident photon (Raleigh), or with a change in energy (Raman). This light is then collected with a lens and directed to an interference filter to obtain the Raman spectrum. The amount of energy lost is seen as a change in wavelength of the incident photon. Since only about 0.001% of incoming photons produce Raman scattering, the main challenge of this technique is differentiating Raman from the intense stray light that produces Raleigh scattering. This is usually accomplished with a Raleigh filter, which increases the signal to noise ratio.

Raman spectroscopy is typically used for identifying phases, chemical composition, and crystal structure, but the technique can also be used to measure stress [129-135]. If we consider a monochromatic laser light with angular frequency \( \omega \), the light is then scattered inelastically by the crystal. The Raman effect is given by:

\[
\omega = \omega' \pm \Omega
\]  

(2-8)

where \( \omega' \) is the angular frequency of the scattered photon and \( \Omega \) is the angular frequency of the interacting phonon. The inelastically scattered photons will thus display a Raman shift equal to the frequency of the lattice vibration \( \Omega \). This method is unique in the fact that it is the only non destructive, spectroscopic technique that can offer information about stress. When a crystalline semiconductor is under compressive stress, the reduction in lattice spacing causes the frequency of oscillation to decrease. This can be seen if we consider a one dimensional lattice with a
2 masses \( m_1 \) and \( m_2 \) positioned alternately, the frequencies of oscillation \( v \) can be expressed as:

\[
v_{\pm} = \alpha \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \pm \alpha \left[ \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin(kd)}{m_1 m_2} \right]^{1/2}
\]

where \( \alpha \) is a force constant, \( k \) is the wavenumber, and \( d \) is the lattice constant [136].

From this equation, it is evident that a smaller lattice constant results in a shift to lower frequencies. The opposite is true for tensile stresses; therefore, the Raman spectrum shifts to lower frequencies when under compressive stress and higher frequencies when subjected to tensile stress [137]. This shift in the Raman spectrum is linear with applied stress and can be expressed for Ge by:

\[

\tau_{Ge} = (40 MPa) \cdot \Delta \omega (cm^{-1})
\]

where \( \tau \) is the residual stress and \( \Delta \omega \) is the change in frequency from the unstressed to stressed conditions. Most recently, Raman spectroscopy has been used to quantify stresses in patterned Si devices caused by mask edge defect formation [135, 138]. This work uses Raman spectroscopy to do a similar experiment, but with patterned Ge substrates.

### 2.3 Simulation Techniques

#### 2.3.1 Level Set Methods and FLOOPS

The level set method is a numerical method that can accurately monitor the evolution of curved interfaces by embedding the position of the interface as a higher order equation. The level set method has a distinct advantage over traditional techniques that incur positive feedback error as the interface progresses. Level set methods have been used to simulate etching, deposition, surface diffusion, and the propagation of an \( w/c \) interface. The level set approach minimizes error by embedding
the interface position within a higher dimensional function. This is done by first initializing the interface in a Cartesian grid using the following equation:

$$\phi(x, y, z, t = 0) = \pm d$$  \hspace{1cm} (2-11)

where $\phi$ is the higher dimensional function. The function $\phi$ then evolves using an equation that contains the velocity of the interface.

$$\phi_t + F |\nabla \phi| = 0$$  \hspace{1cm} (2-12)

where $F$ is the velocity of the interface, $\phi_t$ is the time derivative of $\phi$ and $\nabla \phi$ is the spatial derivative of $\phi$. In this fashion, the value of $\phi$ is calculated for each time instant. The level set technique is especially useful in this work, where the epitaxial growth front moves in two dimensions simultaneously around a curved interface.
Figure 2-1. Schematic of a RIE chamber. A RIE consists of two electrodes (1 and 4) that create an electric field (3) meant to accelerate ions (2) toward the surface of the samples (5).

Figure 2-2. Schematic of the tube furnace used for annealing experiments.
Figure 2-3. SEM images at 52° of the FIB procedure for XTEM sample preparation showing platinum deposition (a), trench milling (b), sample thinning and undercut (c), and final thinned sample (d).
Figure 2-4. SEM and ion beam images at 52° of the FIB procedure for PTEM sample preparation. A SEM image of Pt deposition at sample edge with trench mill is shown in (a), SEM image of the undercut (b), Ion beam image of omniprobe liftout (c), and SEM image of sample mounted on omniprobe grid (d).
Figure 2-5. Schematic of a TEM column.
Figure 2-6. Schematic of the Tencor film stress measurement system. The radius of curvature (R) is measured by scanning multiple points across the wafer. The film thickness (t_f) and substrate thickness (t_s) are indicated above.
CHAPTER 3
AMORPHIZATION OF GERMANIUM AND SUBSTRATE ORIENTATION DEPENDENCE ON SPEG

3.1 Amorphization and TDD of Germanium

This section provides a summary of the amorphous layer depths measured by XTEM for implants that produced a continuous amorphous layer in this work. By performing a full damage density simulation using the SRIM code [139], the vacancy profile can be overlaid onto the XTEM images to determine the vacancies/(cm•ion) at the α/c interface. This can then be used to determine the critical damage $D_c$ (vacancies/cm$^3$) by multiplying by the dose. The critical damage is a measure of the critical vacancy population needed for amorphization to occur. In this way, the TDD (keV/cm$^3$) can be calculated using the following equation:

$$TDD = D_c \cdot E_d$$  \hspace{1cm} (3-1)$$

where $E_d$ is the displacement energy of Ge (15 eV). Since TDD is independent of energy and dose, a wide range of implant conditions can be directly compared. As seen in Table 3-1, the average TDD for Ge was calculated to be $2.7 \pm 1.2 \times 10^{22}$ keV/cm$^3$, which is significantly less than the reported TDD for Si ($7.5 \pm 1.5 \times 10^{22}$ keV/cm$^3$). This result indicates that it is easier to amorphize Ge than Si, which is consistent with literature findings [117]. The average critical damage was determined to be $1.8 \pm 0.8 \times 10^{22}$ vac/cm$^3$, which is roughly half of the atomic density for Ge ($4.42 \times 10^{22}$ /cm$^3$).
Table 3-1. Amorphous layer depth measured by XTEM along with critical damage and TDD calculated using SRIM. All substrates are (001) Ge for this table.

<table>
<thead>
<tr>
<th>Implant Energy (keV)</th>
<th>Dose (Ge/cm²)</th>
<th>α Layer Depth (nm)</th>
<th>Critical Damage (vac/cm³)</th>
<th>TDD (keV/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.0E+13</td>
<td>18.1</td>
<td>1.03E+22</td>
<td>1.54E+20</td>
</tr>
<tr>
<td>20</td>
<td>1.0E+14</td>
<td>21.8</td>
<td>1.09E+22</td>
<td>1.63E+20</td>
</tr>
<tr>
<td>30</td>
<td>2.0E+15</td>
<td>44.8</td>
<td>1.41E+22</td>
<td>2.11E+20</td>
</tr>
<tr>
<td>60</td>
<td>2.0E+15</td>
<td>73.6</td>
<td>2.14E+22</td>
<td>3.21E+20</td>
</tr>
<tr>
<td>90</td>
<td>5.0E+14</td>
<td>81.0</td>
<td>3.15E+22</td>
<td>4.72E+20</td>
</tr>
<tr>
<td>90</td>
<td>2.0E+15</td>
<td>107.0</td>
<td>1.26E+22</td>
<td>1.88E+20</td>
</tr>
<tr>
<td>120</td>
<td>2.0E+15</td>
<td>131.4</td>
<td>1.40E+22</td>
<td>2.10E+20</td>
</tr>
<tr>
<td>150</td>
<td>1.0E+14</td>
<td>118.9</td>
<td>9.13E+21</td>
<td>1.37E+20</td>
</tr>
<tr>
<td>150</td>
<td>2.0E+14</td>
<td>128.5</td>
<td>1.54E+22</td>
<td>2.31E+20</td>
</tr>
<tr>
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<td>5.0E+14</td>
<td>138.8</td>
<td>1.50E+22</td>
<td>2.25E+20</td>
</tr>
<tr>
<td>150</td>
<td>1.0E+15</td>
<td>145.8</td>
<td>2.11E+22</td>
<td>3.16E+20</td>
</tr>
<tr>
<td>150</td>
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<td>160.5</td>
<td>1.73E+22</td>
<td>2.60E+20</td>
</tr>
<tr>
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<td>234.3</td>
<td>3.89E+22</td>
<td>5.83E+20</td>
</tr>
<tr>
<td>1000</td>
<td>1.0E+15</td>
<td>828.6</td>
<td>1.70E+22</td>
<td>2.55E+20</td>
</tr>
<tr>
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<td>2.0E+15</td>
<td>856.7</td>
<td>2.14E+22</td>
<td>3.21E+20</td>
</tr>
</tbody>
</table>

AVG 1.80E+22 2.70E+20
STD DEV 8.09E+21 1.21E+20

3.2 Substrate Orientation Dependence of Ge

3.2.1 Introduction

Amorphization caused by ion implantation and subsequent solid phase epitaxial growth (SPEG) [37] is a common technique used to dope the source and drain regions of field effect transistors (FETs) [140]. With the renewed interest in Ge as an alternative material in complementary metal-oxide-semiconductor devices [2, 141-144], it is important to understand the recrystallization process and defects that form for this material. The SPEG orientation dependence for Si has been well studied, but relatively little knowledge is known for Ge. The SPEG process for Si shows a clear dependence on orientation where the regrowth in the [001] direction is about 25 times greater than
the [111] and about 3 times greater than the [011] [24, 59, 81, 82]. It is believed that the difference in SPEG rate is attributed to the number of amorphous atoms at the amorphous crystalline (α-c) interface that are needed to attach to a crystalline atom with 2 undistorted bonds. This number is 1, 2, and 3 for [001], [011], and [111], respectively [60, 62, 65]. It is also theorized that twin defect formation affects SPEG. Csepregi et al. has noted high defect densities within 16º of the [111] orientation for Si [59], and Monte Carlo simulations match reasonably well with the experiments [60].

The entire orientation dependence has been measured from [001] to [011] for Si, but so far, only 3 relative velocities along the major indices have been reported for Ge [59, 66]. The goal of this work is to measure the SPEG orientation dependence for Ge and characterize the resulting defect structures upon crystallization. In this regard, this work will also attempt to compare the SPEG process of Ge with past work done for Si.

3.2.2 Experimental

(001) Ge wafers with a resistivity of 0.02 Ω•cm and (011) Ge wafers with a resistivity of 56 Ω•cm were implanted with 1×10^{15} Ge^+/cm^2 at 1MeV using a 5SDH-4 tandem accelerator at Australian National University. The low background doping (<1×10^{17} As/cm^3) for these Ge wafers was not expected to affect SPEG velocities in this experiment [9]. A set of (001) Ge wafers were mechanically polished to a mirror finish at angles of 15º, 25º, 40º, 54.7º, 70º, and 80º away from the [001] and then implanted normal to the polished surface with the same implant (Figure 3-1). In this way, the polished surface was normal to the ion beam during implant. For all samples, this implant resulted in a continuous amorphous layer extending approximately 800 nm from the surface. The samples were then annealed in a tube furnace with flowing N_2 at 330ºC and the amorphous depths were measured at various times via cross-sectional
transmission electron microscopy (XTEM). Plan-view transmission electron microscopy (PTEM) was also used to characterize and quantify defect formation of the fully recrystallized structures for all orientations. An FEI DB235 focused ion beam (FIB) was used to prepare both XTEM and PTEM samples. A JEOL 2010F microscope operated at 200 kV was used for imaging XTEM samples, while a JEOL 200CX microscope operated at 200 kV was used for imaging PTEM samples.

3.2.3 Results

Figure 3-2 shows an XTEM annealing sequence of the SPEG process for (001) Ge (0°). The distance from the surface to the α/c interface marks the thickness of the amorphous layer, which gives rise to a SPEG velocity over many anneals. The regrowth of the amorphous layer was then measured at 330°C in this fashion for all 8 orientations.

The progression of the α/c interface for the 3 main directions ([001], [111], and [011]) is graphed in Figure 3-3. The SPEG velocities were relatively linear for these orientations. Unlike Si, which had a bimodal growth regime for the [111], the SPEG velocity for [111] Ge was constant throughout the annealing sequence [59, 82].

