Empirical correlation of minority carrier lifetime to detect density profile in germanium on silicon heteroepitaxy

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EMPIRICAL CORRELATION OF MINORITY CARRIER LIFETIME TO DEFECT DENSITY PROFILE IN GERMANIUM ON SILICON HETEROEPITAXY

by

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DISSERTATION

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DEDICATION

I would like to dedicate this to my parents George and Christy Sheng, and to my in-laws, Richard and Charlotte Mobarak. If it wasn’t for your faith and encouragement, I might have given up a long time ago. I would like to dedicate this to my maternal grandmother in Taiwan, to my paternal grandmother who is no longer here with us, and to my extended family and friends; thanks for believing in me.

And finally, I would like to dedicate my dissertation to my husband, Jason Mobarak, and our two beautiful little girls, Adelene Yuan and Thelia Fei. I love you guys so much! Addie, mommy is finally done and can now spend more time playing tea party and doing arts and crafts with you.
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ABSTRACT

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near infrared (NIR) photodetectors and integration with III-V films for multijunction photovoltaics. However, challenges such as thermal expansion coefficient mismatch and lattice mismatch between Ge and Si often leads to a high density of defects which can propagate through any III-V material grown subsequently. Introducing annealing steps prior to and after full Ge island coalescence are found to reduce the defect density. It has been observed that the defect density in Ge also decreases with increasing dopant density in Si substrates, likely by the defect pinning near the Ge/Si interface by dopants. Using the effective minority carrier lifetime measured as a function of Ge film thickness, an empirical correlation is established between the minority carrier lifetime and the defect density in the Ge film as a function of distance from the Ge/Si
interface and relating the surface recombination velocity on Ge film surface average lifetime within Ge film, and recombination velocity at the Ge/Si interface. Two photoconductance decay techniques were used in this work: quasi-steady-state photoconductance decay and microwave photoconductance decay. The interface recombination velocity for Ge films grown on low-doped, high resistivity (HDLR) and high-doped, low resistivity (LDHR) Si substrates were found to be 370 cm/sec and 0.22 sec/cm$^2$, respectively. Also established is an empirical correlation between minority carrier lifetime of the Ge film ($\tau_{Ge}$) and the defect density ($\rho_D$) within the Ge film as a function of distance from the Ge/Si interface: $\tau_{Ge} = C/\rho_D$, where C is a proportionality constant and a fitting parameter which is determined to be 0.17 sec/cm$^2$ and 0.22 sec/cm$^2$ for Ge films grown on LDHR Si substrates and HDLR Si substrates, respectively.
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Chapter 1

Introduction

1.1 Motivation

Since its 1960 debut, silicon-based metal-oxide-semiconductor-field-effect-transistors (MOSFET) have been the driving force in the semiconductor industry. MOSFETs are used by companies such as Intel and Apple in their microprocessors as well as in handheld devices such as the new iPad2. Moore’s Law states that the number of transistors that can be placed inexpensively on an integrated circuit doubles approximately every two years. Therefore, transistor sizes are shrinking down into the low nanometers range, increasing leakage currents due to thinner gate oxides, lowering output resistances between the gate and drain electrodes due to close proximity, and complicating fabrication without process variations. As silicon (Si) MOSFETs are quickly approaching their performance limit, this allows for the development of novel materials and architectures to boost device performance. With Germanium’s (Ge) higher hole mobility in comparison to other semiconductor materials such as Si and gallium arsenide (GaAs), a nanoscale Ge p-type MOSFET, or pMOS for short, is a promising candidate as a replacement for the current Si pMOS, and a GaAs n-type MOSFET (nMOS) would be the ideal complementary MOSFET (CMOS) (Fig. 1-1). However, integration of Ge pMOS and GaAs nMOS with the current Si fabrication process is not a simple task.
Epitaxial growth of lattice-mismatched III-V semiconductor materials on Si has been actively researched for decades\textsuperscript{,6-13} The materials engineering solutions to circumvent the lattice mismatch include metamorphic growth\textsuperscript{,14,15} graded buffer layers\textsuperscript{,16} selective epitaxial overgrowth\textsuperscript{,17,18} and a variety of defect filtering strategies\textsuperscript{,19-25} One of these engineering solutions is the use of virtual substrates that consists of low-dislocation-density Ge grown on Si\textsuperscript{.17,26-28} Including Ge pMOS, such engineering solutions may enable a variety of applications, such as (1) high-electron-mobility transistors (HEMTs)\textsuperscript{15} integratable with the current Si CMOS platform, (2) light-weight, low-cost multijunction photovoltaics (Fig. 1-2)\textsuperscript{,29-31} and (3) Ge quantum wells\textsuperscript{32} and infrared detectors\textsuperscript{33-35} for photonic applications.
Figure 1-2. A simplified schematic of a triple junction solar cell consisting of three layers in order of largest to smallest bandgap from top to bottom. Each layer collects a range of the solar spectrum shown in the inset at the lower right. All three layers are closely lattice matched to one another.

Despite the promising applications, growing low-dislocation-density Ge on Si continues to present two key technological challenges: lattice mismatch and thermal expansion coefficient mismatch between Ge and Si. The 4% lattice mismatch between Ge and Si typically leads to a high density of threading dislocations, when the epitaxial film is grown beyond its critical thickness (4 monolayers). These threading dislocations can propagate through subsequently grown GaAs layers. The thermal expansion coefficient mismatch causes microcracks and eventual delamination of Ge as
the thickness of the Ge epilayer continues to increase. Various techniques have been
developed to reduce threading dislocations. These techniques include compositional
grading,\textsuperscript{17} Ge condensation,\textsuperscript{38} aspect ratio trapping,\textsuperscript{25} and selective epitaxial growth over
templates,\textsuperscript{39} including the "touchdown" growth technique in which we have previously
developed.\textsuperscript{26-29, 40} The touchdown technique will be described later in Chapter 4. Han's
Research Group has also presented an engineering solution to reduce the thermal stress
by introducing voids around the surfaces of a SiO\textsubscript{2} nanotemplate inserted in the
epitaxially grown Ge layer.\textsuperscript{41} Herein, this dissertation will focus on the touchdown

Growth of a GaAs/AlAs heterostructure on engineered Ge-on-Si (GoS) virtual
substrates has been characterized by room-temperature photoluminescence (PL),\textsuperscript{42} and
have found to be comparable to that of the same structure grown on GaAs and Ge
substrates.\textsuperscript{38} Although success of III-V growth on GoS has been demonstrated, this
dissertation takes a step back to assess the quality of the Ge films. As a figure of merit,
the effective minority carrier lifetime is measured using quasi-steady-state
photoconductance decay (QSSPCD) and microwave photoconductivity decay (MWPCD).
Transmission electron microscopy (TEM) characterizations have shown that the defect
density in engineered GoS is not uniform; the defect density at the Ge/Si interface is
orders of magnitude higher than at the film surface. Therefore, the Ge bulk lifetime is
varies with Ge film thickness and is inversely proportional to the defect density. This
dissertation presents the analysis and results of a minority carrier lifetime study on
molecular beam epitaxially (MBE) grown Ge on Si heterostructures, extracting Ge bulk
lifetime as a function of distance from the Ge/Si interface. This study also includes the development of a patented Ge polishing technique.

1.2 Dissertation Outline

This dissertation is broken up into seven chapters. Chapter 2 gives a literature review describing and comparing selected methods of acquiring minority carrier lifetimes. It also describes the technological issues of growing Ge on Si in more detail. Chapter 3 describes the experimental and characterization techniques used: MBE, chemical mechanical polishing (CMP), MWPCD, inductance PCD, Fourier transform infra-red spectroscopy (FTIR), etch pit density, atomic force microscopy (AFM), secondary electron microscopy (SEM), and TEM. Chapter 4 delves into the deposition methods used and film analysis including procedures for sample preparation, various growth recipes, CMP procedures, etch pit density procedures, and measuring film thicknesses using FTIR. Chapter 5 derives the lifetime equations used to fit the experimental data and reports the Ge bulk lifetime as a function of distance from the Ge/Si interface for both QSSPCD and MWPCD. A summary and conclusion of this study are found in Chapter 6. All references in this dissertation can be found in Chapter 7.
CHAPTER 2

BACKGROUND

2.1 Technological Issues for Ge on Si Heteroepitaxy

Two key technological issues to integrating a thick, high quality Ge epilayer on Si is the lattice and thermal mismatch between the Ge and the Si substrate. The thermal mismatch between Ge and Si can be as high as 116%, leaving microcracks in the Ge films thicker than 4 µm when cooled from a growth temperature of 853K to room temperature. Pure Ge and pure Si, diamonds near the bottom of Fig. 2-1, have a lattice mismatch of 4.2%. Figure 2-1 shows a diagram of bandgap versus lattice constant of many important semiconductor materials. Figure 2-2 shows a simple 2-D representation of one possible defect due to Ge/Si lattice mismatch.

The low lattice mismatch allows for direct deposition of Ge on a Si substrate follows a Stranski-Krastanov (SK) growth. Above the critical thickness (order of 1-10 monolayer), direct deposition initially forms a Si and Ge mixed (SiGe) wetting layer, frequently dominated by subsequent faceted island growth coalescing to form misfit dislocations. These misfit dislocations form at the film and substrate interface, propagating upwards as threading dislocations. Direct Ge on Si growth can result in threading dislocation densities (TDD) on the order of $10^9$-10$^{10}$ cm$^{-2}$. These threading dislocations are undesirable, causing both detrimental electrical and morphological effects such as introducing electrical traps and creating surface roughness, rendering the material unusable for many practical applications. For example, threading
Dislocations in a Ge/Si heterostructure diode are associated with generation-recombination centers, thus a significant contributor to the diode dark current. A correlation between increases in threading dislocation densities and reverse saturation current has been well documented in literature.\textsuperscript{50, 51} To achieve optimal detector sensitivity, dark current must be reduced; hence it is necessary to develop Ge/Si heterostructures with lower recombination velocities.

Fig. 2-1. A diagram of bandgap versus lattice constant for many important semiconductors.
2.2 Carrier Lifetime

In 1952, Hall, Shockley, and Read introduced the theory of electron-hole-pair (ehp) recombination through defect traps, or recombination centers, located in the forbidden-energy bandgap.\textsuperscript{52-54} The Shockley-Read-Hall (SRH) theory describes the statistics of recombination and generation electrons and holes in semiconductors through trapping.\textsuperscript{55} When quoting a numerical lifetime value, not only does it describe the semiconductor and the temperature it is measured at, the value also encompasses a weighted average of the behaviors of carriers influenced surfaces, interfaces, energy barriers, and the density of carriers. The term lifetime, itself, is also misleading since most people think of carrier recombination when hearing the word. However, carrier lifetime is a combination of recombination lifetime and generation lifetime.\textsuperscript{52, 53} Recombination lifetime is the measurement of excess carrier decay through recombination. Recombination occurs in the bulk as well as on the surface and interfaces. Both bulk and surface recombination occur simultaneously, making their
individual extraction sometimes difficult. The measured lifetimes are always an effective lifetime of bulk and surface components. In this work, we will only focus on recombination lifetime. As novel technologies continuously emerge, recombination of minority carriers via defect imperfections in the bulk, surfaces, and interfaces are becoming a major issue.\textsuperscript{56} In this review section, the dominant focus will be on Si substrates to explain the theory of minority carrier lifetime.