A linear regression analysis was performed for all 8 Ge orientations, shown in Figure 4-4. The measured velocity for [001] was the fastest among the different orientations at 1.04 nm/min, which corresponds well to previous reports of 0.93 nm/min at 330°C [145]. The measured velocities can then be normalized to the [001] as seen in Figure 3-5. In addition, the normalized values from Csepregi’s data (obtained by RBS) are graphed on the same plot. Due to the difference in activation energies between Si and Ge, the recrystallization temperature for Si was 550°C. The shape of the
orientation dependence for Ge mimics that of Si reported in the literature [59], except the normalized values were higher for Ge compared to Si. The [001] velocity for this work was measured to be 16 times faster than the [111] velocity, and only 1.4 times faster than the [011] velocity. This is significantly faster than the normalized data for Si.

The normalized Ge velocities obtained by Csepregi at 331.5°C compare well to what was observed in this work. The absolute velocities; however, differed by a factor of 3. This is likely due to temperature calibration errors since both sets of Ge samples had relatively low doping levels [9-11]. The absolute velocities from other literature reports matched well with the present work, validating the results [11, 14, 112].

Figure 3-6 shows XTEM images for an isochronal anneal for all 8 orientations. The difference in amorphous layer thickness for an 11 hr anneal at 330°C illustrates a clear orientation dependence. Type III defects were uncommon to find within the regrown layers, which is evidenced in the clean regrowth in Figure 3-6. Interestingly, no significant difference in roughness of the α/c interface was observed among the 8 orientations (Figure 3-6). This is unique to Ge, since an increase in interface roughness was observed for [111] Si relative to other Si orientations [82].

In order to characterize defect formation, PTEM samples were made for all 8 orientations (Figure 3-7). Anneal times were chosen based on each orientation’s SPEG velocity in order to image the nearly recrystallized layers. 2 beam BF conditions were chosen to maximize diffraction contrast from hairpin dislocations. These dislocations were observed within the recrystallized layers for all Ge orientations in this work with an average density of $2.7 \times 10^8 \pm 1.6 \times 10^8$ cm$^{-2}$. The density did not vary significantly among the different orientations. Hairpins nucleate when the advancing α/c interface
encounters microcrystalline pockets at a slightly different orientation than the bulk substrate \[102\]. This is common for high energy implants, which produce a rough \(\alpha\)-\(c\) interface \[57\]. It is not surprising that similar hairpin concentrations exist for different orientations since each sample had the same implant, and presumably the same \(\alpha\)-\(c\) interface morphology.

In addition to hairpin dislocations, stacking faults and twins were observed in the (111) orientation only (54.7\(^\circ\)). For Si substrates, Csepregi \textit{et al.} noticed a high concentration of twins within 16\(^\circ\) of the [111] axis \[59\], but this was not the case for Ge. PTEM images indicate that these stacking faults and twins lie on the 3 inclined \{111\} planes, as seen in Figure 3-8. The density of these defects was only \(\sim 1 \times 10^8\) cm\(^{-2}\), and was not great enough to produce twin spots in diffraction, as observed in Si \[57\]. Upon tilting to the [110] zone axis, the defects either appear wider or narrower, as seen in Figure 3-8(b). The angle between the set of defects that appear narrower is 109.5\(^\circ\), which is the angle between the \{111\} planes in the [110] zone. The set of defects that appear wider is inclined 35.3\(^\circ\) to the [110] zone, which also resides on a \{111\} plane. This confirms the twins and stacking faults form on inclined \{111\} planes.

Figure 3-9 shows a 2 beam tilting sequence to identify the burgers vector of the defects in the 54.7\(^\circ\) Ge samples. The group of defects that are highlighted in Figure 3-9(a) disappear when \(g \cdot b = 0\) is satisfied, as seen in Figure 4-9(b)-(d). By tilting to 3 unique \(g\) vectors, the fault vector for these defects was determined to be of the \(a/6[211]\) type, where “\(a\)” is the lattice constant of Ge (0.565 nm). In this manner, the defects residing on other 2 inclined (111) planes were determined to have fault vectors of \(a/6[211]\) type as well.
Figure 3-10 shows XTEM images of the completely recrystallized 54.7º sample. The weak beam dark field (WBDF) image of Figure 3-10(a) illustrates the inclined nature of the twins residing on (111) planes, residing 70.5º from the surface. Hairpin dislocations are also evident in this image, spanning vertically within the recrystallized layer. Figure 3-10(b) shows a higher magnification image of a twinned region, with an inset of the [011] zone fast fourier transform (FFT). The pattern shows satellite spots appearing at positions 1/3 the distance between the {111} matrix spots, which is characteristic of twins on {111} planes. Also evident from this micrograph is a widening of the twin as it progresses up to the surface. The twin widens from 18 to 23 atomic columns in Figure 3-10(a), and widens up to 44 atomic columns near the surface (not shown). The twin changes thickness near the core of the twinning partial dislocations [146]. The thickness of the twin is therefore defined by the number of {111} planes that have been sheared by partial dislocations. This gives the inclined twins a “trapezoidal” shape in PTEM, as seen in Figure 3-8. Stacking faults arranged in a 2 layer structure were sometimes observed within the twin itself, evident in the bottom of Figure 3-10(b). Similar polytype structures have been observed to form during SPEG on {111} planes in Ge [97].

Stacking faults in the 54.7º orientation were also observed to form parallel to the (111) surface. These defects were usually very small (~10-20nm) in length and less than 10 monolayers thick. These defects appeared at a constant concentration throughout the regrown layer, but only for the 54.7º orientation. A high resolution XTEM image of these defects is shown in Figure 3-11. Unlike Si, no large twins were observed to form parallel to the surface. Due to the small size and weak diffraction
contrast from these parallel stacking faults, they were not able to be resolved or quantified by PTEM [147]. It is important to note that recrystallization temperature for this work was chosen to reflect the same fraction of the melting temperature ($T_m$) as work done for Si in the literature ($\sim 0.35 T_m$). In this regard, the effect of temperature on defect formation should be relatively the same for Ge and Si.

### 3.2.4 Discussion

The use of TEM in this work offered the advantage to measure SPEG velocity as well as defect concentration. This allowed for correlating a structure property relationship for Ge SPEG. While hairpin dislocations were observed for all orientations, their density did not vary significantly among the orientations. Elghor at al. have shown that hairpin concentrations of $\sim 1 \times 10^{11}$ cm$^{-2}$ can cause a 30% reduction in SPEG rate[118], but this density is roughly 3 orders of magnitude larger than what was observed in this work. Moreover, the [001] SPEG velocity compared well with previous SPEG experiments in Ge, where no hairpin dislocations were observed [145]. This evidence supports the conclusion that the low density of hairpin dislocations did not contribute to the orientation dependence on SPEG for this work.

Previous studies have shown 2 velocity regimes for Si [111], where the initial 150 nm of SPEG is 3 times slower than the remaining growth [24, 59, 82]. This was attributed to a high density of small twins near the initial $\alpha$-c interface, followed by a lower density of larger twins near the surface [57]. In contrast, only one [111] velocity existed for Ge. The constant SPEG velocity in the [111] is likely a reflection of the constant twin and stacking fault concentration throughout the regrown layer observed in XTEM. The density of inclined stacking faults and twins in this work was estimated to be $\sim 1 \times 10^{13}$ cm$^{-3}$ (assuming a sample thickness of 200 nm), where the density in Si was
reported as high as $\sim 1 \times 10^{16} \text{ cm}^{-3}$ [57]. It follows that a lower density of stacking faults and twins could lead to a less evident change in the [111] SPEG velocity. It could also be that the transition between the phases occurred so rapidly that it was not observed or not great enough to produce an appreciable change in velocity.

Recent theories have suggested that the SPEG velocity for orientations close to the [111] is limited by the formation of twin defects [60, 65]. Compared with Si, this work showed a smaller concentration of defects for Ge in such orientations [57]. The higher normalized SPEG velocities near the [111] seem to confirm this theory. Thus, it is likely that the geometrical effect of amorphous atoms bonding at the interface controls the overall shape of the orientation dependence in Figure 3-5, while twin defect concentration influences the degree of curvature around the [111] orientations. Since Ge has smaller concentrations of twins than Si, the normalized velocities are higher than those in Si.

The reason for a decreased concentration of defects along {111} Ge could stem from a difference in stacking fault energies compared with Si. First principles calculations have shown that the stacking fault energy of Si ranges from 26-33 mJm$^{-2}$, while Ge is 46-56 mJm$^{-2}$ [148]. The larger stacking fault energy means that the defect would be harder to form, which correlates well with experimental results.

### 3.2.5 Conclusion

The solid phase epitaxial growth process has been studied at 330ºC by transmission electron microscopy (TEM) for Ge wafers polished at 10-15º increments from the [001] to [011] orientations. The velocity showed a strong dependence on substrate orientation with the [001] direction displaying a velocity 16 times greater than the [111] direction. Cross sectional (XTEM) and plan view transmission electron
microscopy (PTEM) revealed stacking fault and twin defect formation in the [111] orientation where all other orientations showed only hairpin dislocations. The twin defects formed from Ge SPEG were comparatively less dense than what has previously been reported for Si, and unlike Si, Ge [111] SPEG showed a constant SPEG velocity throughout the entire annealing sequence. The structural results indicated that low defect densities on {111} planes gave rise to higher normalized SPEG velocities for Ge. The decreased defect densities in Ge could result from a larger stacking fault energy compared with Si.
Figure 3-1. Photograph of the 2 polishing stubs used for obtaining different Ge orientations. Implants were done normal to the top surface of the polishing stubs. XTEM samples were fibbed perpendicular to the edge of the wafer.

Figure 3-2. XTEM micrographs of an annealing sequence at 330°C of the 0° (001) Ge orientation. Sample was implanted at 1 MeV with $1 \times 10^{15}$ Ge$^+$/cm$^2$ (a) and annealed for 30 minutes (b), 150 minutes (c), and 330 minutes (d).
Figure 3-3. Graph of the progression of the α/c interface over annealing time at 330°C for the 3 main orientations in Ge.

Figure 3-4. Measured SPEG velocities for Ge at different orientations at 330°C. Each data point represents measurements from roughly 5 XTEM samples.
Figure 3-5. SPEG velocities for Ge and Si normalized to the [001] direction. Values for this work were measured by TEM at 330°C, while Csepregi measured Si SPEG at at 550°C and Ge SPEG at 331.5°C by RBS [59].

Figure 3-6. XTEM images for an isochronal anneal of all 8 orientations done at 330°C for 11 hrs. The [111] direction (54.7°) is noticeably the slowest orientation, while [001] (0°) is the fastest. The orientations are 0° (a), 15° (b), 25° (c), 40° (d), 54.7° (e), 70° (f), 80° (g), and 90° (h).
Figure 3-7. PTEM images of all 8 orientations taken under various 2 beam conditions. Orientations and annealing times were 11 hrs for 0° (a), 14 hrs for 15° (b), 46.3 hrs for 25° (c), 71.5 hrs for 40° (d), 7.5 days for 54.7° (e), 71.5 hrs for 70° (f), 71.5 hrs for 80° (g), and 27.1 hrs for 90° (h).

Figure 3-8. PTEM images of (111) Ge annealed at 330°C for 7.5 days taken with B= [111] (a), and B= [110] (b). The red and white arrows serve to guide the eye to identical regions in the sample. The red (white) arrow points to a defect that becomes wider (narrower).
Figure 3-9. PTEM images of (111) Ge annealed at 330°C for 7.5 days taken under different g vectors. The highlighted box in (a) indicates a set of defects with a [211] fault vector. This set of defects disappear when g·b=0 is satisfied (b-d).
Figure 3-10. XTEM images of (111) Ge annealed at 330°C for 7.5 days. A WBDF image with B= [011] of the regrown layer containing hairpin dislocations and twins (a). A HRTEM multibeam image of a twinned region with an FFT inset (b).