Excess ehps can be generated by photons or particles of energy higher than the material bandgap or by forward biasing a pn junction.\textsuperscript{52} After excitation, there are more carriers than at equilibrium, and the system returns to equilibrium through recombination. There are three main recombination mechanisms used to determine the recombination lifetime: (1) Shockley-Read-Hall or multi-phonon recombination ($\tau_{SRH}$), radiative recombination ($\tau_{rad}$), and Auger recombination ($\tau_{Auger}$). These three recombination mechanisms are related by:\textsuperscript{52}

$$\tau_r = \frac{1}{\frac{1}{\tau_{SRH}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Auger}}} \quad (\text{Eq. 2.1})$$

The below figure (Fig. 2-3) illustrates each recombination mechanism. Each recombination mechanism will be further described in the following subsections.
The bulk recombination rate \( R \) depends non-linearly on carrier densities departing from their equilibrium values. Confining up to third order terms, \( R \) can be written as:

\[
R = A(n - n_0) + B\left(p n - p_0 n_0\right) + C_n\left( p n^2 - p_0 n_0^2 \right) + C_p\left( p^2 n - p_0^2 n_0 \right) \quad \text{(Eq. 2.2)}
\]

\[
n = n_0 + \Delta n, \quad p = p_0 + \Delta p \quad \text{(Eq. 2.3)}
\]

where \( A \) is area (cm\(^2\)), \( B \) is the radiative recombination coefficient (cm\(^3\)/sec), \( C_{n,p} \) are the Auger recombination coefficients for \( n \)-type and \( p \)-type respectively (cm\(^6\)/sec), \( n \) and \( p \) are electron and hole densities (cm\(^{-3}\)), \( n_0 \) and \( p_0 \) are equilibrium carrier densities (cm\(^{-3}\)).
and $\Delta n$ and $\Delta p$ are the excess carrier densities (cm$^{-3}$). If there are no traps, $\Delta n = \Delta p$ and assuming a $p$-type material, $R$ can be reduced to:

$$R = A\Delta n + B\left(p_0 + \Delta n\right)\Delta n + C_p\left(p_0^2 + 2p_0\Delta n + \Delta n^2\right)\Delta n + C_n\left(n_0^2 + 2n_0\Delta n + \Delta n^2\right)\Delta n$$

(Eq. 2.4)

The recombination lifetime ($\tau_r$) is defined as:

$$\tau_r = \frac{\Delta n}{R}$$  (Eq. 2.5)

Substituting in $R$:

$$\tau_r = \frac{1}{A + B\left(p_0 + \Delta n\right) + C_p\left(p_0^2 + 2p_0\Delta n + \Delta n^2\right) + C_n\left(n_0^2 + 2n_0\Delta n + \Delta n^2\right)}$$  (Eq. 2.6)

### 2.2.1 Shockley-Read-Hall Recombination

Traps, or deep level impurities, within the bandgap can act as a recombination center trapping both electrons and holes with equal probability, meaning that the capture cross section for electrons and holes are approximately equal. Since there are always impurities and defects in semiconductor materials, SRH recombination is always active. In other words, SRH recombination is controlled by the cleanliness of the material.

There are four basic processes that can occur at a single—assuming acceptor type—trap (Fig. 2-4):$^{54}$

1. The capture of an electron from $E_c$ by an initially neutral empty trap.
(2) The inverse of (1)—the emission of an electron from a trap to \( E_c \).

(3) The capture of a hole from \( E_v \) by the empty trap.

(4) The inverse of (3)—the emission of a hole to \( E_v \).

Fig. 2-4. The four basic trapping and emission processes for the case of an acceptor type trap.

During SRH recombination, the energy released is dissipated by lattice vibrations or phonons, as shown in Fig. 2-3. SRH recombination is inversely proportional to defect density and electron and hole capture cross section. Although it is not directly dependent on the recombination center energy levels, it is indirectly dependent through capture cross sections. The capture cross section tends to be highest for impurities with traps
near the center of the bandgap, and lowest near the valence and conduction bands. The SRH lifetime for a $p$-type material is given by:

$$\tau_{SRH} = \frac{\tau_p \left( n_0 + n_1 + \Delta n \right) + \tau_n \left( p_0 + p_1 + \Delta p \right)}{p_0 + n_0 + \Delta n} \quad (\text{Eq. 2.7})$$

where $n_1$, $p_1$, $\tau_n$, and $\tau_p$ are defined as:

$$n_1 = n_i \exp \left( \frac{E_T - E_i}{kT} \right); \quad p = n_i \exp \left( -\frac{E_T - E_i}{kT} \right) \quad (\text{Eq. 2.8})$$

$$\tau_p = \frac{1}{\sigma_p v_{th} N_T}; \quad \tau_n = \frac{1}{\sigma_n v_{th} N_T} \quad (\text{Eq. 2.9})$$

and $n_i$ is the intrinsic carrier density (cm$^{-3}$), $E_T$ is the trap energy (eV), $E_i$ is the intrinsic energy (eV), $k$ is the Boltzmann constant (8.617 x 10$^{-5}$ eV/K), $T$ is temperature (K), $\sigma_{n,p}$ is the capture cross sections for electrons and holes (cm$^2$), $v_{th}$ is the thermal velocity (cm/sec), and $N_T$ is the trap density (cm$^{-3}$).

### 2.2.2 Radiative Recombination

Radiative recombination is a form of spontaneous emission; a photon is emitted with a wavelength corresponding to the energy released.$^{57}$ The $ehps$ combine directly from band to band (Fig 2-3). This effect is the basis of LEDs. The photons can either be absorbed, generating an $ehp$, or they can cause a recombination, generating more photons of similar properties. Absorption is the active process in photodiodes, solar cells, and
other semiconductor photodetectors, while stimulated emission is responsible for laser action in laser diodes. The radiative lifetime for a $p$-type material is:

$$\tau_{rad} = \frac{1}{B\left(p_o + n_o + \Delta n\right)} \quad \text{(Eq. 2.10)}$$

where once again $B$ is the radiative recombination coefficient (cm$^3$/sec). The radiative lifetime is inversely proportional to the carrier density since both an electron and hole must be present at the same time. However, the photon carries relatively little momentum, radiative recombination is significant only in direct bandgap materials.$^{56, 57}$ Since Ge has an indirect bandgap, $\tau_{rad}$ is very high, therefore it approaches zero in the general recombination lifetime equation.

### 2.2.3 Auger Recombination

During Auger recombination, the emitted recombination energy is absorbed by a third carrier. The third carrier usually loses its excess energy to thermal vibrations.$^{57}$ Since this process is a three-particle interaction, it is normally only significant in non-equilibrium conditions when the carrier density is very high. The Auger effect process is not easily produced, since the third particle would have to begin the process in the unstable high-energy state. Figure 2-3 shows two methods for Auger recombination.

Auger recombination can be found in both direct and indirect bandgap materials. It requires very high doping densities or very high excess carrier densities, but
independent of the impurity density. Auger recombination is also dominant in narrow bandgap materials. It is an intrinsic property of the semiconductor.

The Auger lifetime is inversely proportional to the carrier density squared.\(^{53}\) The Auger lifetime for a \(p\)-type material is given by:

\[
\tau_{\text{Auger}} = \frac{1}{C_p \left(p_0^2 + 2p_0 \Delta n + \Delta n^2\right) + C_n \left(n_0^2 + 2n_0 \Delta n + \Delta n^2\right)} \approx \frac{1}{C_p \left(p_0^2 + 2p_0 \Delta n + \Delta n^2\right)}
\]

(Eq. 2.11)

where \(C_{n,p}\) are the Auger recombination coefficients for electrons and holes (cm\(^6\)/sec).

### 2.2.4 Injection Level

The injection level (\(\eta\)) is very important during lifetime measurements. Low level injection is valid when the excess carrier injection density is lower than the equilibrium majority carrier density (\(\Delta n = \Delta p \ll p_0\) for \(p\)-type material). High level injection is just the opposite (\(\Delta n = \Delta p \gg p_0\)). Here, we are assuming that the electron and hole excess carrier concentrations are equal to neglect traps. Trapping is a mechanism in which some of the \(ehps\) are trapped temporarily at impurity levels. When trapping is an issue, background illumination is used to reduce the effect. Trapping is typically a major problem in large bandgaps, and hence not a major concern in semiconductors like Si.\(^{53}\) An approximation for low-level (\(ll\)) and high-level (\(hl\)) injection expressions are:
\[ \tau_{SRH}(ll) = \frac{n_1}{p_0} \tau_p + \left(1 + \frac{p_1}{p_0}\right) \tau_n \approx \tau_n ; \quad \tau_{SRH}(hl) = \tau_p + \tau_n \]

\[ \tau_{rad}(ll) = \frac{1}{Bp_0} ; \quad \tau_{rad}(hl) = \frac{1}{B\Delta n} \]  
(Eq. 2.12)

\[ \tau_{Auger}(ll) = \frac{1}{C_p p_0^2} ; \quad \tau_{Auger}(hl) = \frac{1}{(C_p + C_n) \Delta n^2} \]

where the second expression of in \(\tau_{SRH}(ll)\) is valid when \(n_1, p_1 << p_0\) and \(\tau_{SRH}(hl)\) is valid for \(\Delta n = \Delta p >> p_0, n_0, p_1, n_1\). Figure 2-5 shows \(\tau_{SRH}\) versus \(E_T\) for \(N_T = 10^{12} \text{ cm}^{-3}, p_0 = 10^{16} \text{ cm}^{-3}, \sigma_n = 5 \times 10^{-14} \text{ cm}^2, \) and \(\sigma_p = 5 \times 10^{-15} \text{ cm}^2\) with the normalized injection level in \(\eta = \Delta n/p_0\). It suggests that \(\tau_{SRH}\) increases for impurities with energy levels toward the band edges even at low \(\eta\). However, for \(n_1, p_1 >> \Delta n = \Delta p >> p_0, n_0\), the lifetime increases with \(\eta\). Therefore, \(\tau_{SRH}\) does not always increase with increasing injection level, as often stated.

Fig. 2-5. \(\tau_{SRH}\) versus \(E_T\) for \(N_T = 10^{12} \text{ cm}^{-3}, p_0 = 10^{16} \text{ cm}^{-3}, \sigma_n = 5 \times 10^{-14} \text{ cm}^2, \) and \(\sigma_p = 5 \times 10^{-15} \text{ cm}^2\) with the normalized injection level in \(\eta = \Delta n/p_0\).
2.2.5 Surface Recombination Velocity (SRV)

Any defects or impurities within or at the surface of the semiconductor promote recombination. When a single-crystal semiconductor is abruptly terminated, it disrupts the periodic-potential function resulting in allowed energy states distributed within the bandgap (Fig 2-4). In other words, dangling bonds at the surface create surface traps. High rate of surface recombination depletes this region of minority carriers. The surface recombination rate is limited by the rate in which minority carriers can move towards the surface, called surface recombination velocity (SRV). If there is no recombination at the surface, no carriers are moving towards the surface, hence SRV is zero. However, if the surface is highly defective, SRV is limited by the rate in which carriers can traverse towards the surface. For most semiconductors, the maximum velocity is on the order of $10^7$ cm/sec.58

Fig. 2-6. Distribution of surface states within the bandgap.
If the trap density at the surface is greater than the trap density in the bulk, the surface lifetime is lower than the bulk lifetime. For an $n$-type semiconductor, the rate of excess carrier recombination can be greatly simplified to equal the excess minority carrier concentration divided by the excess minority carrier lifetime:

$$R = \frac{\Delta p}{\tau_{p0}} = \frac{\Delta p_B}{\tau_{p0}} = R_B; \quad R_S = \frac{\Delta p_S}{\tau_{p0s}} \quad \text{(Eq. 2.13)}$$

where $B$ denotes the bulk and $S$ denotes the surface. In the steady-state of an homogenous and infinite semiconductor, $R_B = R_S$. Figure 2-7 shows an example of the excess-carrier concentration versus distance from the surface. Since $\tau_{p0s} < \tau_{p0}, \Delta p_s < \Delta p_B$.