Figure 3-11. XTEM images of (111) Ge annealed at 330°C for 85 hrs. A low magnification image of the recrystallized layer (a), and a high resolution image of the stacking faults parallel to the surface with an FFT showing streaks (b).
4.1 Introduction

Solid phase epitaxial growth (SPEG) is a common method of achieving high dopant activation for ultra shallow junctions in Ge [2, 3, 149]. This process describes the layer by layer crystallization of an amorphous layer, which typically takes place in the source and drain regions of CMOS devices. As silicon nears the end of its roadmap, Ge is an attractive alternative material due to its higher free carrier mobility and dopant activation. One dimensional (1D) SPEG has been well documented for Ge [11, 15, 37, 66, 145], but little work has been done on 2D SPEG in Ge substrates.

The velocity of the amorphous-crystalline (α-c) interface for Ge is known to be thermally activated and obeys the Arrhenius-type relationship given by:

$$v = v_0 \exp \left(\frac{-\Delta G}{kT}\right)$$

where $v_0$ is a temperature independent prefactor, $\Delta G = 2.17$ eV is the activation energy, $k = 8.62 \times 10^{-5}$ eV/K is Boltzmann’s constant, and $T$ is the absolute temperature [7, 8, 15, 37, 150]. Additionally, SPEG is affected by the crystallographic orientation at the α-c interface, dopant impurities, and applied stress [10, 11, 17, 25, 151].

Unlike 1D SPEG for blanket implants, implants around the source and drain regions typically involve masked regions which results in curved α-c interfaces. This is essentially a three dimensional (3D) process, but in the case of one of the dimensions of the structure being very long, it can be simplified to a two dimensional (2D) process. In this study, a line pattern was chosen where the length (dimension into the page for all
the figures) is very long (hundreds of microns), which is a good assumption for many devices.

The crystallographic orientation dependence is important to consider for 2D SPEG. The normalized regrowth velocity $f(\theta)$ for Ge has been measured by TEM from [001] to [011], as discussed in the previous chapter. The SPEG velocity as a function of $\theta$ can be expressed as:

$$v(\theta) = v_{[001]} \cdot f(\theta)$$  \hspace{1cm} (4-2)

where $v_{[001]}$ is the value of $v$ along the [001] and $f(\theta)$ is temperature independent and can be fit using a fourth order polynomial fit. For Ge, the [001] regrowth velocity is 16 times faster than the slowest regrowth direction of [111] and 1.4 times faster than the [011] direction.

The SPEG velocity of the [001] direction is much faster than that of the [111] and [011]. This causes the vertical and lateral epitaxial fronts to meet when a masked implant recrystallizes. The [111] front becomes pinched off, resulting in what is known as a mask edge defect [55, 85, 86]. These defects are highly sensitive to stress, and tend to be more pronounced when formed under compressive stress [152]. From a modeling perspective, it is important to be able to predict the formation of mask edge defects as they can affect the short channel mobility and drive current of devices [138, 153-155].

The goal of this work is to study and simulate the 2D SPEG process for Ge in order to gain an understanding of how Ge crystallizes and the mask edge defects that form during this process.
4.2 Experimental

4.2.1 Sample Processing

For this work, a (001) Ge wafer was patterned with 110 nm of Si₃N₄ using a plasma enhanced chemical vapor deposition (PECVD) tool at 300°C. The wafer was then spin coated with 250 nm of PMMA A4 (polymethylmethacrylate, anisole 4) resist and baked at 170°C for 30 min. E-beam lithography was used to create line regions on the wafer aligned along [011] directions using a 10 keV electron beam from a working distance of 7 mm. For 250 nm of resist, an exposure dose of 100 μC/cm² was used. Since PMMA A4 is a positive resist, the exposed resist was removed when treated with a developer solution of 1:3 MIBK (methyl isobutyl ketone). Reactive ion etching (RIE) was used to expose 3 different line structures. The different line structures consisted of ~150nm, ~350nm, and ~530nm wide silicon nitride lines as seen in Figure 4-3. For clarity, the simulation results in this chapter will focus on the 350nm sized lines. The etch parameters consisted of gas flow= 30 sccm SF₆, RF1=200W, RF2=1W, pressure= 5mT, time=60 sec. The wafer was purposely under-etched by ~10 nm to prevent damage to the Ge surface. A schematic of the wafer processing for this experiment is illustrated in Figure 4-1.

One set of patterned samples was implanted at 90 keV with a dose of 5×10¹⁴ Ge⁺/cm², which produced an amorphous layer 75 nm deep with a pinned α-c interface under the mask edge, as seen in the cross-sectional transmission electron microscopy (XTEM) image in Figure 4-5(a).

Another set of samples was implanted at 300 keV with a dose of 5×10¹⁴ Ge⁺/cm², which produced an amorphous layer 160 nm under the mask and 235 nm in the
exposed areas as seen in the XTEM image in Figure 4-7(a). In this case, the α-c interface is not in contact with the surface and is therefore not subjected to any surface pinning.

The samples were annealed in a tube furnace at 330ºC in N₂ atmosphere for 44-335 min. Anneal times were chosen to see different points during the regrowth process when the regrowth evolution showed important changes. A set of the samples with interfacial pinning had the Si₃N₄ removed prior to annealing via a 5 minute etch in hydrofluoric acid, as seen in Figure 4-6(a). This was done to observe the effect of pattern induced stress on the α-c interface evolution. It was determined from previous work that the presence of the Si₃N₄ only affected the regrowth of pinned α-c interfaces since simulations have shown that the stress from the silicon nitride is concentrated within the first 100 nm of the surface [47, 67]. An FEI DB235 focused ion beam (FIB) was used to prepare XTEM samples and a JEOL 2010F was used to image the 2D SPEG process.

4.2.2 Wafer Curvature Experiment

Wafer curvature measurements are a commonly used technique for understanding the stresses of thin films, as described in the introduction chapter. For this experiment, a Tencor thin film stress measurement tool was used to map the intrinsic curvature of a bare 4 inch Ge wafer. Then, a 165 nm layer of Si₃N₄ was deposited via PECVD onto the Ge wafer (Figure 4-3). The wafer was then heated from room temperature to 330ºC at a ramp rate of 15ºC per minute while wafer curvature measurements were taken every 12 minutes. The wafer was held at this temperature for 300 minutes, which is approximately the time of the longest SPEG anneal.
4.2.3 Raman Spectroscopy Experiment

3 different Si$_3$N$_4$ pattern spacings (530 nm, 350nm, and 150nm) were chosen as the areas of interest as seen in Figure 4-3. The silicon nitride patterned sample was annealed at 330ºC for 335 minutes, resulting in a stressed $\alpha$/$c$ interface. Another patterned sample was annealed with the silicon nitride removed, resulting in an unstressed $\alpha$/$c$ interface. The 530 nm, 350nm, and 150nm patterned regions were analyzed for both the stressed and unstressed samples. A Horiba Jobin Yvon LabRAM Aramis Raman system equipped with a CCD detector was used for analyzing substrate stress at room temperature. The setup consisted of a 50mW 532 nm laser with a 50 um confocal aperture and 2400 g/mm grating. This resulted in a ~1 um spot size for the laser and penetration depth of about 20 nm [156]. Data acquisition consisted of 10 second exposures, which were averaged 3 times to form a spectrum. Peak shifts were determined by fitting the Raman spectrum with a Lorentzian fit [157].

4.2.4 Implementation of Level Set Methods

As mentioned in the introduction chapter, the Level Set Method is a very accurate numerical technique to simulate the progression of an $\alpha$/$c$ interface. The 2D SPEG process was modeled using level set techniques and implemented in FLOOPS [158]. Level set simulations were used to track the evolution of the propagating interface, where the interface of interest is the $\alpha$-$c$ interface [159].

For the FLOOPS simulations of the patterned Ge structures, Equation (4-2) was modified to be linearly dependent on interfacial curvature via [67, 160],

\[ v(\theta) = v_{[001]} \cdot f(\theta) \cdot (1 + A\kappa) \]  

(4-3)
where \( A \) is the curvature factor with units of length and \( \kappa = \frac{1}{r} \) where \( r \) is the radius of curvature at the mask edge (\( r \approx 80 \text{nm} \)). For the pinned interface nitride patterned samples, \( A = 8 \times 10^{-8} \text{ cm} \) was used, while \( A = 3 \times 10^{-7} \text{ cm} \) was used for the etched samples with a pinned interface. The unpinned interface samples were simulated with a curvature factor of \( A = 1 \times 10^{-6} \text{ cm} \). Equation (4-3) was used for level set simulations of the 2D SPEG process at 330ºC.

Figure 4-4 shows the SPEG velocities as a function of Ge orientation dependence with a fourth order polynomial fit. The data has been normalized to the [001] direction, which was measured to be \( \sim 1 \text{ nm/min} \) at 330ºC. The orientation angle is measured from the [001] direction so that 90º corresponds to the [011] direction. Given the dataset, the fourth order is the least order polynomial that yields a reasonable fit. The polynomial for orientation is given by:

\[
 f(\theta) = (A_1 \cdot \theta^4) + (A_2 \cdot \theta^3) + (A_3 \cdot \theta^2) + (A_4 \cdot \theta) + A_5 \tag{4-4}
\]

where \( A_1 = -1.47 \times 10^{-7}, A_2 = 3.22 \times 10^{-5}, A_3 = -1.92 \times 10^{-3}, A_4 = 1.51 \times 10^2, A_5 = 1.01, \) and \( \theta \) is the angle in degrees. \( f(\theta) \) is valid between 0 and 90 degrees, which was sufficient for modeling the 2D SPEG from the [001] to [110] directions. Since \( f(\theta) \) is unitless, the units of \( A_1 - A_5 \) are degrees\(^{-1}\). Also, since the orientation dependence is independent of temperature [59], the regrowth shapes simulated in this experiment would also be independent of temperature.

4.3 Results and Discussion

4.3.1 Pinned Interface Structure

Figure 4-5 shows XTEM images of the annealing sequence at 330ºC for pinned interface structures with silicon nitride present during the anneal. After 44 minutes, the
α-c interface squares off (Figure 4-5(b)) and after 135 minutes, mask-edge defects form (Figure 4-5(c)). The mask edge defects remain after complete crystallization at 335 minutes (not shown). Similar mask edge defects were observed in Si and were determined to be dislocations aligned along [011]-type directions [47, 85, 161].

Figure 4-6 shows XTEM images of the annealing sequence at 330ºC for pinned interface structure with the silicon nitride etched prior to the anneal. After 44 minutes, the α-c interface becomes obtuse (Figure 4-6(b)) and eventually crystallizes up to the surface defect free (Figure 4-6(d)). This result indicates that the stress from the silicon nitride causes a change in the α-c interface shape, resulting in mask edge defect formation. Wafer curvature measurements revealed that the stress in the silicon nitride was tensile, which would impart a compressive stress on the substrate. This is consistent with previous work, which found that compressive stresses facilitate the formation of mask edge defects by forming an acute angle in the α-c interface [47, 152]. Interestingly, the removal of this film relieved enough stress to eliminate mask edge defect formation in the patterned Ge.

While mask edge defects have been known to cause device leakage [123], recent work has shown that mask edge defects can actually be beneficial if positioned correctly along the edges of the channel [135, 138, 153]. Due to the vacancy-type nature of the mask edge defect, the regions surrounding the defect are put in a state of tension. This implies that annealing with (without) a nitride mask would be beneficial for nMOS (pMOS) planar devices.

Morarka et al. have suggested that the role of the applied stress on Si SPEG evolution may be accounted for by simply changing the curvature factor [151].
Simulations with larger curvature factors matched reasonably well with experiments under tensile stress, and simulations with smaller curvature factors matched reasonably well with experiments under compressive stress. This work has shown that unstressed (stressed) Ge SPEG can be simulated with a curvature factor of $A=3\times10^{-7}$ cm ($A=8\times10^{-8}$ cm), which further supports that the silicon nitride caused a compressive stress in the substrate. This compressive substrate stress is quantified through Raman spectroscopy is section 4.3.5.

It is interesting to note that the presence of a silicon nitride stress reduced mask edge defects for Si [152], but enhanced mask edge defect formation for Ge in this work. One possible explanation for this discrepancy is that the nature of stress in the silicon nitride could be different. This work has shown that a tensile nitride mask produces compressive stresses in the substrate, thus enhancing defect formation. It follows that a compressive nitride mask would produce tensile stress in the substrate and reduce defect formation. The fact that Olson (this work) observed faster (slower) SPEG with the mask present substantiates this argument [152]. It is also possible that mask edge defect formation was suppressed in the Si case due to the location of nucleation. For Si, lateral straggle results in less amorphization under the mask due to a higher amorphization threshold. This results in mask edge defect nucleation further away from the mask edge. Conversely, the low amorphization threshold for Ge results in more amorphization under the masked region. This is an important difference between Si and Ge since it has been demonstrated that the stress concentrates at the mask edge and changes sign as well [130, 131, 162-164]. This would imply that the same tensile
stress could result in tensile or compressive substrate stress depending on exactly where the defect nucleates.