Fig. 2-7. Steady-state excess hole concentration versus distance from the surface.
The bulk and surface SRH recombination rate are:

\[ R_p = \frac{\sigma_n \sigma_p \nu_{ih} N_T \left( p n - n_i^2 \right)}{\sigma_n (n + n_i) + \sigma_p (p + p_i)} = \frac{(pn - n_i^2)}{\tau_p (n + n_i) + \tau_n (p + p_i)} \quad \text{(Eq. 2.14)} \]

\[ R_s = \frac{\sigma_{ns} \sigma_{ps} \nu_{ih} N_{it} \left( p_s n_i - n_i^2 \right)}{\sigma_{ns} (n_s + n_{is}) + \sigma_{ps} (p_s + p_{is})} = \frac{s_n s_p (p_s n_i - n_i^2)}{s_n (n_s + n_{is}) + s_p (p_s + p_{is})} \]

where

\[ s_n = \sigma_{ns} \nu_{ih} N_{it}; \quad s_p = \sigma_{ps} \nu_{ih} N_{it} \quad \text{(Eq. 2.15)} \]

The subscript "s" denotes quantity at the surface. The interface trap density \( N_{it} \) (cm\(^{-2}\)) is assumed to be constant. If it is not constant, the interface trap density \( D_{it} \) (cm\(^{-2}\)eV\(^{-1}\)) would have to be integrated over energy with \( N_{it} \), given by \( N_{it} \approx kT D_{it} \). In this thesis, SRV is synonymous to surface lifetime. Therefore, SRV can be written as:

\[ S = \frac{R_s}{\Delta n_s} \quad \text{(Eq. 2.16)} \]

Plugging in \( R_s \) from above:

\[ S = \frac{s_n s_p (p_s + n_s + \Delta n_i)}{s_n (n_s + n_{is} + \Delta n_i) + s_p (p_s + p_{is} + \Delta p_s)} \quad \text{(Eq. 2.17)} \]

The surface recombination velocity for low-level and high-level inject becomes:

\[ S(II) = \frac{s_n s_p}{s_n \left( \frac{n_{is}}{p_s} \right) + s_p \left( 1 + \frac{p_{is}}{p_s} \right)}; \quad S(HI) = \frac{s_n s_p}{s_n + s_p} \quad \text{(Eq. 2.18)} \]

For SiO\(_2\)/Si interfaces, SRV is strongly dependent on injection level.
Fortunately, there are two popular ways to lower SRV: (1) chemical passivation of the surface or (2) forming a potential barrier that prevents minority carriers from reaching the surface.\textsuperscript{56} Such a potential can be achieved by creating an appropriate heterojunction with low interface recombination rate, or by strong doping of the surface so that it electrostatically bends to confine minority carriers in the bulk. Oxidized Si surfaces have been reported to reduce SRV to $S \approx 20$ cm/sec\textsuperscript{59} but as low as 1 cm/sec has also been observed.\textsuperscript{60} Submerging Si substrates in hydrofluoric acid (HF) and taking measurements while immersed has drastically decreased SRV to 0.25 cm/sec.\textsuperscript{61} Immersing in an iodine/methanol solution has produced results of $S \approx 4$ cm/sec.\textsuperscript{62}

### 2.2.6 Effective Lifetime

The measured or effective lifetime is a combination of the bulk lifetimes and the recombination velocities at the surfaces and at the interfaces. Although each component is independent of the other, they can be related by:\textsuperscript{53}

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_B} + \frac{1}{\tau_s} \quad \text{(Eq. 2.19)}
\]

where the surface lifetime is given by:

\[
\tau_s = \frac{1}{\beta^2 D_n} \quad \text{(Eq. 2.20)}
\]

$D_n$ is the electron diffusion constant and $\beta$ is obtained from
\[
\tan \left( \frac{\beta t}{2} \right) = \frac{S}{\beta D_n} \quad (\text{Eq. 2.21})
\]

where \( t \) is the sample thickness. In the limits of high or low SRV (\( S \)):

\[
\tau_i(s \to 0) = \frac{t}{2S}; \quad \tau_i(s \to \infty) = \frac{t^2}{\pi^2 D_n} \quad (\text{Eq. 2.22})
\]

Samples with impurity concentrations below \( 10^{12} \text{ cm}^{-3} \), SRV must be very low in order to measure the true recombination lifetime. Otherwise, the effective lifetime can be much lower than the bulk lifetime. At higher impurities where the bulk lifetime dominates, the effective lifetime is inversely proportional to the impurity density. For lower impurity concentrations, SRV is dominant and the effective lifetime becomes independent of the trap concentration.\(^5\)

The minority carrier diffusion length (\( L_n \)) is also affected by surface recombination since it is directly related to effective lifetime by:

\[
L_{n,\text{eff}} = \sqrt{\tau_i D_n} \quad (\text{Eq. 2.23})
\]

The longest diffusion length that can be reliably measured is \( t/4 \). Therefore the sample needs to be fairly thick to obtain the true effective lifetime or minority carrier diffusion length, especially for samples with low impurity densities.

### 2.3 Lifetime Measurement Systems

Recombination lifetime measures can be broke down into two categories: optical and electrical. The more common measurements today are performed optically. Optical
measurements include surface photovoltage (SPV), photoconduction decay (PCD) and quasi-steady-state photoconduction (QSSPC), photoluminescence decay (PL), and short circuit-current/open-circuit voltage decay (SCCD/OCVD). Electrical measurements include diode current-voltage, reverse recovery (RR), and open-circuit voltage decay (OCVD). The following sub-sections will give a brief tutorial on some of the measurement techniques just listed.

2.3.1 Surface Photovoltage (SPV)

Surface photovoltage (SPV) is an attractive technique because (1) it is nondestructive and contactless, (2) simple sample preparation (no contacts, junctions, or high temperature processing required), (3) a steady-state method relatively immune to slow trapping and detrapping effects, and (4) is commercially available. SPV is defined as the illumination-induced change in the surface potential. It is a specific variant of the photovoltaic effect which is the result of charge transfer and/or net charge redistribution due to optical excitation. SPV is a widely used method to determine the minority carrier length of semiconductors. Measurements involve monitoring the potential of a semiconductor surface while generating electron-hole pairs with a light source. The absorbed photons cause the formation of free carriers by creating electron-hole pairs via band-to-band transitions and/or release captured carriers via trap-to-band transitions. When the free carriers are generated deep in the semiconductor, the electron-hole pairs must diffuse through the bulk before reaching the surface. The photogenerated minority carriers have a much shorter diffusion length than the majority carriers, with which they can radiatively recombine. The change in surface potential after excitation is hence a
measure of the ability of minority carriers to reach the surface, or the minority carrier diffusion length.

SPV measurements are performed by placing a sample on a ground electrode and positioning a kelvin probe a small distance above the sample. A typical schematic of the setup is shown in Fig. 2-8. The top surface is chemically treated to induce a surface space charge region. Note that the space charge region is from surface charges, not from a bias voltage. The optical source is a chopped monochromatic light of energy higher than the bandgap of the sample. The light is chopped to enhance the signal to noise ratio using lock-in techniques. Only the top surface is illuminated with the back surface kept in the dark. During the measurement, the wavelength is varied. The absorption depth of the light source wavelength is monitored since fewer minority carriers that will reach the surface as the absorption depth deepens, leading to a lower photovoltage. If the spectral absorption coefficient is known, the minority carrier diffusion length can in principle be extracted from a measurement of photovoltage versus wavelength. This diffusion length, \( L_{\text{measured}} \), is approximately related to bulk lifetime by:

\[
L_{\text{measured}} = \sqrt{D\tau_{\text{bulk}}} \quad (\text{Eq. 2.24})
\]

where \( D \) is the diffusion coefficient and \( \tau_{\text{bulk}} \) is the bulk lifetime. Note that the diffusion length is independent of any built-in fields in contrast to drift behavior of carriers. The photogenerated majority carriers will also diffuse towards the surface but their fraction is minimal compared to thermally generated majority carrier density in a moderately doped semiconductor. Both carrier types will also diffuse towards the rear contact where their collection can confuse interpretation of the data if the diffusion lengths are larger than the
film thickness. In reality, the $L_{measured}$ includes the effects of surface recombination. Therefore Eq. 2.24 needs to be rewritten as:

$$L_{measured} = \sqrt{D \tau_{effective}} \quad \text{(Eq. 2.25)}$$

where $\tau_{effective}$ is the effective lifetime related to the bulk lifetime and surface recombination velocity by the following equation:

$$\frac{1}{\tau_{effective}} = \frac{1}{\tau_{bulk}} + \frac{2S}{d} \quad \text{(Eq. 2.26)}$$

where $S$ is the surface recombination velocity (SRV) and $d$ is the substrate thickness. Unfortunately, even for well characterized materials, uncertainty of SRV values reduce the accuracy with which the diffusion length can be determined for thin films.
2.3.2 Photoconductance Decay (PCD)

Photoconductance decay (PCD) was first proposed in 1955. It utilizes optical excitation to generate electron-hole pairs, typically a xenon strobe lamp or a single frequency laser, to increase the conductivity of the semiconductor material. The enhancement of the electrical conductivity under the excitation of light is called photoconductivity effect. Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as optical light. To cause the excitation, the light that strikes the materials surface must have enough energy to raise electrons from the valence band to the conduction band or to excite impurities within the bandgap. The duration of
the strobe light must be short in comparison to the expected lifetime of the carriers.\textsuperscript{60} Once excitation ceases, the carriers recombine, returning the sample to its quiescent state and in the process, producing a transient decay. The latter part of the decay is monitored as a function of time, often referred to as the asymptotic decay lifetime or the lifetime of the fundamental mode of decay.\textsuperscript{68} The decay of the excess carriers is described as a summation of an infinite numbers of modes \( m \) each characterized by a lifetime, \( \tau_m \). The higher order modes \((m > 0)\) die out rapidly after excitation has ceased. Therefore, the measured lifetime is dominated by the decay of the fundamental mode, \( \tau_0 = \tau_{\text{eff}} \), for time \( t > \tau_{\text{eff}} \) after the excitation has stopped. Depending on the material quality and the injection level, the decay can a combination of various recombination mechanisms described earlier in this chapter.\textsuperscript{60}

Conductivity is given by the following equation:\textsuperscript{52}

\[
\sigma = q \left( \mu_n n + \mu_p p \right) \quad (\text{Eq. 2.27})
\]

where \( q \) is the magnitude of electron charge \((1.6 \times 10^{-19} \text{ C})\), \( \mu_{n,p} \) is the electron or hole mobility, \( n = n_0 + \Delta n \), and \( p = p_0 + \Delta p \). It is assumed that the equilibrium carriers and the excited carriers have the same mobility. However, this is only true under low level injection where \( \Delta n \) and \( \Delta p \) are small compared to the equilibrium majority carrier density. Under high injection, this is no longer true due to carrier-carrier scattering which lowers mobility.

Some PCD techniques will measure the time-dependent excess carrier density directly. For low trapping density \((\Delta n = \Delta p)\), the relationship between conductivity and excess carrier density is given by:\textsuperscript{52}
\[
\Delta n = \frac{\Delta \sigma}{q(\mu_n + \mu_p)} \quad \text{(Eq. 2.28)}
\]

provided that the mobilities are constant during the measurement. PCD can be monitored using contacts or contactless. With contacts, the current through the sample is monitored. Figure 2-9 is a schematic measurement circuit for direct contact PCD measurement.\footnote{52}

The contacts should not inject minority carriers, hence the illumination area should be away from the contacts to avoid minority carrier sweep-out. The electric field in the sample should be held at \( E = 0.3/(\mu \tau_r)^{1/2} \), where \( \mu \) is the minority carrier mobility. The excitation light should penetrate the sample as well.

![Fig. 2-9. Schematic diagram for contact PCD measurement.](image)

The change in output voltage between the sample in the dark and the sample illuminated is given by:

\[
\Delta V = (i_{ph} - i_{dk}) R \quad \text{(Eq. 2.29)}
\]
where $i_{ph,dk}$ are measured photocurrent and dark current. The change in conductance is given by:

$$\Delta g = g_{ph} - g_{dk} = \frac{1}{r_{ph}} - \frac{1}{r_{dk}} = \Delta \sigma \frac{A}{L} \quad (\text{Eq. 2.30})$$

where $r_{ph,dk}$ are the steady-state photo-resistance and the dark resistance. Eq. 2.29 can now be rewritten as:

$$\Delta V = \frac{r_{ph}^2 R \Delta g V_0}{(R + r_{ph})(R + r_{ph} + R \Delta g)} \quad (\text{Eq. 2.31})$$

Contact PCD can be split up into two main versions: the constant current method and the constant voltage method. For constant voltage, the load resistor, $R$, is chosen to be very small:

$$\Delta V \approx \frac{R \Delta g V_0}{1 + R \Delta g} = R \Delta g V_0 \left(1 - \frac{\Delta V}{V_0}\right) \quad (\text{Eq. 2.32})$$

For low-level injection ($AgR \ll 1$ or $\Delta V \ll V_0$), $\Delta V \sim \Delta g \sim \Delta n$. Therefore the voltage decay is proportional to excess carrier density. For constant current, $R$ is very large and:

$$\Delta V \approx \frac{(r_{ph}^2 / R) \Delta g V_0}{1 + r_{ph} \Delta g} = r_{ph} \Delta g V_0 \left(\frac{r_{ph}}{R} - \frac{\Delta V}{V_0}\right) \quad (\text{Eq. 2.33})$$

For $r_{dk} \Delta g \ll 1$ or $\Delta V/V_0 \ll r_{dk}/R$, $\Delta V \sim \Delta g \sim \Delta n$ again.