4.3.2 Unpinned Interface Structure

Figure 4-7 shows XTEM images of patterned Ge SPEG with an unpinned α-c interface. Unlike the structures with convex interfaces (κ>0) shown in Figure 4-5(a) and 4-6(a), the as implanted structure shown in Figure 4-7(a) produced an α-c interface with both concave (κ<0) and convex (κ>0) α-c interfaces. A negative κ value would yield smaller SPEG velocities for concave interfaces according to Equation (4-3). In fact, this is exactly what is observed experimentally since the interface curvature decreases over time. This implies that interfaces with positive κ grow faster than interfaces with negative κ. Throughout the annealing sequence, the FLOOPS simulations matched well with the XTEM images. This shows that Equation (4-3) can be used to simulate both concave and convex interfaces for Ge.

Figure 4-7(d) shows the recrystallized structure for the unpinned interface free of mask edge defects. This could be due to the fact that the initial α-c interface in the unpinned case had less curvature than the pinned case, suggesting that the formation of mask edge defects is also highly dependent on the initial interfacial curvature. This is also why a different curvature factor needed to be used. The defect-free nature of this sample could also be due to the absence of stress near the initial α-c interface. Simulations have shown that the stress from the nitride is concentrated within the first 100 nm of the surface [47], which could explain why the deep implant in this case recrystallized free of defects.

It is interesting to note that analogous structures in Si formed mask edge defects in the unpinned case. The triangular amorphous regions near the surface in Si were not
observed in Ge. This stems from the different SPEG dependence on substrate orientation, notably the higher [110] velocity in Ge. The more isotropic SPEG orientation dependence for Ge leads to a more uniform and defect free regrowth up to the surface.

Unlike similar reports for Si [67], there was minimal diffraction contrast from end of range damage in Ge throughout this annealing sequence. This is consistent with reports in the literature, suggesting a small size and density of EOR in Ge [111, 112, 165]. Since Ge has a reduced threshold for amorphization (as determined in chapter 3), it makes sense that less interstitials would contribute to defects in the EOR.

4.3.3 Comparison of Si and Ge

Mask edge defect formation is important for creating tensile stress for planar nMOS devices [138, 153]; however these defects may be undesirable for pMOS devices where a compressive stress is wanted [166]. Since Ge has gained attention as an alternative source drain material, it is important to be able to predict mask edge defect formation in these structures to optimize performance.

Figure 4-8 shows FLOOPS simulations for identical Si and Ge structures. The curvature factor for the simulations is also kept constant at $8 \times 10^{-8}$ cm for both structures, so the only difference is the substrate orientation factor for Si and Ge. It is evident from the simulations that $a/c$ interface is less pinched than its Si counterpart. This means that Ge would be less prone to mask edge defect formation. While this may be inconvenient for utilizing stress memorization technology in nMOS Ge devices, it may be advantageous for the use of Ge in pMOS devices since mask edge defects would be undesirable in this case. From this comparison, it is clear that the orientation
factor plays an important role in mask edge defect formation. Since Ge has a more isotropic orientation dependence on SPEG, the structure recrystallizes with less defects.

Perhaps a more dramatic comparison of SPEG orientation dependence between Ge and Si lies in the unpinned interface structure. Figure 4-9 (a)-(b) shows annealed samples for Ge and Si. Both structures had similar initial $\alpha/c$ interfaces where the difference in amorphous depth under the masked and unmasked areas was 75 nm and 100 nm for Ge and Si respectively. Upon annealing, Ge crystallizes defect free, whereas Si forms well defined mask edge defects and end of range defects. Since the initial interface was deeper in the unpinned case, there is more room for the $[100]$ front to overwhelm the other orientations in the case of Si. This leads to the creation of amorphous regions faceted on $\{111\}$ planes. This was not observed in unpinned Ge structures due to a more isotropic orientation dependence.

4.3.4 Wafer Curvature Measurement Data

The wafer curvature method measures the residual stress of the deposited nitride, as discussed in chapter 2. Figure 4-10 shows the residual tensile stress of the nitride during thermal cycling from room temperature to $330^\circ$C. The film stress initially decreases due to thermal relaxation of the film. The decrease is minimal (<20 MPa), which is primarily due to the small difference between the deposition and anneal temperatures. This essentially minimized the thermal component of the residual stress as seen in Equation (2-7). The tensile stress in the nitride then increases over the 300 minutes at the anneal temperature, which is then retained in the film upon cooling. Low temperature deposited nitrides ($300^\circ$C) have a smaller surface diffusivity, which ultimately creates a relatively porous microstructure. Since the nitride deposition
involves silane (SiH\(_4\)) and ammonia (NH\(_3\)), it is possible that upon annealing, residual gases are removed from the nitride, causing it to densify [167-170]. This irreversible change in microstructure would cause a permanent increase in the tensile stress generated in the film, as seen in Figure 4-10. Ultimately, this graph shows that stress was still retained in the film at the anneal temperatures studied in this work. It is important to note that several thermal cycles were performed during the annealing of patterned Ge samples since XTEM samples needed to be made, while the nitride stress was only measured for one thermal cycle. However, it can be assumed that the stress of the nitride did not increase for further thermal cycling based on comparison with literature results [167-170].

4.3.5 Raman Spectroscopy Data

In addition to wafer curvature measurements, Raman Spectroscopy was used as a second technique to measure stress. As described in the introduction chapter, Raman spectroscopy can be used to measure stress in semiconductor crystals by measuring the shift of vibrational modes within the lattice. The stress for Ge scales linearly with frequency shift according to the following equation:

\[
\tau_{Ge} = (40MPa) \cdot \Delta \omega (cm^{-1})
\]  

where \(\tau\) is the residual stress and \(\Delta \omega\) is the change in frequency from the unstressed to stressed conditions [137]. For this experiment, a 532 nm laser was focused on a section of patterned Ge with (stressed) and without the nitride (unstressed). The Raman peak for the 3 unstressed Ge patterns averaged at 300.8±0.1 cm\(^{-1}\), which compares well with the reported Ge peak at 300.7 cm\(^{-1}\) [137]. The Raman peak shifted for the nitride patterned samples, indicating pattern induced stress in the substrate
The Raman shifts and corresponding compressive stresses for the large, medium, and small patterns were 300.5±0.01 cm⁻¹ (10.0 MPa), 300.2±0.01 cm⁻¹ (21.6 MPa), and 299.9±0.02 cm⁻¹ (31.3 MPa) respectively. This increase in substrate stress with decreasing pattern spacing is consistent with similar studies in Si [164].

The Raman stress from a nitride cap was found to influence the α-c interface shape upon SPEG. The unstressed patterned Ge SPEG was virtually free of mask edge defects, while the stressed patterned Ge formed a mask edge defect upon SPEG. The 2D SPEG process for Ge was studied using TEM and modeled using level set techniques. Stress from a nitride cap was found to influence the α-c interface shape as nano beam diffraction (NBD) data of in plane stresses around patterned structures [135, 172-174]. The beam spot of the laser is roughly an order of magnitude larger than the feature size, so line scans could not be performed across the patterned structures. Other techniques, such as nano beam diffraction (NBD) and high spatial resolution (10nm) techniques could not be performed across the patterned structures. The beam spot of the laser is roughly an order of magnitude larger than the feature size, so line scans could not be performed across the patterned structures. Other techniques, such as nano beam diffraction (NBD) and high spatial resolution (10nm) data of in plane stresses around patterned structures [135, 172-174].

4.4 Conclusions

The 2D SPEG process for Ge was studied using TEM and modeled using level set techniques. Stress from a nitride cap was found to influence the α-c interface shape upon SPEG. The unstressed patterned Ge SPEG was virtually free of mask edge defects, while the stressed patterned Ge formed a mask edge defect upon SPEG.
unpinned $\alpha$-c interface was found to recrystallize defect free as well. The ability to control defect formation through stress and $\alpha$-c interface curvature shows promise for use of Ge in device structures. FLOOPS simulations were accurate in predicting the evolution of the $\alpha$-c interface and the curvature factor was modified to account for the stress of the nitride and the initial curvature of the $\alpha$-c interface. Wafer curvature experiments measured tensile film stresses, which caused compressive substrate stresses of the same magnitude as measured by Raman spectroscopy. Moreover, there was a measured stress dependence that scaled inversely with nitride pattern width. As the nitride pattern width increased to 530 nm, the stress in the substrate was insufficient for mask edge defects formation. This supports the theory that the presence of compressive stresses promotes mask edge defect formation in Ge. In comparison to Si, mask edge defects are less likely to form in Ge since Ge has a more isotropic SPEG orientation dependence. Simulations were found to match reasonably well with experimental data to support this theory.
Figure 4-1. Schematic of wafer processing for multidirectional growth. Deposition of Si$_3$N$_4$ and PMMA resist (a), exposure of Si$_3$N$_4$ using E-beam lithography (b), and etching of the Si$_3$N$_4$ using RIE (c).
Figure 4-2. XTEM image of the continuous 165 nm Si$_3$N$_4$ film used for wafer curvature measurements.
Figure 4-3. Plan view SEM image of the 3 nitride patterns with widths of 530nm (a), 350nm (b), and 150nm (c). The red circle indicates the approximate laser spot size for Raman measurements.
Figure 4-4. The Ge orientation dependence on SPEG velocities normalized to the [001] direction (0º) with a fourth order polynomial fit. The [111] and [011] directions exist at 54.7º and 90º, respectively.

Figure 4-5. XTEM images of nitride stressed patterned Ge implanted with 90 keV 5×10^{14} Ge⁺/cm² and annealed at 330ºC for (a) 0, (b) 44, (c) 135, and (d) 235 minutes. The corresponding FLOOPS simulations are shown below in (e) through (h) using a curvature factor of A=8×10⁻⁸ cm. A mask edge defect is produced in the stressed case.
Figure 4-6. XTEM images of unstressed patterned Ge implanted with 90 keV $5\times10^{14}$ Ge$^+/\text{cm}^2$ and annealed at 330ºC for (a) 0, (b) 44, (c) 135, and (d) 235 minutes. The corresponding FLOOPS simulations are shown below in (e) through (h) using a curvature factor of $A=3\times10^{-7}$ cm. No mask edge defect is produced in the unstressed case.

Figure 4-7. XTEM images of patterned Ge implanted with 300 keV $5\times10^{14}$ Ge$^+/\text{cm}^2$ and annealed at 330ºC for (a) 0, (b) 44, (c) 235, and (d) 335 minutes. The corresponding FLOOPS simulations are shown below in (e) through (h) using a curvature factor of $A=1\times10^{-6}$ cm. No mask edge defect is produced in the unpinned case.
Figure 4-8. FLOOPS simulations for pinned interface structures for Si at 500°C (a)-(d) and Ge at 330°C (e)-(h). The curvature factor was kept constant for both structures at $8 \times 10^{-8}$ cm as well as the $\alpha/c$ initial interface.

Figure 4-9. XTEM images for unpinned interface structures in Ge annealed for 335 minutes at 330°C (a), and Si annealed for 600 minutes at 500°C. The white dashed line indicates the initial $\alpha/c$ interface for Ge in (a). Reprinted and modified with permission from S. Morarka, N.G. Rudawski, M.E. Law, K.S. Jones, R.G. Elliman, J. Appl. Phys. 105 (2009), Copyright [2009], American Institute of Physics.
Figure 4-10. Evolution of residual tensile stress in the Si$_3$N$_4$ film upon annealing at 330°C as calculated from wafer curvature measurements. Arrows indicate the heating and cooling cycle. The sample was held at temperature for 300 minutes.
Figure 4-11. Raman spectroscopy data showing the unstressed peak near 300.7 cm\(^{-1}\) and a progressive shift for smaller nitride line widths.
Figure 4-12. The effect of line width on substrate stress calculated from equation 4-5.