Contactless PCD techniques include using an RF bridge circuit under the sample or a microwave circuit in the reflected or transmitted microwave mode. These two circuitries will be explained in detail in the next chapter.
2.3.3 Quasi-steady-state Photoconductance (QSSPC)

The quasi-steady-state photoconductance (QSSPC) method has the capability to measure lifetimes in the nanosecond to millisecond range.\textsuperscript{69} QSSPC measurements on wafers have been used to investigate trapping and Fe concentrations as well as lifetime. It has been used to measure the lifetime of wafers, block, boules, and ingots.\textsuperscript{70} It utilizes a flash lamp with a decay time of several milliseconds, and illuminates areas of several centimeters. Because of the long decay time, the sample is under a quasi-steady-state as the light intensity varies from its maximum to zero. The generation of electron-hole pairs must be in balance with the recombination of these same pairs.\textsuperscript{69} In other words, the excess carrier concentration must be in equilibrium with the external light intensity at every point in time.\textsuperscript{71} The steady-state condition is maintained as long as the flash time is longer than the measured lifetime. This allows the feasibility to obtain the photoconductance under a large range of illumination intensities in a short time without significant sample heating. The time-varying photoconductance is measured by inductive coupling, and the excess carrier density is calculated from the photoconductance signal. The carrier generation rate is determined from the light intensity measured with a calibrated detector. However, semiconductor materials only absorb a fraction of the incident photons depending on the wafer surfaces and thickness. The absorption fraction of a polished, bare Si wafer is \( f \approx 0.6.\)\textsuperscript{52} QSSPC setups measure the total photoconductance of the sample, therefore making it difficult to separate out bulk lifetimes of multiple films.

Assuming that the flash lamp decay is exponential in time, the generation rate is:
\[ G(t) = 0 \text{ for } t \leq 0; \ G_0 \exp\left(-\frac{t}{\tau_{\text{flash}}}\right) \text{ for } t > 0 \quad (\text{Eq. 2.34}) \]

Therefore, the excess carrier density as a function of time is:

\[ \Delta n(t) = \frac{\tau_{\text{eff}}}{1 - \frac{\tau_{\text{eff}}}{\tau_{\text{flash}}}} G_0 \left[ \exp\left(-\frac{t}{\tau_{\text{flash}}}\right) - \exp\left(-\frac{t}{\tau_{\text{eff}}}\right) \right] \quad (\text{Eq. 2.35}) \]

For \( \tau_{\text{eff}} < \tau_{\text{flash}} \), the sample is in quasi steady-state. Therefore the flash lamp decay time must be sufficiently long for the QSSPC measurement to be valid. Figure 2-10 is an example of a QSSCP plot showing the increasing SRH lifetime with injection level followed by a lifetime decrease due to Auger recombination.\(^{52}\) The decay time constant of the flash lamp is usually adjustable by the user. For QSSPC, the user usually selects the longest time constant possible.\(^{31}\)

Fig. 2-10. Effective recombination lifetime versus injection level obtained with the QSSPC technique.\(^{52}\)
2.3.4 Time-resolved Photoluminescence (TRPL)

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. When the incident photon energy is sufficient ($h\nu > E_G$), the material absorbs the photon and electronic excitations are created.\textsuperscript{52, 72} Photoluminescence decay can be used to monitor the time dependence of excess carriers generated by a short pulse of incident photons. The excess carrier density is monitored by the recombination of electron-hole pairs. PL signal is higher for light-emitting direct bandgap semiconductors such as GaAs and InP. PL analysis is also non-destructive.

The time-resolved photoluminescence (TRPL) technique uses a pulsed light source to excite luminescence from a sample, and then measures the subsequent decay in PL as a function of time. Most setups use a pulsed laser source and detect PL with either a photodiode, streak camera, or photomultiplier tube (PMT) setup for up-conversion, or single-photon counting.\textsuperscript{73} System response time, wavelength range, sensitivity, operational difficulty, and cost vary widely for each configuration. The commonly used PL detection method is the single-photon counting technique. With this technique, the laser pulse is split into two beams with a beam splitter. One beam triggers a time-amplitude converter (TAC) to start ramping up a voltage. The other beam excites PL from the sample. Some of the PL is passed through a long pass filter and a monochromater on to a PMT. Once the PMT detects an emitted photon, it sends a stop signal to the TAC. The TAC voltage is read and stored by a pulse height analyzer. This is repeated at a repetition rate of the laser, typically 250,000 times per second. A single photon is detected approximately once every 200 pulses, leading to a collection time of
about 10 minutes. With appropriate electronics, the system response time is on the order of 30 to 100 ps.

The PL intensity is proportional to the rate of radiative recombination. For direct bandgap recombination, the radiative recombination rate per unit volume is given by: \(^{73}\)

\[
R_{\text{rad}}(t) = B[p(r,t)n(r,t) + p_0(r)n_0(r)] \quad \text{(Eq. 2.36)}
\]

where \(B\) is the radiative recombination coefficient and \(p_0, n_0\) are the equilibrium hole and electron concentrations, respectively. For \(p\)-type material \((p_0 \gg n_0)\) and substituting in \(p = p_0 + p\) and \(n = n_0 + n\),

\[
R_{\text{rad}}(t) = B[p_0(r) + p(r,t)]n(r,t) \quad \text{(Eq. 2.37)}
\]

where \(p\) and \(n\) are excess hole and electron concentrations, respectively. Under low-injection, the radiative recombination rate is linearly proportional to the number of minority carriers. Under high-injection, the PL intensity is proportional of \(p^2\), hence still tracking the decay of excess carriers. By varying sample temperature, sample dimensions, and injection levels, TRPL can determine which recombination process is dominant. TRPL has been used to study the PL decay of CdTe, CIGS, GaAs, InGaAsP, GaInP, GaAsN, GaInAsN, GaNP, GaInN, amorphous-Si, carbon nanotubes, and III-V quantum dots. \(^{73}\)
2.3.5 Short-Circuit Current/Open-Circuit Voltage Decay (SCCD/OCVD)

The overall energy conversion efficiency of a photovoltaic (PV) cell is critically dependent upon the base region minority carrier lifetime of the cell.\textsuperscript{74} The open-circuit voltage decay (OCVD) technique uses either a flash of light or a brief forward current to generate excess minority carriers. The open-circuit voltage ($V_{oc}$) is monitored after the excitation is terminated. This technique assumes that all of the recombination takes place in the base of the PV cell. However, PV cells with base widths shorter than the minority carrier diffusion length and/or low-resistivity at the base\textsuperscript{75} also have recombination occurring in the space charge region as well as in the heavily doped $n^+$ emitter. This complicates the measurement by adding in a surface recombination velocity component.\textsuperscript{76} Measuring both the short-circuit current decay (SCCD) and OCVD, the recombination lifetime and the surface recombination velocity can be determined.\textsuperscript{52}

The theory of this technique is based on a solution of the minority carrier differential equation subject to boundary conditions:\textsuperscript{52}

\[
\frac{1}{\Delta n(x,t)} \frac{\partial \Delta n(x,t)}{\partial x} = -\frac{S_r}{D_n} \quad \text{for } x = d \quad \text{(Eq. 2.38)}
\]

\[
\Delta n(0,t) = 0
\]

for the short-circuit current method where $S_r$ is the surface recombination velocity, and

\[
\frac{\partial \Delta n(x,t)}{\partial x} = 0 \quad \text{for } x = 0 \quad \text{(Eq. 2.39)}
\]

for the open-circuit voltage method.
As noted earlier, with shorter base width, the recombination in the space charge region and the emitter plays a role in the PV cell lifetime. The minority carriers are swept out of the space charge region by the electric field in times on the order of $10^{-11}$ sec under short-circuit conditions. Since the emitter is highly doped, its lifetime is much shorter than the base. Recombination in the emitter causes carriers from the base to be injected into the emitter, where they recombine at a faster rate. Voltage decay is used to determine the recombination rate of the emitter.

Current decay is found to be exponential with time. Its time constant is determined by the time dependence of the excess carrier density. Voltage decay is influenced by the junction RC time constant, but can be reduced by measuring the small-signal decay with a steady-state bias light. For PV cells with a base region thicker than the minority carrier diffusion length, the current and voltage decays are the same since surface recombination is negligible.

### 2.3.6 Open-Circuit Voltage Decay (OCVD)

Figure 2-11 shows a simplified circuit schematic of an open-circuit voltage decay (OCVD) setup and the diode output waveform. The diode is in forward bias by applying a constant current pulse, injecting minority carriers into the base region. At $t=0$, switch $S$ is opened, open-circuiting the diode. The voltage decay at the diode is detected. In Fig. 2-11b, there is a voltage step due to the ohmic voltage drop in the diode from a cease in current flow. This can be used to determine the device series resistance ($\Delta V_d = I_f r_s$, where $I_f$ is the forward bias current and $r_s$ is the series resistance).
Fig. 2-11. Open circuit voltage decay (a) simple circuit schematic and (b) voltage waveform.\textsuperscript{77}

All of the excess carriers in this technique recombine; none are swept out of the device by a reverse current since the current is zero. For a $p$-type substrate, the junction voltage is:\textsuperscript{52}

$$V_j(t) = \frac{kT}{q} \ln \left( \frac{\Delta n_p(t)}{n_{p0}} + 1 \right) \quad \text{(Eq. 2.40)}$$

where $n_{p0}$ is the equilibrium minority carrier density and $\Delta n_p$ is the excess minority carrier density in the quasi-neutral region at the edge of the space charge region. $\Delta n_p$ is related to time-varying junction voltage ($V_j(t)$) by:

$$\Delta n_p(t) = n_{p0} \left[ \exp \left( \frac{qV_j(t)}{kT} \right) - 1 \right] \quad \text{(Eq. 2.41)}$$

The diode voltage is $V_d = V_j + V_b$, where $V_b$ is the base voltage. Voltage in the base, or Dember voltage, is due to the unequal electron and hole mobilities even though
there is no current flow. However, this voltage is negligible for low-injection levels, making $V_d(t) \approx V_j(t)$. The device voltage at low-level injection:

$$V(t) = V(0) + \frac{kT}{q} \ln \left( \text{erfc} \frac{t}{\tau_r} \right) \quad (\text{Eq. 2.42})$$

where $V(0)$ is the diode voltage before opening of the switch. Figure 2-12 is a plot of the above equation. The curve has an initial rapid decay followed by a linear region with a constant slope which can be used to extract the recombination lifetime:

$$\frac{dV(t)}{dt} = -\left( \frac{kT}{q} \right) \exp \left( \frac{-t}{\tau_r} \right) \approx -\frac{kT / q}{\sqrt{\pi \tau_r \text{erfc} \frac{1}{\tau_r}}} \frac{1}{\tau_r \left( \tau_r / 2t \right)} \quad (\text{Eq. 2.43})$$

Figure 2-12. Open circuit voltage decay waveform with $V(0) = 0.55$ V.52
CHAPTER 3

FUNDAMENTALS OF EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

3.1 Introduction

This chapter will describe the fundamentals experimental and characterization techniques used in this dissertation. The growth of all Ge films on Si is done using a molecular beam epitaxy (MBE). Two lifetime techniques were used: (1) microwave photoconductance decay (MWPCD) and (2) quasi-steady-state photoconductance (QSSPC). Characterization tools and techniques include: Fourier transform infra-red spectrometry (FTIR) for Ge film thicknesses, etch pit density (EPD), atomic force microscopy (AFM), secondary electron microscopy (SEM), transmission electron microscopy (TEM), and Hall effect.

3.2 Molecular Beam Epitaxy (MBE)

A molecular beam epitaxy (MBE) setup is used to grow the Ge films used in this research. Figure 3-1 shows a schematic of the substrate holder and heater assembly. Si substrates are clamped down on top of the substrate heater with tungsten clips. The maximum substrate size this assembly can accommodate is 2 inches. The substrate heater is a 50 mm x 50 mm pyrolytic boron nitride (PBN) plate encasing a pyrolytic graphite filament made by Momentive Performance Materials. The power leads of the
heater are connected via high vacuum rated banana plugs. The substrate assembly is loaded into the load lock that is vented with pure N\textsubscript{2} gas. A turbo-molecular pump operating at 240 L/s pumps down the load lock with the pressure monitored by a thermocouple and cold-cathode gauge.