Figure 4-13. XTEM images of different nitride pattern widths implanted with 90 keV, 5×10^{14} Ge/cm^2 and annealed at 330°C for 335 minutes: 530 nm (a), 350 nm (b), and 150 nm (c). The mask edge defect becomes more apparent as the pattern spacing decreases.
CHAPTER 5
SPEG WITH NON-PLANAR SURFACES AND TRENCH EDGE DEFECT FORMATION IN GERMANIUM

5.1 Introduction

The previous chapter discussed 2D SPEG in patterned substrates with a planar surface. Recent CMOS device structures have moved to more complicated 3D structures, such as the finFET (Figure 5-1). In this light, it is often useful to understand how SPEG behaves around non-planar surfaces. SPEG in Si fin structures consists of epitaxial growth in the lower portion of the fin, stacking fault formation in the middle of the fin, and polycrystalline homogenous nucleation in the upper portion of the fin [94, 96, 97]. The stacking fault defects are known to be highly stable, even after rapid thermal annealing (RTA) at 600°C [97]. It is therefore desirable to understand the mechanism of this defect formation and control it, if possible.

It is known that 2D SPEG from amorphized trench-like structures in Si can result in defective regrowth in the [111] direction [55, 98, 175]. In addition, the presence of an oxide on the (110) face of the trench can noticeably affect defect formation in the corner of the trench [99]. It is believed that having an oxide present near the trench edge hinders SPEG by forcing Si-O bonds to rearrange at the α/c interface. Thus, annealing without SiO₂ near the sidewall results in a less defective structure.

So far, there has not been an analogous study for the effect of a surface oxide on trench edge defect formation in Ge. In contrast to Si, the thermally grown oxide for Ge is known to be highly unstable, and growth rates vary throughout the literature [96, 176-180]. While the oxidation of Si can be predicted well by the Deal-Grove model [181], the oxidation of Ge behaves very differently. The growth of GeO (Ge²⁺) is more
preferable than \( \text{GeO}_2 \) (\( \text{Ge}^{4+} \)) and above 450°C, the monoxide state tends to desorb from the surface, resulting in substrate loss. For this reason, all anneals in this experiment are kept below this temperature.

5.2 Experimental

Similar to the previous chapter, a (001) Ge wafer was patterned with 110 nm of \( \text{Si}_3\text{N}_4 \) using a plasma enhanced chemical vapor deposition (PECVD) tool at 300°C. The wafer was then spin coated with 250 nm of PMMA A4 (polymethylmethacrylate, anisole 4) resist and baked at 170°C for 30 min. E-beam lithography was used to create line regions on the wafer aligned along [011] directions using a 10 keV electron beam from a working distance of 7 mm. For 250 nm of resist, an exposure dose of 100 \( \mu \text{C/cm}^2 \) was used. Since PMMA A4 is a positive resist, the exposed resist was removed when treated with a developer solution of 1:3 MIBK (methyl isobutyl ketone). Reactive ion etching (RIE) was used to purposely over-etch and create a trench structure with a height to width ratio of 0.25. The etch parameters consisted of gas flow= 30 sccm \( \text{SF}_6 \), \( \text{RF1}=200\text{W} \), \( \text{RF2}=1\text{W} \), pressure= 5mT, time=150 sec. A schematic of this wafer processing is depicted in Figure 5-2.

The samples were implanted at 300 keV with a dose of \( 5 \times 10^{14} \text{ Ge}^+/\text{cm}^2 \), which produced an amorphous layer 230 nm deep, as seen in the cross-sectional transmission electron microscopy (XTEM) image in Figure 5-3(a). Samples were etched for 5 minutes in HF to remove any native oxide on the surface. One set of samples was immediately coated with a 90nm layer of \( \text{SiO}_2 \) via PECVD, while another set was left uncoated. The two sets of samples were then annealed in a tube furnace in a reducing ambient of 5% \( \text{H}_2 \), 95% \( \text{Ar} \) for times ranging from 88 minutes to 1 day at
temperatures between 330−400ºC. Times and temperatures were chosen to monitor key changes in the evolution of the α/c interface with TEM. An FEI DB235 focused ion beam (FIB) was used to prepare XTEM samples and a JEOL 2010F was used to image the structures.

5.3 Results

The as implanted structure created α/c interface that was unpinned from the surface (Figure 5-3(a)), similar to what was observed in the previous chapter. The RIE process resulted in an overetched surface, which created some irregularities in the corner regions of the trench; however, this did not significantly affect the shape of the original α/c interface. The evolution of the α/c interface can be seen in Figure 5-3(b)-(d). After 665 minutes at 330ºC, amorphous Ge remains in the corner regions. The α/c interface then facets to {111} planes in the corner regions, as seen in Figure 5-3(d). This type of faceting is similar to what has been observed for analogous structures using a Si substrate [98].

In order to completely recrystallize the structure, the anneal temperature was increased to 400ºC. The fully recrystallized structures of the SiO₂ coated and uncoated samples are seen in Figure 5-4. For the coated sample, the amorphous layer regrew epitaxially about halfway up the sidewall, while the upper 50 nm was marked by defective growth. The defects in the corner regions were characteristic of stacking faults lying on {111} planes (Figure 5-4(b)). A high resolution XTEM image of the stacking faults formed in the coated sample is shown in Figure 5-5. Interestingly, the removal of native Ge oxide from an HF etch eliminated defect formation all together in the uncoated sample shown in Figure 5-4 (c)-(d). This is different than what was
observed in Si structures, where the uncoated trench Si sample still displayed stacking fault formation upon SPEG [99].

5.4 Discussion

Since defects were only observed in the oxide coated samples, it is believed that the presence of the oxide influences the defect formation. Since SPEG in the [111] has the slowest velocity [59, 82], the a/c interface gets pinned in the corner regions. From there, the a/c interface must then template from an oxide, which further inhibits the epitaxial process. The fact that the amorphous layer regrew defect free partially up the sidewall is an interesting finding and was not observed for analogous Si structures reported in the literature [99]. In Si, stacking faults were observed to form in the entire trench corner where the a/c interface was pinned. Also, unlike Si, SPEG with a free surface prevented the formation of stacking faults in Ge. This finding supports similar conclusions where SPEG in Ge fins was found to be less defective than Si [94, 96, 97]. This difference between Si and Ge is consistent with the results from chapter 3, where Ge had a lower {111} defect concentration than Si. The reason for that Ge is less defective than Si could be due to a higher stacking fault energy for Ge, as discussed in chapter 3. This implies that it is harder for the 3 amorphous Ge atoms to rearrange in a faulted configuration along the {111} crystalline ledge than Si. Alternatively, it could be that crystalline bonds are easier to form in the case of Ge. From a bond breaking perspective, it makes sense that the Ge/SiO₂ bond is slightly less covalent and thus weaker than the SiO₂ bond, thus allowing for easier regrowth along the coated edge for Ge. Due to the low annealing temperatures employed in this work, it is possible that a strong bond was never created between the Ge/SiO₂. Research has shown that
anneals up to 700-800°C are needed to strengthen the Ge/SiO₂ bond [182]. In this case, the amorphous layer would recrystallize before the Ge/SiO₂ bond strengthened, allowing for easier SPEG.

5.5 Conclusions

SPEG was investigated for self amorphizing implants in non-planar Ge substrates. The trench corner defects that formed during SPEG result from pinning the α/c interface against an oxide layer. Upon removal of this surface oxide, Ge SPEG improved and corner defects did not form. Compared with similar trench structures in Si, Ge proved to be less defective upon SPEG. The reason that Ge is less defective than Si could be related to a higher stacking fault energy for Ge or weak bonding at the Ge/SiO₂ interface. This work shows encouraging results for using SPEG to create highly doped Ge FinFET structures.
Figure 5-1. Schematic of a finFET device structure.
Figure 5-2. A schematic of wafer processing for the trench Ge structures. Deposition of Si$_3$N$_4$ and PMMA resist (a), exposure of Si$_3$N$_4$ using E-beam lithography (b), and overetching of the Si$_3$N$_4$ using RIE (c).

Figure 5-3. An XTEM annealing sequence for the uncoated trench structure at 330°C. The as implanted structure with 5×10$^{14}$ Ge$^+$/cm$^2$ is shown in (a), along with annealed samples of 88 minutes (b), 235 minutes (c), and 665 minutes (d).
Figure 5-4. XTEM images of the trench structures annealed at 400°C for 1 day. The SiO$_2$ coated trench (a) and a zoomed in image of the SiO$_2$ coated corner (b). The uncoated trench (c) and zoomed in image of the etched corner in (d).
Figure 5-5. High resolution XTEM image of the stacking faults for the SiO$_2$ coated sample.

Figure 5-6. Si trench structure pinned against an SiO$_2$ layer. Implanted with $1 \times 10^{15}$ Si$^+$/$\text{cm}^2$ at 40 keV (a), and annealed at 700°C for 1 minute with SiO$_2$ present (b), and with SiO$_2$ removed (c). Reproduced and modified with permission from Burbure, Electrochem. Solid-State Lett.10, H184 (2007). Copyright © 2007 by the Electrochemical Society. Reprinted by permission of the Electrochemical Society.
CHAPTER 6
THE INFLUENCE OF IMPLANT ENERGY AND DOSE ON SPEG

6.1 Introduction

Recently, Ge has received renewed interest as an alternative source/drain and channel material in CMOS devices due to higher dopant activation and free carrier mobility compared to Si [144, 183, 184]. However, the knowledge base and understanding of CMOS-related processing of Ge is still relatively small compared to that of Si. Pre-amorphization using self-implantation to create a continuous amorphous (α) layer is a commonly used processing step which reduces channeling effects and results in higher activation of subsequently implanted dopants during SPEG [2, 141, 142, 185]. Moreover, understanding the SPEG process is crucial to optimizing the performance of CMOS devices [25, 47]. The SPEG process has been studied extensively for Si and is known to be influenced by many variables [7, 8, 10, 17, 18, 28, 51, 59, 80, 81, 150, 186], though comparatively minimal similar research has been performed for Ge. A key difference between Ge and Si is that Ge is known to become highly porous at doses above $4 \times 10^{15}$ cm$^{-2}$ [49, 187-192]. Such behavior suggests the atomistic nature of the α-Ge phase can be altered with dose or implant energy [193], which may possibly lead to dependence of the SPEG kinetics on self-implantation conditions, in contrast with Si where no such dependence is observed [7]. The goal of this chapter is to investigate the effects of implantation conditions on Ge SPEG.

6.2 Experimental

Two sets of (001) Ge samples with background B concentrations of $5.0 \times 10^{17}$ cm$^{-3}$ were self-implanted at room temperature using a VILSta 900XP ion-implanter. The first set of samples was implanted at a fixed energy of 150 keV with doses of $1.0 \times 10^{14}$ –
2.0×10^{15} \text{ cm}^{-2} \text{ while the second set was implanted at a dose of either } 1.0×10^{14} \text{ or } 2.0×10^{15} \text{ cm}^{-2} \text{ with implant energies of 20–150 keV. Samples were furnace annealed at } 330\text{°C in } \text{N}_2 \text{ ambient for times between 22–176 min. Cross-sectional transmission electron microscopy (XTEM) and plan view transmission electron microscopy (PTEM) samples, prepared by focused ion beam (FIB) milling, were used to investigate the evolution of the SPEG process and provide a quantitative means of measuring the growth velocity, similarly as described elsewhere [51].}

6.3 Results

Figure 6-1 shows a sequence of XTEM micrographs depicting the growth process of a sample implanted at 90 keV to a dose of 2.0×10^{15} \text{ cm}^{-2}. The as-implanted structure shown in Figure 6-1(a) indicates an initial \( \alpha \)-Ge layer 107±3 nm thick. With subsequent annealing for 44, 88, and 132 min, the \( \alpha \)-Ge layer has crystallized and reduced in thickness 66±10, 36±5, and 15±5 nm, respectively. For some samples implanted to a dose of 2.0×10^{15} \text{ cm}^{-2}, voids 15±6 nm in diameter spaced randomly a few hundred nm apart appeared just below the surface and tended to swell the surface above the void. Thus, the \( \alpha \)-Ge layer depths were measured in non-swelled regions to obtain the most accurate measurement of SPEG kinetics.