![Fig 3-1. a schematic of the substrate holder and heater assembly.](image)

The substrate holder assembly is transferred from the load lock into the deposition chamber by a magnetically coupled manipulator. Figure 3-2 shows a schematic diagram of the MBE system with its major components. A receiver mounting in the deposition chamber guides the substrate holder assembly's banana plugs into the female plug receptacles that are connected to a power feed-through vacuum fitting. The deposition chamber is pumped down via a 500 L/s turbo-molecular pump and a 400 L/s ion pump
producing a base pressure of $5 \times 10^{-10}$ Torr measured by a nude ion gauge. The effusion cell has a dual-filament and heats up a double-walled PBN crucible filled with Ge source material of 99.9999% purity. The effusion cell temperature is monitored by two thermocouples near the outside of the PBN crucible.

Fig 3-2. Schematic diagram of the MBE chamber and its major components.

3.3 Lifetime Setups

Minority carrier lifetime measurements can be quick, easy, and inexpensive. They are often an indication of the quality of the material since lifetimes are extremely sensitive to mid-gap defect states; the longer the lifetime, the better the quality of the film. Two lifetime techniques were used: (1) microwave photoconductance decay ($\mu$PCD
or MWPCD) and (2) quasi-steady-state photoconductance (QSSPC). MWPCD was performed by Steven Johnston at the National Renewable Energy Laboratory (NREL) in Golden, Colorado. The QSSPC setup is located at Sandia National Laboratories (SNL) in Albuquerque, New Mexico.

### 3.3.1 Microwave Photoconductance Decay (µPCD or MWPCD)

There are many techniques to measure excess carrier lifetime by means of photoconductance decay, differentiated by the method used to detect change in photoconductance or carrier concentration. Among these techniques are ohmic contacts, photoluminescence, radio-frequency, inductive-coupling, and microwave reflection; each technique having its particular advantages. MWPCD uses high frequency microwaves combined with high-speed laser optical excitation. The generation of excess carriers increases conductivity, causing a change in the microwave reflectivity. ⁷⁹

A typical MWPCD setup consists of a microwave source, a waveguide, and a circulator which separates the reflected component. The end of the waveguide directs the microwave through a glass plate onto the bottom of the wafer. The microwaves are essentially planar and normally incident on the dielectric plate and wafer, thus the microwaves follow simple one-dimensional wave theory for lossy dielectrics, with the exceptions of energy loss by diffraction from the metal plate and the fixed reflectance from an abrupt waveguide termination. ⁸⁰ The reflected microwave signal is detected by rectification, by converting AC to DC. A DC voltage proportional to the amplitude of the reflected microwave beam is created across a load resistor. The DC voltage is dependent
on the sample conductance and reflection plate position. A small variation from the laser excitation is imposed on top of DC voltage. This variation is linearly proportional to change in the sample conductance which in turn is proportional to the change in excess carrier concentration. In order to amplify this small signal, a high pass filter (AC coupling) is used to block out all of the DC components.\textsuperscript{80} MWPCD also utilizes a sampling method where the laser pulses repeatedly and one point of the decay curve is measured in each pulse. However, substantial waveform shifts can be introduced if the carrier lifetime approaches the laser repetition period because not all of the excess carriers have recombined by the time the next pulse arrives. Therefore carriers build up with each successive laser pulse.

The metal "backstop" reflector also plays a very important role in MWPCD measurements. The metal reflectors reflect all of the microwaves not absorbed by the sample, creating a standing-wave pattern.\textsuperscript{81} The spacing between the sample and the metal reflector determines the position of the standing-wave electric field maximum relative to the lossy sample. Samples with low conductivity are highly transparent to microwaves, thus the net reflectance is large since all of the microwaves are being reflected by the metal reflector. Samples with high conductivity will reflect most of the microwaves themselves, also leading to a large net reflectance. The reflected microwave for samples with intermediate conductivity is greatly influenced by the distance between the metal reflector and the sample.\textsuperscript{81}

The NREL MWPCD setup has a frequency range from a few to tens of GHz. The sample is coupled to the end of a microwave waveguide or an antenna structure. Changes in the reflected microwave power are sensed as short light pulses illuminate the sample
and modulate its photoconductivity. In this setup, a tunable laser is used as a pulsed light source to generate excess carriers. Figure 3-3 shows the experimental setup of the MWPCD. The microwave power is supplied by a signal generator which travels through an isolator before entering a directional coupler. Following is a circuitry containing an E and H tuner, which are sliding shorts in each plane of the waveguide, used to match the impedance of the sample to the attached waveguide. For each sample, impedance matching is performed without excess carrier generation; the circuit’s null response corresponds to no power reflection. The sample’s conductivity is changed with each light pulse, disrupting the balanced circuit, and resulting in reflected power. The reflected power returns through the directional coupler and is coupled out to an amplifier and a subsequent diode detector. The detector output is amplified by a high bandwidth pulse amplifier and displayed on an oscilloscope.
3.3.2 Quasi-steady-state Photoconductance (QSSPC)

The QSSPC setup used is the WTC-120 from Sinton Instruments. As explained in chapter 2, this technique uses a pulse of light from a strobe lamp, which optically injects carriers into the Si or Ge to increase carrier concentration. Without contacting the wafer, $\sigma(t)$ is sensed by an RF bridge which inductively couples the wafer photoconductivity.

The physical setup consists of a computer, a flash lamp, and a measurement stage. Hardware and software requirements for the computer includes: (1) Pentium or faster processor, (2) full-sized PCI card slot, (3) National Instruments 6111 card, and (4) Excel 2000. The flash lamp is a Quantum Q-paq flash system with a QFlash X5D flash head and power supply. The setup also uses a 1000 nm IR-pass filter, which is inserted.
between two white diffusers installed between the reflector and retaining rings. The IR-pass filter controls the peak lamp intensity. The measurement stage detects the light level and photoconductance. The stage has a plastic housing which encloses a light level sensor, an RF inductor, and a RF bridge circuit. The light level sensor detects the flash intensity, and the information is directly sent to channel 1 (CH1) of the oscilloscope or computer. A 3-turn RF coil with an estimated inductance of ~0.16 µH is placed directly under the wafer. The inductance is calculated by measuring radius of the inductor to determine the coil length. The equation used for the calculation was that of an air coil.85 The inductor is attached to the stage via two steel screws.

Before measurements were taken, the system’s calibration was checked with an undoped wafer, tuning the instrument to 100 mV by adjusting a variable capacitor and a variable resistor which are parallel to the inductor. The RF frequency is generated by a crystal oscillator at 13.56 MHz by Vectron.86 Figure 3-4 shows a schematic diagram of the setup.
There are two measurement techniques available for the WTC-120: the (1) transient photoconductance decay method and the (2) quasi-steady-state method. In the transient case, the effective lifetime is only valid if the carrier lifetime is significantly longer than the decay time of the flash. The transient flash duration in this setup is 15 µs. The transient decay method is a “stand-alone” method that does not require precise calibration of the photoconductance, and the results are also independent of the pulse intensity. An example of a measurement taken using the transient photoconductance decay method is shown in Fig. 3-5(a). The figure shows the photoconductance (PC) signal and intensity signal from the light level sensor of a p-type, high resistivity, floating zone (FZ), Si substrate with hydrogen surface passivation. The photoconductance signal (PC) is a voltage pulse that corresponds to a change in the RF bridge, which is proportional to conductivity. Note the very short flash duration in blue compared to the
PC signal in red. Figure 3-5(b) is an exponential decay fit of the photoconductance, giving a lifetime ($\tau$) of 150 $\mu$s.

Fig. 3-5(a). PC signal and light level intensity (in transient mode) for a high resistivity, FZ, Si substrate which received a 2 minute DHF dip, rinse, and spin dry.
Fig. 3-5(b). Exponential decay fit of the photoconductance, giving a measured lifetime of 150 µs.

The exponential time dependence of the transient decay curve was used to measure lifetimes in the wafer that are greater than 130 µs for our wafers. However, for Si and Ge/Si samples with shorter effective lifetimes, meaningful steady-state lifetimes were difficult to extract due to effects such as minority-carrier spreading that have a similar or longer transient time as the recombination lifetime itself. That is, transport transients become equally or more important than the recombination transient in determining the rate of decay of the photoconductance signal. This was undesirable when trying to probe the recombination lifetime in the material. An alternative approach to overcome this problem is the QSS measurement. The QSS method uses a longer pulse time (i.e., pulse time >> $L_{\text{substrate}}^2 / D_{n,p}$) to drive the system into a quasi-steady-state, which allows much shorter recombination lifetimes to be examined. However, this
method requires that the conductance be calibrated to the exact carrier concentration. Figure 3-6 shows the QSS PC signal and the intensity signal for a sample that has nominally 600 Å of recrystallized a-Ge:H on a p-type Si substrate. Note that the flash duration is comparable to the PC time. All lifetime measurements for Ge/Si heterostructures are taken from the backside of the Si substrate.

![Illumination at Reference Cell and PC Signal](image)

Fig. 3-6. Intensity and PC signals of a Ge/Si heterostructure in QSS mode.

3.4 Characterization Tools and Techniques

3.4.1 Fourier Transform Infra-red Spectrometry (FTIR)

In Fourier transform infra-red spectrometry (FTIR), IR radiation is passed through a sample with some of the IR absorbed by the sample and the rest transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a
molecular fingerprint of the sample. The absorption peaks correspond to the frequencies of vibrations between the atomic bonds making up the material. Each molecular structure has its own IR spectrum since different material is a unique combination of atoms. The size of the peaks in the spectrum is a direct indication of the amount of material present. FTIR is also a nondestructive technique with only one moving part.

Before FTIR, IR instruments were of the dispersive type. The instruments separated the individual frequencies of energy emitted from the IR source using a prism or a grating. The detector measured the amount of energy at each frequency after it has passed through the sample, resulting in a plot of intensity vs. frequency. However, this process is very slow, and a process in which all of the IR frequencies are measured simultaneously is needed. The solution was a Michelson interferometer. The interferometer produces a unique type of signal where all of the IR frequencies are encoded into it. Most interferometers use a beam splitter which takes the incoming beam and splits it into two optical beams. One beam is reflected off a fixed flat mirror while the other beam is reflected off a mobile flat mirror. The two beams reflect off their respective mirrors and recombine back at the beam splitter. Since one beam travels a fixed length while the other is constantly changing as its mirror moves, the resulting recombination of these two beams is an interference with each other called an interferogram. This recombined beam is then sent to the sample and detector. Figure 3-7 is a schematic diagram of a Michelson interferometer, configured for FTIR. An interferogram cannot be interpreted directly, but goes through a mathematical technique called a Fourier Transform converting the data encoded in the interferogram into a spectrum.
A typical sample analysis process starts at the source. IR energy is emitted from a glowing black-body source and passes through an aperture that controls the amount of energy presented to the sample. The beam enters the interferometer to be "spectrally encoded" before entering the sample compartment where it is transmitted through or reflected off the surface of the sample, depending on the type of analysis desired. The beam finally passes through a detector designed to measure the interferogram signal. The interferogram is sent to a computer for Fourier Transform, and an IR spectrum is computed. A background spectrum is usually taken to remove any contributions from the system, resulting in a FTIR spectrum strictly due to the sample. A sample analysis process diagram is shown in Fig. 3-8.88

---

Fig. 3-7. A schematic diagram of a Michelson interferometer, configured for FTIR.90
FTIR is typically used to identify unknown materials, determine the quality or consistency of a sample, and to determine the amount of components in a mixture. However, FTIR is used in this research to measure Ge film thickness. A description of how Ge film thickness is extrapolated from the FTIR spectrums is found in the next chapter.