Figure 6-2(a) shows an XTEM micrograph of a sample self-implanted at 90 keV to a dose of 2.0×10^{15} \text{ cm}^{-2} exhibiting clusters of small voids just below the surface and an \( \alpha \)-Ge layer 107±3 nm thick (as measured in regions without voids). PTEM imaging of the same sample, shown in Figure 6-2(b), indicates an average of 9±4 voids per cluster. Approximately 0.07% of the surface of this sample was covered by voids. After annealing the sample in Figure 6-2(b) at 330 °C for 176 min, the amorphous layer crystallized, but the void clusters remain with the same area distribution and size as
shown in Figure 6-2(c). It should be noted that trapped gas is likely not a possible explanation for the formation of voids, since only self implants were performed in this experiment. This is consistent with prior reports indicating the stability of porous regions formed from high dose self-implantation upon annealing [141, 191, 192, 194-197]. Behavior similar to that presented in Figure 6-2 was also observed for other samples self-implanted at 30 – 120 keV to a dose of \(2.0 \times 10^{15}\) cm\(^{-2}\). It is apparent from Figure 6-2 that voids were not present uniformly across the entire sample, but were clustered randomly. This observation is surprising considering the dose uniformity is estimated at <1% across the sample [198].

The measured \(\alpha\)-Ge layer thickness versus time for samples implanted at 150 keV with doses of \(1.0 \times 10^{14} – 2.0 \times 10^{15}\) cm\(^{-2}\) is shown in Figure 6-3(a), and for samples implanted with energies of 20 – 150 keV with a dose of \(1.0 \times 10^{14}\) or \(2.0 \times 10^{15}\) cm\(^{-2}\), shown in Figure 6-3(b). The average growth velocity from each set of thickness versus time data was calculated using least-squares regression analysis from 22 to 88 min as shown in Figure 6-4. The linear regression analysis was performed on data from 22 to 88 min in order to reduce the error in SPEG velocity calculations from the initial planarization of the \(\alpha\)/crystalline interface as well as the final crystallization near the surface. For samples implanted at 150 keV with doses of \(1.0 \times 10^{14} – 2.0 \times 10^{15}\) cm\(^{-2}\), presented in Figure 6-4(a), the growth velocity was nearly identical for all doses with an average growth velocity of \(0.93 \pm 0.02\) nm/min, which agrees well with the values reported in the literature for similar implant conditions [11, 14, 112]. In terms of energy-dependence, the growth kinetics of samples implanted at a dose of \(1.0 \times 10^{14}\) cm\(^{-2}\) showed little variation with energy. However, for samples implanted with a dose of
2.0×10^{15} \text{ cm}^{-2}$, the growth velocity clearly decreased with decreasing implant energy. This behavior differs considerably from that of self-amorphized Si, where the SPEG kinetics are independent of implantation conditions [7].

### 6.4 Discussion

It is interesting that implantation conditions affect SPEG kinetics for self-amorphized Ge when since no such effect has been observed in Si. It is known that H and/or O contamination in the near-surface region during annealing can slow SPEG [7, 11, 37, 66], though the depth into which such contamination is known to occur (several hundred nm) would imply such an effect would be identical for all α-Ge layer thicknesses used in this work. For a given implant condition, the growth rate was independent of the growth interface depth [32, 112], which again contradicts the notion of contamination reducing the growth velocity. Additionally, the presence of electrically-active dopants [11, 17-19] alters growth kinetics but this effect is typically only observed with dopant levels exceeding 4.0×10^{18} \text{ cm}^{-3}$, which is much higher than the background concentrations used in this work. Also, this background concentration should be uniform throughout the wafer for all samples.

A possible explanation of the variation of SPEG with implant energy is implant-induced stress since the presence of stress at the growth interface is known to alter SPEG kinetics [47, 51, 199, 200]. One study showed that compressive stresses in the plane of the growth interface are generated during Kr+ implantation into Ge, where the generated stresses increased with dose at a fixed implant energy [49]. While the implanted ion in the present study is different, a reduction of the implant energy at a fixed dose leads to a higher density of implanted ions, similarly to the previous work. Strain could be attributed to an increase in three and five-fold configurations upon
implantation, leading to an increase in average bond length [201-203]. Additionally, the
generation of compressive stresses resulting from implantation is consistent with current
models of stress-altered SPEG [51] where in-plane compressive stresses tend to retard
growth kinetics. This is further supported by the observation that growth retardation
was not observed at low doses (corresponding to lower damage densities) since less
stress would be generated at lower doses.

Furthermore, the structural transition of α-Ge to a porous structure at high damage
densities may support the observed implantation-dependent SPEG kinetics being
influenced by stress [49, 187-192, 198]. As stated earlier, high dose/low implant energy
conditions generated sparse, but microscopic voids (a precursor to the porous structure)
and possibly, these voids are preceded by smaller, submicroscopic voids. As
suggested by Mayr and Averback [49], the presence of these voids is responsible for
the generation of in-plane compressive stresses during implantation, and an incident ion
transferring energy to the substrate over a smaller volume increases the probability of
void formation. Thus, at high doses and low implant energies, the volume over which
the energy is deposited decreases, resulting in a higher probability of void formation in
the α-Ge network. The in-plane compressive stress generated from void formation then
could possibly slow the growth kinetics in regions between voids [199].

Finally, it should be noted that in the case of group-IV semiconductors, it is known
that the amorphous phase can exist in a so-called “unrelaxed” state where short-range
order is not maintained and bond lengths/angles are excessively distorted [201, 203-
206]. Presumably, if the amorphous phase is not “relaxed” during SPEG, the nature of
bond breaking/rearrangement in the growth interface, which mediates SPEG would be
affected [5]. However, the relaxation of α-Ge from the unrelaxed state is expected to occur very rapidly at the thermal budget used in this work [204, 206]. A structural relaxation argument also does not account for the fact that the pores and voids in Ge are highly stable upon annealing [141, 191, 192, 194-197]. Thus, voids (and void-generated stresses) remain even after short-range order is restored and bond lengths/angles relaxed in the non-voided material.

6.5 Conclusion

The effects of implantation energy and dose on Ge solid-phase epitaxial growth kinetics were studied using (001) Ge substrates self-implanted at energies of 20−150 keV and doses of $1 \times 10^{14} - 2 \times 10^{15}$ cm$^{-2}$. It was shown that implant conditions generating the greatest ion density (low energy/high dose) tended to produce the greatest reductions in growth kinetics. In conjunction with the nature of α-Ge to become highly porous at high damage densities, it was postulated that the implant produced both microscopic and sub-microscopic voids, resulting in stress and altering the growth kinetics.
Figure 6-1. XTEM micrographs of the solid-phase epitaxial growth process at 330 ºC of (001) Ge self-implanted at 90 keV to a dose of $2.0 \times 10^{15}$ cm$^{-2}$: a) the as-implanted structure, b) after annealing for 44 min, c) after annealing for 88 min, and d) after annealing.

Figure 6-2. (001) Ge self-implanted at 90 keV to a dose of $2.0 \times 10^{15}$ cm$^{-2}$: a) XTEM micrograph of the as-implanted structure (surface indicated by the dotted line), b) PTEM micrograph of the as-implanted structure (inset diffraction pattern indicates sample is amorphous) and c) PTEM micrograph of the sample in b) following annealing at 330°C for 176 min (inset diffraction pattern indicates sample is single crystal). Red arrows in parts b) and c) indicate the same void clusters in each sample.
Figure 6-3. Amorphous layer thickness versus annealing time behavior at 330 ºC of self-implanted (001) Ge: a) samples implanted at 150 keV with doses of 1.0×10^{14} – 2.0×10^{15} cm^{-2} and b) samples implanted with energies of 30 – 150 keV with a dose of 2.0×10^{15} cm^{-2}.

Figure 6-4. The solid-phase epitaxial growth velocity at 330 ºC of self-implanted (001) Ge: a) the effect of implanted dose for samples implanted at 150 keV and b) the effect of implant energy for samples implanted at a dose of 1.0×10^{14} or 2.0×10^{15} cm^{-2}.
CHAPTER 7
HIGH DOSE SELF ION IMPLANTATION IN GERMANIUM

7.1 Mechanisms and Proposed Theories for Porous Formation in Bulk Ge

7.1.1 Introduction

There is renewed interest in Ge as an alternative channel material in complementary metal-oxide-semiconductor devices due to its higher free carrier mobility and dopant activation compared to Si. However, the evolution of damage in ion-implanted Ge as a function of implantation conditions remains poorly understood. It is known that for a critical dose, Ge undergoes a crystalline (c-Ge) to amorphous (α-Ge) phase transition[112], and at significantly higher doses exhibits voiding within the α-Ge layer forming a porous structure with surface cavitation [187, 190-192, 198]. However, the threshold ion implantation conditions for void formation remain basically unknown.

Over the past 30 years, there has been much debate as to what mechanism governs formation of the porous structure in ion-implanted Ge. Currently, there are two main theories of void formation for Ge: vacancy clustering and so-called “microexplosions”. The vacancy clustering theory invokes the inefficient recombination of Ge point defects during ion-implantation[207], where once a critical point defect population is created by ion-implantation, excess vacancies cluster into pores [188, 192, 202, 208-212] in order to minimize the dangling bond density. In contrast, the microexplosion theory is based on the creation of voids through pressure waves and thermal spikes caused by the overlap of ion cascades [213-215]. In principle, it is possible to determine which theory better models void formation by selecting appropriate implant conditions and observing the resulting microstructure after implantation. If vacancy clustering is the governing mechanism, then varying depth and
concentration of the vacancy profile should have an effect on the size and depth of the voids. If the microexplosion theory governs the formation process, then a small fraction of implanted ions (<0.1%) would produce microexplosions that result in voids. This implies that dose is the critical parameter that controls the void formation process, which should occur at the surface regardless of the implant energy [213-215]. In this work, the influence of ion dose and implant energy on void formation in ion-implanted Ge is investigated in an attempt to better understand the threshold conditions for the formation of a porous microstructure as well as which theory best explains void formation in Ge.

7.1.2 Experimental

Two sets of (001) Ge samples with background B concentrations of 5.0×10^{17} cm^{-3} were self-implanted at room temperature using a VIISta 900XP ion-implanter with beam current density of 0.38 μA/cm^2. The first set of samples was implanted at implant energies ranging from 20−300 keV with doses ranging from 1.0×10^{13} − 1.0×10^{15} cm^{-2} while the second set was implanted with ion energies of 30−150 keV at a fixed dose of 2.0×10^{15} cm^{-2}. The samples were then annealed at 330°C in a tube furnace in N_2 ambient for 22−176 min. A third set of samples was self-implanted at 130 keV with doses between 1.0×10^{16} − 1.0×10^{17} cm^{-2} using a 5SDH-4 tandem accelerator at Australian National University. Implantation for this set was performed at room temperature using a beam current density of 0.14 μA/cm^2. The α-Ge layers and voids were characterized using a JEOL 2010F transmission electron microscope at 200 kV in cross-section (XTEM) and plan-view (PTEM). An FEI DB235 focused ion beam (FIB) was used to prepare both XTEM and PTEM samples via a 30 keV Ga^+ beam. Scanning electron microscopy (SEM) in the FIB was used to characterize the surface morphology
of the samples at 5 keV. A Multimode Nanoscope III was used for Atomic force microscopy (AFM) to characterize surface roughness as a function of energy and dose.

7.1.3 Results

As discussed in chapter 6, random clusters of voids were observed for implant conditions of 30–120 keV to a dose of $2.0 \times 10^{15}$ Ge$^+$/cm$^2$. At this dose, the average void diameter was measured to be 15±6nm via PTEM. These void clusters covered roughly 0.07% of the surface with 9±4 voids per cluster.

Interestingly, the average depth of the voids (measured by XTEM) in samples self-implanted at energies of 30–120 keV to a dose of $2.0 \times 10^{15}$ cm$^{-2}$ appears to be independent of implant energy, as shown in Figure 7-1. This is in contrast to the approximate linear dependence of the α-Ge layer thickness and depth of the vacancy concentration profile peak ($R_d$) with implant energy predicted with SRIM [139]. Furthermore, there is a complete lack of voids upon increasing the self-implantation energy to 150 keV.