3.4.2 Etch Pit Density (EPD)

Etch pit density (EPD) is commonly used as a measure of quality for semiconductor wafers. An etch solution is applied on the surface of the wafer where the etch rate is increased at dislocations of the crystal resulting in pits. Typically, a thin layer of the sample surface is oxidized by a first reagent (sulfuric or nitric acid) and subsequently dissolved by a second reagent (hydrofluoric acid). Often, the etch rate is controlled by diluting the etchant with acetic acid or de-ionized water. Internal excess
stress at defects (stacking faults, threading dislocations, twin, etc.) lowers the bond strength in those areas, allowing the etchants to more easily break those bonds, then oxidize and dissolve the material. Advantages of using EPD is that it gives you an inexpensive, quick, and reliable statistical count of defects that intersect the surface of the material, especially for indirect bandgap semiconductors that cannot utilize cathodoluminescence (CL), normally used for defect counting. Unfortunately, with epitaxial films, the defect density is not uniform from the interface to the surface of the film. The defect density must also be below $10^9 \text{ cm}^{-2}$ so that the etch pits can be resolved by an optical microscope or secondary electron microscopy (SEM). Higher defect densities must be determined using transmission electron microscopy (TEM) which has a lower limit of $10^7 \text{ cm}^{-2}$. Figure 3-9 shows an example of etch pits; it is a SEM image of a Ge film grown on Si by MBE.

Fig. 3-9. SEM image of etch pits and stacking faults in a Ge/Si MBE grown film.
3.4.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM), also known as scanning force microscopy (SFM) or scanning probe microscopy (SPM), measures the force between a very sharp probe mounted on a cantilever and a sample surface. The cantilever can have a spring constant more than an order of magnitude lower than the spring constant between two atoms.\footnote{In this research, AFM is used to measure surface roughness after CMP.}

The AFM has three basic imaging modes: contact, non-contact, and tapping mode. Contact mode imaging is greatly influenced by tip attraction; an image is formed by dragging the tip across the sample surface. This mode is best for hard materials. Because surface tension forces can pull the tip down, the sample can be damaged, distorting the image. Additionally, small particles on the sample surface can also contaminate the tip, resulting in a misrepresentation of the sample surface.

In tapping mode, the cantilever is oscillating in ambient air near the cantilever’s resonant frequency at very high amplitudes. The tip is lowered towards the surface until it is slightly touching or tapping the surface. The tip then rasters across the surface, decreasing in amplitude when it encounters a bump since there is less room to oscillate. When the tip encounters a divot, its amplitude increases due to more oscillating room. The amplitude changes are sensed by a laser and a detector. A laser beam is focused on the cantilever and reflected towards a detector. Subsequently, the detector sends the data to a computer which records and maps the amplitude change.\footnote{Since we do not have access to tapping mode, non-contact mode is used in this research. In non-contact mode, the tip is brought within a close proximity of the surface}
such that van de Waals forces between the sample and the tip causes the tip to be
deflected. It is usually preferred for soft materials such as Ge. Like tapping mode, the
cantilever is also held oscillating above the sample and uses a feedback loops system to
maintain constant oscillation. Although the resolution is not as good as contact mode, it
does not have contact mode's drawbacks.

There are some limitations to AFM. One limitation is imaging deep fissures. If
the tip is not long enough, or thin enough, to reach the bottom of the recess, a square
fissure will be misrepresented as a wedge trench. The AFM also cannot properly image
undercuts [Fig. 3-10(a)] since the tip cannot access the area, nor can it accurately
interpret angles steeper than the tip’s own angle [Fig. 3-10(b)].

Fig. 3-10. Tapping Mode AFM cannot properly image (a) angles steer than the tip, and
(b) undercuts.
3.4.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was used to characterize the quality of the Ge lattice structure and its defect density. Although it is a destructive technique with laborious sample preparation steps, TEM has many advantages over other microscopy techniques. Phase contrast TEM can resolve as low as 2.5 Å (all-purpose TEM) along the low index direction for lattice imaging, and less than 2 Å in high resolution TEM or HRTEM.\textsuperscript{92, 97}

A TEM sample is prepared by first using an epoxy to glue two small pieces (device or film side) of the wafer together and on to a piece of glass work that is mounted on to a tripod polishing jig. A subsequent mechanical polish using polymer sheets impregnated with silicon carbide crystals of varying sizes thins down the sample to about 15 µm. Ion milling thins the sample thickness down to less than 250 nm thick. This step is performed using low energy (250-500 V) Ar ions with a low incident beam angle (< 9°) to minimize the sample surface damage (amorphization). Argon ion milling can thin the sample down to as low as 1.5 nm\textsuperscript{98-100} which does not affect image obtainability. Once the sample is ready, it is loaded into the TEM and bombarded with a highly-focused, monoenergetic (100 keV to 3 MeV) electron beam.\textsuperscript{92} The energy from the beam propagates through the sample and a series of magnetic lenses (above and below the sample) which magnify the transmitted electron signal (Fig. 3-11).
When the incident beam is incident upon the sample, not all of the electrons are transmitted. Figure 3-12 shows some of the scattering mechanisms found. Transmitted and diffracted (elastic) electrons are used for imaging, while x-rays and inelastic electrons are used by an energy dispersive spectrometer (EDS) and electron energy loss spectrometer (EELS) for elemental analysis. Elements in a sample are determined by the amount of energy incident electrons has lost and the characteristic x-rays each element produces. Electron diffraction allows analysis of crystallinity, grain orientation, texture, and phase identification. Since the samples are on the order of sub-micron thickness and that Ge can tolerate high temperature, transmitted electrons pass through Ge without causing much damage.
TEM imaging is basically formed by 3 mechanisms: (1) thickness-mass contrast, (2) diffraction contrast, and (3) phase contrast. Figure 3-13 shows three TEM images of Ge/Si grown by plasma enhanced chemical vapor deposition (PECVD). The contrast between Ge and Si is due to the difference in mass, therefore known as mass contrast. Mass contrast is independent of the crystal structure. Its intensity is based on the scattering power of the element, where lighter elements absorb fewer electrons than heavier elements. Diffraction contrast can image crystallinity and defects such as threading dislocations induced by strain from lattice mismatch [Fig. 3-13(b)]. Especially in single crystalline material, defects disturb the order of the lattice diffracting electrons differently than the lattice. The contrast in poly-crystalline materials is due to the orientation of the adjacent grains relative to the incident beam [Fig. 3-13(c)]. High-resolution TEM (HRTEM) is used to image crystal structure. The sample is tilted so that a low-index direction is perpendicular to the incident beam. This allows all of the lattice
planes parallel, or close to parallel, to the incident beam to be close to the Bragg position, diffracting the incident beam. The diffracted beams are at a different phase with respect to the incident beam, thus the name, phase contrast. All of the diffracted beams and the incident beam are collected by a series of magnetic objective lenses. The interference between the beams lead to an enlarged image of the periodic potential [Figure 3-13(b)].

![Fig. 3-13](image)

(a) (b) (c)

Fig. 3-13. (a) TEM image of Ge/Si showing the mass contrast of Ge and Si. (b) HRTEM image showing epitaxial Ge on Si and threading dislocations via diffraction contrast. (c) TEM image of poly-crystalline Ge on Si by diffraction contrast.

3.4.5 Secondary Electron Microscopy (SEM)

A scanning electron microscope (SEM) can give a highly magnified “quick look” at surface structures when the object of interest cannot be resolved by an optical microscope. The SEM is often compared to the TEM since both tools use focused
electron beams. Although SEM magnification ranges from 10x to 100,000x (300,000x to 500,000x for HRTEM) with a minimum resolution of about 20 Å, plan-view SEM imaging and analysis are nondestructive.\textsuperscript{92,97}

A focused electron beam is raster-scanned over a small rectangular area, producing signals that create an image or for elemental analysis. Signals include secondary electrons, backscattered electrons, Auger electrons, beam-induced electron pair generation (EBIC), and voltage-field enhancement (voltage contrast).\textsuperscript{97} Secondary electrons are collected by detectors whose outputs modulate the brightness of a cathode ray tube (CRT), producing a 3-D image on the screen. Figure 3-14 shows the beam interaction with a sample. Like TEM, the incident electron beam does not damage the sample.

Fig. 3-14. When a focused electron beam hits the sample, both electrons and photons are emitted from the surface.\textsuperscript{103}
The diameter of the electron probe is 1 to 2 nm, however, the excited volume of the sample may be up to 1 µm in diameter depending on the energy of the incident electrons. Using lower electron energies to excite a smaller sample volume can increase the resolution to 1 to 3 nm in some materials. Figure 3-15 shows a depiction of sample excitation due to absorption of high energy electrons. It compares the excitation volume between 5 keV electrons and 30 keV electrons.

![Figure 3-15](image1)

Figure 3-15. Comparison of sample volume excitation between 5 keV electrons and 30 keV electrons.

SEM is used in this work to view the Ge surface morphology and to estimate Ge film thickness. Figure 3.11(a) is a plan-view SEM image of PECVD grown Ge on Si
with craters and blisters that formed during Ge deposition. A cross-sectional SEM is used to determine the origin of the blisters on the Ge surface [Figure 3-16(b)]. The image shows blisters where the Ge delaminated at the Ge/Si interface.

Fig. 3-16. (a) Plan-view (surface scan) SEM image of Ge with craters and blisters. (b) Cross-section SEM of one of the blisters from (a), showing Ge delamination. Images are from Lot MC054904A, compiled by Dr. Kent Childs.

3.4.6 Hall Effect

The key feature of Hall measurements is the ability to determine carrier density, type, and mobility. Discovered in 1879 by Edwin H. Hall, the Hall effect is a voltage difference (Hall voltage) across a conductor that is transverse to an electric current running through the conductor and has a magnetic field perpendicular to the current.\textsuperscript{105}

\textsuperscript{106} When a magnetic field is not applied parallel to the moving charges in a conductor,
the charges follows the Lorentz force. If no magnetic field is applied, the charges take a straight-line path which can lead to collisions with impurities, phonons, etc. But if a magnetic field is applied perpendicular to the moving charges, the magnetic field exerts a transverse force on the moving charges curving the path of the carriers, pushing them to the edge of the conductor.\textsuperscript{105, 106} The positive charges are moved to one side and the negative charges on the other. The separation of charges establishes an electric field, further forcing the opposing charges to stay on their side of the conductor. As the current continues to flow, charges continue to accumulate, building a measurable potential across the conductor. This potential is called the Hall voltage. Figure 3-17 shows a diagram of the forces, fields, and carriers in a Hall measurement setup.

Fig. 3-17. Diagram of fields, forces, and charges of a conductor during a Hall measurement.
The magnetic force and current through the conductor are:

\[ F_m = qv_d B \]  \text{(Eq. 3.1)}

\[ I = qeAv_d \]  \text{(Eq. 3.2)}

\[ F_m = \frac{qIB}{neA} \] \text{(Eq. 3.3)}

@ equilibrium: \( F_m = F_e = \frac{qV_H}{w} \)

where \( I \) is the current, \( B \) is the magnetic field, \( q \) is the carrier charge, \( n \) is the electron carrier density in this case, \( w \) is the width of the conductor \( (A=wd) \), and \( v_d \) is the carrier drift velocity. For a simple metal with only one type of charge carrier (electrons):

\[ V_H = \frac{-IB}{qnd} \] \text{(Eq. 3.4)}

where \( d \) is the thickness of the conductor. The polarity of the Hall voltage is different for negative and positive carriers. The Hall coefficient is (in SI units):

\[ R_H = \frac{E_x}{j_x B} = \frac{V_H d}{IB} \] \text{(Eq. 3.5)}

For extrinsic \( p \)-type \((p >> n)\):

\[ R_H = \frac{1}{qp} \] \text{(Eq. 3.6)}

For extrinsic \( n \)-type \((n >> p)\):
\[ R_H = \frac{-1}{qn} \] (Eq. 3.7)

For semiconductors with a moderate magnetic field applied:

\[ R_H = \frac{-n\mu_e^2 + p\mu_h^2}{q(n\mu_e + p\mu_h)^2} \] (Eq. 3.8)

where once again, \( n \) is the electron density, \( p \) is the hole density, and \( \mu_{e,h} \) are the electron and hole mobilities. For semiconductors with a large magnetic field applied, the single carrier expression holds:

\[ R_H = \frac{p - nb^2}{q(p + nb)^2}, \quad b = \frac{\mu_e}{\mu_h} \] (Eq. 3.9)

Theoretically, there is a scattering factor, \( r \), in the numerator, whose value lies between 1 and 2, and is dependent on the scattering mechanisms of the semiconductor.\(^{52}\) In high magnetic fields, \( r \to 1 \). However, this is not achievable in most labs. Typically, the magnetic field is between 0.5 to 10 kG, making \( r > 1 \). Since \( r \) is usually not known, it is assumed to be unity. This assumption gives a less than 30% error.