As the implant dose is increased, the voids transform into open pores. Figure 7-2 presents the evolution of the porous microstructure with dose at implant energy of 130 keV. It is evident that the amorphous layer thickness remains relatively constant over the dose sequence, while the thickness of the porous region increases with dose, as shown in Figure 7-2 (a)–(c). The pore diameter also increases with dose as shown in the SEM micrographs presented in Figure 7-2(d)–(f), which is consistent with literature reports[187, 208]. Interestingly, the pores at the surface appear open at a dose of $1.0 \times 10^{16}$ cm$^{-2}$, but an increasing portion of the pores get covered by a surface layer at $3.0 \times 10^{16}$ and $1.0 \times 10^{17}$ cm$^{-2}$ as seen in Figure 7-2(d)–(f). This leads to an undulating α/c
interface since the ions travel through different thicknesses of material depending on whether a surface layer is present.

Figure 7-3 shows a sequence of $1\mu m^2$ AFM scans for Ge self implanted at various doses. Figure 7-3(a) shows an image of the Ge surface after forming a continuous amorphous layer with a $2\times10^{14}$ Ge$^+/cm^2$ implant. The RMS roughness increased from 1.0 to 1.7 nm at the dose threshold for pore cluster formation ($2\times10^{15}$ Ge$^+/cm^2$) (Figure 7-3(b)). This increase in roughness is a precursor to porous formation in Ge [216]. Upon increasing the dose to $1\times10^{16}$ Ge$^+/cm^2$, the Ge surface turned porous and the RMS roughness increased to 16 nm.

Implant energy did not have a significant effect on surface roughness in the range of 30–150 keV (Figure 7-4), but the roughness did scale with increasing implant dose (Figure 7-5). The roughness reached a maximum near $1\times10^{16}$ Ge/cm$^2$ and then slowly decreased above this dose, which is consistent with literature findings [196]. At sufficiently high doses, the roughness decreases due to the formation of a surface layer overtop some of the pores, as seen in the SEM image of Figure 7-2(e)-(f).

Figure 7-6 shows a damage map for self-implantation in Ge. The threshold dose for the formation of a continuous amorphous layer in Ge is $5.0\times10^{13}$ cm$^{-2}$ [112], while the threshold implant dose for void formation was determined to be $2.0\times10^{15}$ cm$^{-2}$ with an implant energy of 120 keV. No clusters of voids were observed in XTEM or PTEM above this implant energy or below this dose. This threshold dose compares well with the void threshold doses for ions of similar mass, such as As$^+$ and Ga$^+$ [217].
7.1.4 Discussion

If void formation is governed by a vacancy clustering mechanism alone one would expect a uniform void distribution due the high uniformity of the ion implantation process. This work has shown that at a dose of $2.0 \times 10^{15} \text{ cm}^{-2}$, approximately 0.07% of the surface is covered with clusters of voids. However, it is known that once the dose is increased to $4.0 \times 10^{15} \text{ cm}^{-2}$, the entire surface is covered with voids[187]. By comparison, the microexplosion theory suggests ~0.1% of incoming ions overcome the critical energy to form a microexplosion. However, this cannot explain void formation alone since a two-fold increase in dose leads to an increase in surface coverage by roughly three orders of magnitude. The lateral range [139] (~15 nm) of a 90 keV Ge$^+$ ion into Ge is roughly equal to the average diameter of a single void (15±6nm), which means that the clusters of voids seen in Figure 6-2 cannot be formed by a single ion. In addition, the voids observed in this work were several orders of magnitude larger than those predicted with single ion molecular dynamics simulations [213-215, 218]. These results indicate that neither the vacancy clustering or microexplosion theory can solely explain void formation.

It is possible that the initial microexplosion serves as a nucleation point for vacancy clustering; once a single void is formed, the formation energy decreases for neighboring voids, resulting in a cluster. Therefore, the number of voids a cluster contains would increase with dose, resulting in even more nucleation points. In this manner, the percentage of the surface covered in voids would increase nonlinearly with dose after the initial void formation. Furthermore, it is known that the individual void size increases with dose [187, 208], which strengthens the argument that voids nucleate
through a microexplosion mechanism, and then a vacancy clustering mechanism could govern the growth process.

Additionally, the fact that voids were observed in the near surface region well above $R_d$ indicates that vacancy clustering alone cannot explain void formation. If vacancy clustering solely governed void formation, then the void depth dependence on ion energy, shown in Figure 7-1, should be centered on the vacancy $R_d$. Instead, the void depth is roughly the same value for all ion energies. In terms of the microexplosion explanation, there is a critical density of cascades required for a void to form. As the depth of the cascade increases, the cascade volume increases as well, and thus the critical energy to produce a microexplosion increases rapidly with the depth of the cascade below the surface [215]. This could possibly explain the observation of voids at the same distance from the surface, regardless of implant energy. It is possible that self-implantation at 150 keV to a dose of $2.0\times10^{15}$ cm$^{-2}$ produces a cascade density just below the critical value, thus resulting in no void formation at the surface.

Upon increasing the dose into the porous regime, several factors determine the surface morphology, including sputtering, redeposition, swelling, and ion beam annealing. It is likely that a combination of these factors contribute to the surface layer formation and surface roughness as shown in Figure 7-3(d)–(f). Mayr et al. showed that high dose implantation in Ge results in compressive stresses, which plateau around 500 MPa [49]. These high compressive stresses lead to the increase in surface roughness with dose seen in AFM. Interestingly, the amorphous depth remains relatively constant, whereas the depth of the porous layer increases with dose. It is speculated that
vacancies continue to cluster with increasing dose, leaving the interstitials to migrate out from the surface, causing the surface to swell.

### 7.1.5 Conclusions

This work has shown that void formation in ion-implanted Ge does not occur uniformly across the surface of the samples. Rather, void formation at the threshold implant conditions exists in random clusters, which may be explainable via a combination of both the vacancy clustering and microexplosion theories of void formation. Once the voids nucleate through a microexplosion mechanism, the voids grow into open pores through a vacancy clustering mechanism. A implantation map diagram for amorphous and porous formation in Ge has been presented. Since the voids form after amorphous threshold, but do not require annealing to nucleate, they do not fit into any of the 5 defect types presented by Jones et al \[102\].

This work suggests that implant conditions must be chosen carefully in any type of Ge-based device processing; since common p- and n-type dopants (Ga\(^+\) and As\(^+\)) have similar masses to Ge\(^+\). Dopant doses that approach \(2.0 \times 10^{15} \text{ cm}^{-2}\) could result in void formation at low implant energies which cannot be removed via annealing. In addition, the work presented in chapter 6 revealed that the presence of void clusters reduces SPEG velocities by exerting in-plane compressive stress on the amorphous layer. These effects make high dose implantation in Ge undesirable for device processing.

### 7.2 High Dose Ion Implantation in Sputtered and Evaporated Ge

#### 7.2.1 Introduction

Although high dose implantation is not desirable in the semiconductor industry, there are other applications which might take advantage of such high surface area porous materials. Recently, there is renewed interest in porous Ge due to several
emerging applications, such as high performance lithium ion battery anodes [219], gas sensors [220], thermoelectrics [221, 222], and thermal insulators for MEMS devices [223]. For many of these applications, deposited Ge films present several advantages over single crystal Ge including lower cost and the ability to use a variety of substrates. In addition, the ability to control and predict the final microstructure is important for different application.

The previous chapter proposed that the porous formation in crystalline Ge is governed by a nucleation and growth process. Since the formation of an amorphous layer precedes the formation of the porous layer, the number of nucleation sites within this amorphous layer should be critical for the evolution of the final microstructure. This chapter focuses on qualitatively changing the initial microstructure of deposited Ge to test the theory of nucleation and growth for porous formation in ion implanted Ge.

### 7.2.2 Experimental

For this experiment, 300-500 nm layers of Ge were sputtered and evaporated onto thermally grown layers of SiO₂. Sputtering was done using a KJL-CMS18 tool, while a Temescal E-beam evaporator was used for the evaporation. The samples were implanted with doses ranging from $1 \times 10^{16}$ to $1 \times 10^{17}$ Ge⁺/cm² at 130 keV. Implantation was performed at room temperature using 5SDH-4 tandem accelerator with a beam current density of 0.14 μA/cm². An FEI DB235 focused ion beam (FIB) was used to prepare XTEM samples and a JEOL 2010F was used for imaging. Scanning electron microscopy (SEM) was used to characterize and quantify sample microstructure.

### 7.2.3 Results

Figure 7-7 shows a cross sectional view of the evaporated and sputtered Ge substrates implanted with 130 keV $1 \times 10^{16}$ Ge⁺/cm². Similar to (001) crystalline Ge, it is
clear that columnar pores develop in the evaporated Ge; however, spherical pores form for the sputtered Ge. Closer examination of the film microstructure through XTEM revealed spherical pores with 1nm diameter within the sputtered film (Figure 7-7(d)), while the evaporated film consisted of a void-less amorphous layer (Figure 7-7(b)). It is likely that the small pores in the sputtered film act as nucleation sites during the implant process, whereby vacancies agglomerate to form larger spherical pores [216]. For the implanted sputtered film, the void size varied as a function of depth, where larger voids were found near the peak of the damage profile (R_d=40 nm), and smaller voids were found at the end of the projected range.

The structure of the evaporated Ge samples was similar to the (001) crystalline Ge shown in the previous chapter. This is likely due to a low concentration of nucleation sites within the starting substrates. This resulted in a columnar growth of the pores from the surface downwards. This implies that the nucleation and growth process is highly dependent on the initial microstructure of the film [208, 209].

Figure 7-8 shows the evolution of the pores formed in the sputtered Ge as a function of dose. The depth of the porous layer increases with dose (Figure 7-8(a)-(c)), which is expected since the vacancy concentration increases with dose. The amount of swelling in the sputtered film was not able to be accurately measured since the thickness of the deposited layer varied by tens of nanometers across the sample. As the porous depth increased with dose, so did the size of the pores, as seen in the plan-view SEM images (Figure 7-8(d)-(f)). The reduced contrast from secondary electrons is due to the presence of a ~7nm surface layer for the implanted sputtered Ge. This
surface layer was also observed for the evaporated Ge implants as seen in Figure 7-7(a).

The pore diameters of the different Ge substrates were measured using plan view SEM images assuming a circular pore shape. The distributions of the crystalline, sputtered, and evaporated substrates are shown as a function of dose for a 130 keV Ge$^+$ implant in Figure 7-9. The distributions follow a positively skewed Gaussian profile and become wider with increasing dose. The substrates which form columnar pores, i.e. crystalline and evaporated Ge, create larger pores than the spherical pores for sputtered Ge at the same dose. This indicates that the final pore size of ion induced porous Ge is highly dependent on the starting substrate.

### 7.2.4 Discussion

It is known that porous Ge forms within an amorphous layer, regardless of the starting substrate, thus it is difficult to define vacancies in an amorphous solid [197]. However, there is still a difference in the amount of deposited energy within the amorphous layer, as simulated with SRIM [139]. For purposes of explanation, vacancies will be discussed in the sense of damage created by the ion profile.

The difference in pore morphology for sputtered and evaporated films for the same implant conditions highlights the importance of nucleation sites for the formation of porous Ge. When a Ge film does not have pre existing nucleation sites, voids nucleate at the surface and then grow in a columnar shape from the surface downwards, as demonstrated with the schematic in Figure 7-10. Once the voids at the surface nucleate, it is possible that vacancies migrate from the bulk to the bottom of the void in order to minimize the dangling bond density. This results in anisotropic growth of columnar voids, as seen with the (001) Ge and evaporated Ge.
The presence of ~1 nm voids existing within the sputtered film effectively created a spherical pore morphology within the implanted layer. An abundance of pre-existing voids likely causes a competition between nucleation sites. This results in isotropic growth of spherical pores, as seen with the sputtered Ge. A schematic of this process is illustrated in Figure 7-11. The final size of each spherical pore then depends on the vacancy concentration at different depths caused by the ion profile.

It is interesting to note that crystalline, evaporated, and sputtered Ge all nucleate spherical voids at first, but these voids turn into columnar voids for crystalline and evaporated Ge for increasing dose. The location of the nucleation sites likely cause this change in morphology. The nucleation sites for crystalline Ge were highly localized near the surface. From here, the vacancies from the bulk cluster to the bottom of the void and the forward momentum of the ion beam elongates the void to create a columnar shape. If the entire amorphous film has a uniform concentration of pre-existing voids, such as in the case of sputtered Ge, then the voids expand isotropically as vacancies cluster on all sides of the voids.