The Hall Effect is used to measure the carrier density, resistivity, and mobility at a given temperature, and the carrier density is a function of temperature to extract additional information. For a \( p \)-type semiconductor with doping \( N_A \) compensated with donors of \( N_D \), the hole density is determined by:\(^{52}\)

\[ \frac{p \left( p + N_D \right) - n_i^2}{N_A - N_D - p + n_i^2/p} = \frac{Nv}{g} \exp\left( -\frac{E_A}{k_BT} \right) \] (Eq. 3.10)
Equation 3.10 can be simplified for certain conditions.

1. At low temperatures where \( p << N_D, p << (N_A - N_D), \) and \( n_i^2/p \approx 0 \)

\[
p \approx \frac{(N_A - N_D) N_v}{g N_D} \exp \left( -\frac{E_A}{k_B T} \right) \quad \text{(Eq. 3.11)}
\]

2. When \( N_D \) is negligibly small,

\[
p \approx \sqrt{\frac{(N_A - N_D) N_v}{g}} \exp \left( -\frac{E_A}{k_B T} \right) \quad \text{(Eq. 3.12)}
\]

3. At higher temperatures where \( p >> n_i \),

\[
p \approx N_A - N_D \quad \text{(Eq. 3.13)}
\]

4. At still higher temperatures where \( n_i >> p \),

\[
p \approx n_i \quad \text{(Eq. 3.14)}
\]

Hall measurements are generally made on samples from which an average carrier density is derived. For a uniformly doped sample, a true density is derived. For a non-uniformly doped sample, the carrier density is only an average. In this work, Hall measurements were made to estimate the Ge film mobility and carrier type.
CHAPTER 4

EXPERIMENTAL AND CHARACTERIZATION METHODS

4.1 Introduction

Low-defect Ge/Si heterostructures require the minimization of contaminants such as carbon and oxygen at the Si surface so that when Ge is deposited, these elements are not trapped at the interface. Residual oxygen and carbon concentrations have been correlated with an increase in defects and undesirable formation of electrically active defects. Native oxide and organic contamination degrades device performance. Different surface cleans are available to remove the native oxide formed from long exposure to air. However, not all cleans prevent re-oxidation. This chapter begins with a description of the steps taken to prepare the Si substrates for each growth method, followed by the various growth methods characterized by minority carrier lifetime, our patented CMP procedure, etch pit density measurements, and using FTIR to extrapolate Ge film thicknesses.

4.2 Sample Preparation Steps

The first step to growing a good Ge/Si heterostructure is to remove the native oxide and organic contaminants on the bare Si substrate surface. Si (100), p-type wafers are used in this research unless otherwise noted. The resistivities of the Si substrates used are as following: 0.003-0.005 Ω-cm, 1-10 Ω-cm, 500-1000 Ω-cm, and 1000-4000 Ω-cm
(semi-insulating, SI). In order to remove as much of the organic contaminants as possible, all wafers are first submerged in a piranha solution consisting of 3 volumetric parts of 96 wt% sulfuric acid (H$_2$SO$_4$) and 1 part of 30 wt% hydrogen peroxide (H$_2$O$_2$) heated to 373 K for 5 minutes. Subsequent dip in a buffered oxide-etch solution (20 parts 40 wt% NH$_4$F:1 part 49 wt% HF) diluted in deionized (DI) water by 1:6 volumetric ratio removes the chemical oxide. A second Piranha solution is used to grow a 1.4-nm-thick chemical oxide, followed by a DI water rinse, and blown dry with N$_2$. Once the sample is loaded into the deposition chamber, the substrate temperature is ramped up to the growth temperature and sits at the temperature for 10 minutes without exposure to the effusion cell to degas. The effusion cell temperature is increased to 1473 K to maintain a Ge growth rate of 9.3 nm/min (6.8×10$^{14}$ atoms cm$^{-2}$s$^{-1}$). The pressure in the chamber remains below 1.3×10$^{-6}$ Pa during the deposition. The substrate temperature for all samples used in this research is 853 K.

4.2.1 Piranha Solution and Thin Film Oxide Growth

The piranha solution is known to be a very effective solution in removing organic residues, and does so in two distinct processes.$^{109}$ The first and much faster process is a rapid dehydration process where concentrated H$_2$SO$_4$ removes oxygen and hydrogen as units of water. This process also exhibits a rapid carbonization process of common organics such as carbohydrates. When large amounts of organics are immersed in a piranha solution, the organics are dehydrated so quickly and so violently that it resembles a piranha feeding frenzy, thus getting its name. The second process is the ability of the piranha solution to dissolve elemental carbon in the form of soot and char. Elemental
carbon is notorious for its resistance to room temperature aqueous reactions. The combination of H$_2$SO$_4$ and H$_2$O$_2$ produces the following reaction:

$$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- + \text{O}$$

where hydronium ions, bisulfate ions, and atomic oxygen are formed. Carbon allotropes are highly stable and very difficult to attack chemically. The extremely reactive oxygen atom will attach to a surface carbon to form a carbonyl group:

The oxygen atom disrupts the bonds of the carbon atom with its neighboring carbons, allowing for further oxidation converting the carbonyl group into carbon dioxide and a new carbonyl group on the neighboring carbon:

Although oxidation process (minutes) is slower than the dehydration process, with time, the piranha solution will return to clarity with no visible traces of the original organic materials. The high acidity of the piranha solution also dissolves deposits such as metal oxides and carbonates. The remaining oxygen atoms will oxidize the Si substrate surface forming a self-limiting layer of chemical SiO$_2$. 
4.2.2 Buffered Oxide Etch (BOE)

A diluted buffered oxide etch is used to remove the chemical SiO$_2$ formed in the piranha solution. The overall reactions for etching SiO$_2$ with BOE are$^{110,111}$

\[
\text{SiO}_2 + 4 \text{HF} \rightarrow \text{SiF}_4 (g) + 2 \text{H}_2\text{O}
\]

\[
\text{SiO}_2 + 6 \text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}
\]

The buffering agent, ammonium fluoride (NH$_4$F) in this case, is added to help maintain the HF concentration and to control pH. The buffering reaction is:

\[
\text{NH}_4\text{F} \leftrightarrow \text{NH}_3 + \text{HF}
\]

Although HF is classified as a weak acid due to its low dissociation constant, it is highly corrosive and can be lethal if swallowed.

4.2.3 Degassing

To remove any excess piranha or BOE, substrates are rinsed in DI water and blown dry with an argon (Ar) gun. However, the Ar gun is insufficient at removing all of the water molecules which can lead to defects in the Ge film. Therefore, a degassing step to remove any residual water molecules is required. A typical bake-out temperature to desorb water molecules after the chamber has been subjected to atmospheric pressure is 523 K.$^{112}$ With a minimum Ge growth temperature at 853 K, 10 minutes at this temperature is sufficient to desorb any residual water molecules on the substrate surface.
4.3 Growth Methods

Except for the control sample of direct Ge growth on Si substrates, each growth method is based on our patented Touchdown technique which will be described in the next section. We have found that annealing the Ge film at different stages of island coalescence during the touchdown growth affects the defect density which will be further discussed in the next chapter.\textsuperscript{113} The minority carrier lifetime is measured and compared for four different growth methods, and they will be referred to as: (a) direct Ge-on-Si (Ge/Si) Heteroepitaxy [Method 1], (b) sealed oxide and post-growth annealed [Method 2], (c) unsealed oxide and pre-growth annealed [Method 3], and (d) unsealed oxide and pre/post-growth annealed [Method 4]. The details of each growth method will also be described in this section.

4.3.1 “Touchdown” Technique

The “touchdown” technique uses Ge flux to create nanometer-sized openings in thin SiO\textsubscript{2} film on Si substrates before growing Ge islands out of these holes and coalescing to form low defect Ge films. There are two specific requirements for dislocation-free growth of Ge on Si: (1) the diameter of the Ge islands need to be less than 10 nm, and (2) the spacing between the Ge islands need to be more than 3 nm apart\textsuperscript{114}, which are met by the touchdown technique.

The SiO\textsubscript{2} used in the touchdown technique is chemically formed as the result of a heated (100°C) piranha solution with a thickness of 1.4 nm measured by high resolution cross-sectional scanning transmission electron microscopy (HR-STEM) shown in Fig. 4-
The dark spots in the image are SiO$_2$ patches. Exposure of the chemical SiO$_2$ to a Ge flux creates the following reactions:

$$\text{Ge (g) + SiO}_2\ (s) \rightarrow \text{GeO (g) + SiO (g)}$$

Fig. 4-1. High resolution cross-sectional scanning transmission electron microscopy (HR-STEM) image showing the Ge/SiO$_2$/Si interface, with voids of 3 to 7 nm in diameter in the SiO$_2$.

However, Ge must first diffuse through the oxide to the SiO$_2$/Si interface before the reaction products can propagate laterally outward and upward towards the oxide surface [Fig. 4-2(b)]. Once the void forms, Ge atoms selectively nucleate on the exposed Si substrate surface forming islands [Fig. 4-2(c)], eventually growing out over the remaining SiO$_2$ and coalescing into a complete film [Fig. 4-2(d)]. Planarization is performed afterwards to smooth out the surface [Fig. 4-2(e)].
Fig. 4-2. (a) Ge atoms diffuse through the oxide to the oxide/Si interface before breaking bonds and forming volatile GeO and SiO (b) that propagates outwards and outwards through the oxide (c) forming voids exposing the Si substrate surface. (d) Ge selectively nucleates and grows on the exposed Si (e) eventually growing out of the voids and coalescing to form a continuous film (f) that is subsequently planarized.

4.3.2 Direct Ge-on-Si Heteroepitaxy [Method 1]

For direct Ge grown on Si substrates, the chemical oxide from the piranha etch is removed using a diluted HF solution before loading into the MBE for a 10 minute degassing step followed by exposure to the Ge flux until approximately 3.5 µm of Ge
film is formed [Fig. 4-3(a)]. With direct Ge on Si growth, Ge atoms randomly nucleate on the bare Si substrate surface, forming a high density of Ge islands before coalescing into a continuous film. Figure 4-4(a) shows a TEM image of Ge grown directly onto a Si substrate with a very high density of threading dislocations throughout the Ge film.

Fig. 4-3. Cartoon diagram of the four Ge growth methods are compared by lifetime measurements and referred to as: (a) direct Ge/Si [Method 1], (b) sealed oxide and post-growth annealed [Method 2], (c) unsealed oxide and pre-growth annealed [Method 3], and (d) unsealed oxide and pre/post-growth annealed [Method 4].
4.3.2 Sealed Oxide and Post-Growth Annealed [Method 2]

The sealed oxide and post-growth annealed growth process follows the touchdown process until 450 nm of Ge is deposited, followed by an \textit{in situ} anneal at 1123 K for 30 minutes, before growing another 3.5 \( \mu \)m thick Ge film [Fig. 4-3(b)]. Annealing the 450 nm of coalesced Ge film at 1123 K for 30 minutes propagates the threading dislocations to either the edge of the film or into each other so that they do not further propagate upwards with subsequent film growth. TEM [Fig. 4-4(b)] shows that the threading dislocations are gone, but the film is full of stacking faults.
4.3.2 Unsealed Oxide and Pre-Growth Annealed [Method 3]

For unsealed oxide and pre-growth annealed samples, 10 nm of Ge is first deposited via the touchdown process. In this growth process, the Ge islands have not yet fully coalesced; the 10 nm of Ge is an effective thickness that would have resulted if the Ge had formed a continuous film. The Ge islands are annealed in situ at 1123 K for 30 minutes, followed by a 3.5 µm Ge film deposition [Fig. 4-3(c)]. This annealing step is intended to drive out stacking faults with ease before forming a continuous film that, without annealing, results in a high density of stacking faults. TEM [Fig. 4-4(c)] shows that the stacking faults are gone but the threading dislocations have returned.

4.3.2 Unsealed Oxide and Pre/Post-Growth Annealed [Method 4]

The unsealed oxide and pre/post-growth annealed growth process is the same as unsealed oxide except that another 30 minutes at 1123 K anneal step is added after the 3.5 µm Ge film is deposited [Fig. 4-3(d)]. This second anneal step drastically reduces the number of threading dislocations. TEM [Fig. 4-4(d)] shows that most of the defects are trapped within the first 200 nm of the film from the Ge/Si interface.