Further research is warranted to investigate the formation of the thin Ge surface layer. Interestingly, this layer forms for both sputtered and evaporated films, but not for (001) Ge. This layer is not a result of pore morphology since both evaporated and (001) Ge formed columnar pores. The thickness of the surface layer is consistent with literature reports under different implant conditions [208, 209, 219]. Since the thickness of the surface layer does not evolve with dose or energy, it is possible that surface recombination forms an equilibrium thickness. Thus, it seems plausible that deposited films have a different IV recombination rate than crystalline Ge.
7.2.5 Conclusions

This work has shown that the formation of porous Ge follows a nucleation and growth model. The morphologies of porous Ge can be significantly altered by changing the nature of the initial nucleation sites. The nucleation sites grow with increasing dose due to increased vacancies. This work has shown that the size and location of the initial nucleation sites ultimately determine whether the Ge will form columnar or spherical pore morphologies. This implies that careful engineering of the starting substrate could allow for different porous structures for different applications. The presented work shows promise for using deposited substrates for porous applications since both columnar and spherical pores were achieved with deposited Ge.
Figure 7-1. Average void depth from the surface plotted against α-Ge thickness and depth of peak vacancy concentration (R_d) as determined by simulations [139]. Error bars indicate the average minimum and maximum depth of the voids versus implant energy for the samples self-implanted to a dose of 2.0×10^{15} cm^{-2}. No voids were observed at 150 keV with doses of 1.0×10^{14} – 2.0×10^{15} cm^{-2}.
Figure 7-2. XTEM micrographs illustrating the evolution of porous Ge with dose at 130 keV: (a) $1.0 \times 10^{16}$ Ge$^+/cm^2$, (b) $3.0 \times 10^{16}$ Ge$^+/cm^2$, (c) $1.0 \times 10^{17}$ Ge$^+/cm^2$ (surface indicated by dotted line) and corresponding plan view SEM micrographs (d) $1.0 \times 10^{16}$ Ge$^+/cm^2$, (e) $3.0 \times 10^{16}$ Ge$^+/cm^2$, (f) $1.0 \times 10^{17}$ Ge$^+/cm^2$.

Figure 7-3. AFM dose sequence showing the change in surface morphology from $2 \times 10^{14}$ Ge$^+/cm^2$ 150 keV (a), $2 \times 10^{15}$ Ge$^+/cm^2$ 150 keV (b), and $1 \times 10^{16}$ Ge$^+/cm^2$ 130keV. The z scale is the same for all images.
Figure 7-4. Graph of RMS roughness vs. implant energy measured by AFM. Dose was kept constant at $2 \times 10^{15} \text{Ge}^+ / \text{cm}^2$.

Figure 7-5. Graph of RMS roughness vs. dose measured by AFM. The implant energy was 150 keV between $1 \times 10^{14} \text{Ge}^+ / \text{cm}^2$ – $2 \times 10^{15} \text{Ge}^+ / \text{cm}^2$ and was 130 keV between $1 \times 10^{16} \text{Ge}^+ / \text{cm}^2$ – $2 \times 10^{15} \text{Ge}^+ / \text{cm}^2$. 
Figure 7-6. Implant damage map for self implants into Ge. The threshold dose values are $5.0 \times 10^{13} \text{ cm}^{-2}$ for amorphization, $2.0 \times 10^{15} \text{ cm}^{-2}$ for void formation, and $4.0 \times 10^{15} \text{ cm}^{-2}$ for porous structure formation. Boxed symbol represents crystallinity, filled symbols represent continuous amorphization, half-filled symbols represent void clustering, and open symbols represent porous formation. All implants were done at room temperature [111, 112, 117, 187, 208, 217, 224].
Figure 7-7. XTEM images of a 130 keV $1 \times 10^{16}$ Ge$^+$/cm$^2$ implant into evaporated (a) and sputtered Ge (c) with zoomed in images of the evaporated and sputtered film microstructures in (b) and (d), respectively.
Figure 7-8. XTEM micrographs illustrating the evolution of sputtered porous Ge with dose at 130 keV: (a) $1.0 \times 10^{16}$ Ge$^+/\text{cm}^2$, (b) $3.0 \times 10^{16}$ Ge$^+/\text{cm}^2$, (c) $1.0 \times 10^{17}$ Ge$^+/\text{cm}^2$ and corresponding plan view SEM micrographs (d) $1.0 \times 10^{16}$ Ge$^+/\text{cm}^2$, (e) $3.0 \times 10^{16}$ Ge$^+/\text{cm}^2$, (f) $1.0 \times 10^{17}$ Ge$^+/\text{cm}^2$.

Figure 7-9. Pore diameter histograms for crystalline (001) Ge, sputtered Ge, and evaporated Ge for doses ranging from $1.0 \times 10^{16}$ - $1.0 \times 10^{17}$ Ge$^+/\text{cm}^2$ with a constant implant energy of 130 keV.
Figure 7-10. Porous formation schematic for crystalline and evaporated Ge. Ion implantation creates clusters of voids just below the surface at doses near $2 \times 10^{15}$ Ge$^+$/cm$^2$ (a). Voids then elongate in the direction of the ion beam as vacancies cluster at the bottom of the voids (b). Upon further increasing the dose, the porous layer continues to elongate anisotropically (c).

Figure 7-11. Porous formation schematic for sputtered Ge. The as deposited film contains many nucleation sites (voids) from the deposition process (a). Upon implantation, the voids act as vacancy sinks and expand isotropically (b). The pores then enlarge with dose, and the largest pores are centered on $R_d$ (c).
CHAPTER 8
SUMMARY AND FUTURE WORK

8.1 Overview of Results

The presented work has given insight into the SPEG process and defect formation for Ge. Overall, Ge was determined to have less defects (\{111\} type, EOR, mask-edge defects, and corner defects in trench structures) than Si for similar structures and implant conditions. In contrast to Si, Ge exhibits a porous regime for high dose, heavy ion implants. These defects were not recoverable during the SPEG process.

The orientation dependence on SPEG was studied for the first time in Ge using TEM. This not only allowed for velocity measurements, but also provided information on the types of defects created upon SPEG. Ge showed significantly less \{111\} type defects than what has been reported in the literature for Si. Since these defects only appeared on \{111\} planes for SPEG on (111) substrates, it was speculated that the defects arose from faulty bond rearrangement on \{111\} planes, and contribute to higher normalized SPEG velocities for Ge.

Patterned substrates were created through E-beam lithography and RIE, and for the first time, 2D SPEG for was studied for both pinned and unpinned \(\alpha/c\) interfaces in Ge. The evolution of the \(\alpha/c\) interface was found to heavily depend on the amount of pattern induced stress. As the amount of pattern induced stress increased for pinned interfaces, the mask edge defect became more pronounced. The mask edge defect was found to disappear if the mask was stripped prior to annealing. Again, Ge was found to be less prone to mask edge defect formation than Si, which was attributed to a more isotropic SPEG orientation dependence.
The SPEG orientation dependence was then used to model 2D SPEG for patterned Ge substrates. Level set techniques were used to simulate SPEG in patterned substrates by implementing the orientation dependence $f(\theta)$ along with a curvature factor ($A$). The curvature factor was found to correlate with substrate stress and could be altered to accurately simulate the evolution of the $\alpha/c$ interface and mask edge defect formation.

2D SPEG for non-planar Ge substrates was studied in trench Ge structures. The effect of a free surface was studied for these structures by passivating the surface with an oxide. The presence of an oxide hindered the SPEG process by forcing the Ge to template off the SiO$_2$. This resulted in $\{111\}$ stacking faults in the corner regions of the structure. The amount of corner defects in this work was qualitatively less than similar experiments done with Si substrates. Interestingly, the defects were eliminated by creating free surfaces via a HF etch. Ge was found to be less defective than its Si counterpart and the results show promise for using Ge in non-planar FinFET structures.

1D SPEG has been studied at a variety of implant conditions and was determined to decrease in velocity for low energy, high dose self-implants. This decrease in velocity correlated well with the observation of void clusters within the amorphous layer. This suggests that the voids played a role in the decreased SPEG velocity and that implant conditions should be chosen to avoid this regime. The mechanism of porous formation in Ge was explored and for the first time, the nucleation of void clusters near the threshold conditions was documented in XTEM and PTEM. It was proposed that voids nucleate through a microexplosion mechanism, and then grow with dose following a nucleation and growth model. Implantation into deposited Ge further confirmed this
theory and a physical model was presented for porous formation. The nature of the nucleation sites ultimately determined the final microstructure of porous Ge.

8.2 Future Work

The fact that Ge has a different SPEG substrate orientation dependence than Si is intriguing. This work has shown that SPEG for Ge is significantly less defective than its Si counterpart. This could be advantageous for adopting Ge in CMOS technology since Ge would have to be grown in source and drain regions. It would therefore be interesting to observe the crystal quality of grown Ge on Si as a function of crystal orientation.

Experimentally, the size of the mask edge defect in Ge was smaller relative to Si. This finding warrants more research since the formation of mask edge defects is relevant to strain memorization techniques for device processing. It would be interesting to see whether the mask edge defects in Ge are more/less dependent on stress than Si. This could be tested by creating identical patterned structures on ultrathin Si and Ge substrates and then recrystallizing implanted regions under tensile and compressive stresses by using a bending apparatus. It would also be interesting to see if the mask edge defect in Ge could be enhanced by creating a deep implant, which was pinned to the surface. This would allow more room for the [110] and [100] fronts to overlap each other, thus creating a longer defect. This type of interface engineering has proved to enhance the amount of channel stress in Si [138], but has not yet been tested for Ge.

Further research is also necessary to correlate quantitative stress to the curvature factor. Currently, it is unknown whether the relationship between curvature factor and stress is linear, since there is a limited set of experiments and simulations presented in
this work. It would be desirable to have this relationship for both tensile and compressive stress in order to accurately predict the defect formation in FLOOPS. Further research is also warranted in quantifying the nitride induced stress with NBD instead of Raman spectroscopy. Raman spectroscopy has limited spatial resolution due to the size of the beam, but point scans could be performed using NBD across the pattern width. This could offer information on the magnitude of the different stress tensors in addition to how stress changes spatially.
# APPENDIX

## FLOOPS SCRIPT FOR PATTERNED STRUCTURES

```plaintext
## grid for curvature structure..

line x loc=0.0 spac=0.05 tag=Top
line x loc=0.11 spac=0.002
line x loc=0.28 spac=0.002
line x loc=0.4 spac=0.05 tag=Bottom

line y loc=-0.35 tag=left spac=.05
line y loc=-0.25 spac=.002
line y loc=-0.1 spac=.002
line y loc=0.1 tag=right spac=.05

region germanium xlo=Top xhi=Bottom ylo=left yhi=right

init

#plot.2d grid
#source ~/scripts/params
#foreach Curv {0 1e-8 5e-8 1e-7 2e-7 3e-7 6e-7 8e-7 1e-6 2e-6} {
    #pdbSetDouble Si Curv $Curv
    pdbSetDouble Si Curv 8e-8
```
SPER temp=330 time=4000 spac=0.002 conc=0 level_mat=Level grid=10

movie.plot plot_name=curv_2e-7

#{}
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Blake Darby grew up in Virginia Beach, VA and graduated from the International Baccalaureate program at Princess Anne High School. He went on to study Materials Science and Engineering at Carnegie Mellon University, where he completed internships at Nucor Steel and Arcelormittal. While at CMU, Blake competed on the golf team and lettered all 4 years. After graduating in 2008, he went to the University of Florida and earned his master’s degree in Materials Science and Engineering in 2010. While pursuing a Ph.D. at UF, Blake completed an internship at Varian Semiconductor Equipment Associates in the summer of 2011, where he worked on the deposition and applications of porous semiconductors for lithium ion batteries. While Blake’s dissertation topic is about CMOS technology, he helped file 3 patent applications for lithium ion batteries during his graduate career. In his spare time, Blake enjoys playing golf, tennis, violin, and mandolin. After graduation, Blake plans on accepting a job offer with Intel, where he will make it rain in Portland, Oregon.