4.4 Chemical Mechanical Polishing (CMP)

Chemical mechanical polishing (CMP) is performed on every sample after film growth. AFM measurements of Ge grown on oxidized Si show a root-mean-square (RMS) roughness of about 70 nm due to the coalescence of 3D Ge islands during growth.
For any subsequent processing, it is necessary to planarize the Ge surface using CMP. Commercial slurries made especially for Ge polishing is currently not available, therefore a combination of slurries and polishing pads is tried to try to produce the optimal surface. Since Ge is considered a soft material, a soft pad (Logitech's Chemcloth) is used with varying slurries. Two commercially available slurries are first explored: Chemlox and colloidal silica (Logitech's SF1). Chemlox is typically used to polish III-V compounds. It is a solution mixture of sodium hypochlorite (NaOCl 4-6%) and 70 nm alumina abrasive particles. The initial idea is to first perform a quick polish with diluted Chemlox (10 parts DI H₂O:1 part Chemlox) to remove the rough top surface followed by a colloidal silica polish to produce a specular surface. Unfortunately, Chemlox on Ge produces surface scratches visible to the naked eye.

Fig. 4-5. Touchdown Ge on Si have a surface roughness of about 70 nm RMS.
A diluted SF1 (10 parts DI H$_2$O:1 part SF1) gives an RMS roughness of less than 1 nm. Although no surface scratches were visible to the naked eye, under a Nomarski microscope, a large number of shallow scratches on the Ge surface [Fig. 4-6(a)]. Figure 4-6(b) shows Ge grown on oxidized Si with a 6° offcut towards (110) after SF1 polishing. Using SF1 to polish a specular Ge substrate gives the same result.

![Fig. 4-6. (a) Nomarski image of touchdown Ge on Si (100) after silica-based slurry CMP. (b) Nomarski image of TD GoS (100) with a 6° offcut towards (110).](image)

To prevent scratches, hydrogen peroxide diluted with deionized water [1 part H$_2$O$_2$ (30 wt%): 50 parts DI H$_2$O] is used, producing RMS roughness values between 0.1-0.5 nm. Although the etch rate of Ge is about 11 nm/min in bulk solution, the polish/etch rate is 3 to 5 times faster with a polishing pad depending on the size of the sample. Gravity, pressure from the polishing jig, and the abrasion from the soft polishing pad in contact with the raised features on the Ge surface allows for a faster etch rate of the
features. Figure 4-7 shows a Nomarski and AFM image of touchdown Ge on Si after a diluted H₂O₂ polish. The elongated protrusions in the AFM image are of stacking faults which seems to etch slower than its surroundings.

![Nomarski and AFM images](image)

Fig. 4-7. (a) Nomarski image of touchdown Ge on Si (100) miscut after a diluted H₂O₂ (50:1 DI water: H₂O₂ 30 wt %) CMP. (b) AFM measurements show RMS roughness to be about 0.17 nm. Elongated protrusions in the images are stacking faults.

For samples that required a specular Si backside, such as FTIR film thickness measurements, a 3:1 alumina oxide powder measured using a 90 ml beaker is mixed with DI water slurry is first used to lap the surface until the surface turns into a uniform gray haze, followed by a 2:1 DI water to SF1 slurry to buff the surface specular.
4.5 Etch Pit Density (EPD)

Etch pit density (EPD) is used to give an estimate of the number of defects at a given thickness of Ge film. To produce etch pits in Ge, a mixture of potassium dichromate ($K_2Cr_2O_7$) powder in DI water and HF; 1 part 1M/L $K_2Cr_2O_7$ to 2 part 49 wt% HF. Potassium dichromate is an inorganic oxidizing agent.

The etch rate of Ge films varies with varying defect densities since the etch pit solution has a preference to defects such as threading dislocations in Ge; the higher the defect density, the faster the etch rate. Figure 4-8 shows SEM images of Ge films grown using varying growth methods: (a) direct Ge/Si [Method 1], (b) unsealed oxide and pre-growth annealed [Method 3], (c) sealed oxide and post-growth annealed [Method 2], and (d) unsealed oxide and pre/post-growth annealed [Method 4]. The elongated etch pits are stacking faults. The direct Ge/Si growth sample is submerged in the etch pit solution for about 3 minutes, while unsealed oxide and pre/post-growth annealed sampled stayed submerged in the solution for close to 20 minutes in order to produce any visible etch pits. All Ge films in the Fig. 4-8 are initially about 2.5 µm thick.
Fig. 4-8. SEM images of Ge films grown using varying growth methods: (a) direct Ge/Si (Method 1), (b) unsealed oxide and pre-growth annealed (Method 3), (c) sealed oxide and post-growth annealed (Method 2), and (d) unsealed oxide and pre/post-growth annealed (Method 4). The elongated etch pits are stacking faults.

4.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used in this research to extract Ge film thickness. The Ge film thickness can be calculated using the fringing effect which results from internal reflection in the Ge film (Fig. 4-9). However, the films must be parallel and the surfaces smooth. The fringing effect originates from the constructive and destructive interference of the IR
beam from the parallel surfaces of the sample--in our case, the Ge film on top of the Si substrate. The absorption intensity of a Ge/Si sample is normalized to the absorption intensity of a Si substrate, resulting in an addition of cosine waves produced by the fringing effect (Fig. 4-10). In Fig. 4-10, each maxima is an increase in number of reflectance in the Ge film.

Fig. 4-9. Thin film thickness can be calculated using the fringing effect which results from internal reflection within the film.
Fig. 4-10. The absorption intensity of a Ge/Si sample is normalized to the absorption intensity of a Si substrate, resulting in an addition of cosine waves produced by the fringing effect.

From the fringing effect, thin film thickness can be calculated using the following equation:

\[ dn = \frac{1}{2k} \left( l - \frac{1}{2} \right) \]  (Eq. 4.1)

where \( l = 1, 2, 3..., \) \( n \) is the refractive index, and \( d \) is the film thickness. Let \( k_1, l_1 \) be the first maxima, and let \( k_2, l_2 \) be a maxima not too close. Therefore, \( l_2 = l_1 + m, \) where \( m \) is the number of minima between \( k_1 \) and \( k_2. \) Now we have two equations and two unknowns:

\[ 2dn = \frac{1}{k_1} \left( l_1 - \frac{1}{2} \right) \]  (Eq. 4.2)

\[ 2dn = \frac{1}{k_2} \left( l_2 - \frac{1}{2} \right) = \frac{1}{k_1} \left( l_1 + m - \frac{1}{2} \right) \]  (Eq. 4.3)

Setting the two right hand sides of Eq. 4.2 and Eq. 4.3 equal and solve for \( l_1: \)
Substituting Eq. 4.4 into Eq. 4.2:

\[
2dn = \frac{1}{k_1} \left( \frac{k_2 m}{k_2 - k_1} + \frac{1}{2} - \frac{1}{2} \right) = \frac{m}{k_2 - k_1} \quad (\text{Eq. 4.5})
\]

Therefore, film thickness, \( n \), is:

\[
d = \frac{m}{2n(k_2 - k_1)} \quad (\text{Eq. 4.6})
\]

Since the Ge films are not uniform in thickness, multiples points on each sample are taken and then averaged. Figure 4-11 is an example of a typical FTIR measurement of a touchdown Ge on Si that has been polished on both sides. The refractive index of Ge is 4.00858\textsuperscript{118}. In this example, \( k_1 \) is 1595.238, \( k_2 \) is 3857.143, and \( m \) is 5. Therefore, the Ge film thickness, \( d \), is 2.8 µm.
Fig. 4-11. A typical FTIR measurement of a touchdown sample. In this example, $n$ is 4.00858, $k_1$ is 1595.238, $k_2$ is 3857.143, and $m$ is 5. Therefore, the Ge film thickness, $d$, is 2.8 µm.
5.1 Introduction

A quick, inexpensive, and non-destructive way to extract the Ge film lifetime and the Ge-on-Si (GoS) interface recombination velocity is by photoconductance decay (PCD) lifetime measurements. This chapter will begin with a comparison of the four growth methods. Analysis of the data collected from the two lifetime techniques described in Chapter 3 will also be described in this chapter starting with Quasi-steady-state PCD (QSSPCD) measurements, then followed by microwave PCD (MWPCD).

5.2 Comparison of Ge Films Grown by the Four Growth Methods

Since defects at the Ge film surface will propagate into any subsequent III-V film grown on top, it is necessary to reduce the number of defects. One common solution is thermal annealing. Leonhardt et. al have shown anneal Ge islands on Si substrates will re-orient the Ge islands to lattice match the Si substrate beneath, hence when the Ge islands eventually coalesce, the density of stacking faults decreases. Luan et. al have shown that thermal annealing induces threading dislocation glide leading to the reducing the density of threading dislocations. In relaxed, undoped Ge, dislocations glide at 14 \( \mu \text{m/sec} \) at 1123 K. We believe that it is easier to glide out dislocations in islands
than in a fully coalesced film, hence the four growth methods detailed in Chapter 4 were used.

Figure 5-1 shows TEM images of all four growth methods, a repeat of Fig. 4-4 in Chapter 4. Once again, Fig. 5-1(a) show the Ge/Si interface of direct Ge grown on a Si substrate. The defect density is $\sim 10^{18}$ cm$^{-2}$ with threading dislocations propagating to the surface. Figure 5-1(b) shows the Ge/Si interface of Ge grown using the sealed oxide and post-growth annealed method—450-nm-thick Ge filmed annealed at 1123K for 30 minutes before growing to a 3-µm-thick film. Here, the defect density is in the mid-$10^7$ cm$^{-2}$ but is mostly stacking faults.$^{26, 123}$ Figure 5-1(c) shows the Ge/Si interface of Ge grown using the unsealed oxide and pre-growth annealed method—Ge islands annealed at 1123K for 30 minutes followed by a 3-µm-thick film growth. The defect density is also in the mid-$10^7$ cm$^{-2}$ range, but the defects are all threading dislocations with no stacking faults.$^{123}$ Figure 5-1(d) shows the Ge/Si interface of an unsealed oxide and pre/post-growth sample, which is the unsealed oxide growth method with an additional 1123K anneal for 30 minutes after the film is 3-µm-thick. The defect density is in the low-$10^7$ cm$^{-2}$ range with mostly threading dislocations that are confined to within 200 nm from the Ge/Si interface. The second anneal reduces the defect density by $\sim 73\%$. We predict that the measured lifetime will be inversely proportional to defect density.
Fig. 5-1. Cross-sectional TEM images of each Ge growth method: (a) direct Ge/Si [Method 1], (b) sealed oxide and post-growth annealed [Method 2], (c) unsealed oxide and pre-growth annealed [Method 3], and (d) unsealed oxide and pre/post-growth annealed [Method 4]. TEM images were taken by Darin Leonhardt.

Figure 5-2 compares the MWPCD voltage signal decay characteristics with respect to time for all four growth methods where the effective lifetime is extracted from the decay slope. As predicted, the effective lifetime increases with the decreasing defect density. Method 1, with the highest defect density, has the lowest effective lifetime at 7 ns. Although they have similar defect densities but different types of defects, Method 2 and Method 3 also have similar effective lifetimes at 8.6 and 8.3 ns, respectively. Method 4, which has the lowest defect density, has the highest effective lifetime at 9 ns. The measured lifetimes are virtually the same regardless of defect density or the type of defect suggests that the recombination velocity at the interface, $S_r$, is the main contributor to the effective lifetime.
Fig. 5-2. Comparison of the measured minority carrier lifetimes in 3-μm-thick Ge films grown by the four growth methods.

Minority carrier lifetime varies with injection level due to many different mechanisms (i.e. Auger, radiative, defects producing bandgap states, etc.) acting as recombination centers or trapping sites. Mobility of the bulk can also change with injection level which affects photoconductivity decay. It is often very difficult to precisely know the injection level. The injection level in this case is estimated to be $10^{17}$ cm$^{-3}$, and we believe that it is comparable to the background carrier concentration so that there is minimal change to the bulk mobility. Since it is difficult to determine all of the factors that contribute to errors of the measurement and assign values, error bars may end up being arbitrary depending on how many potential factors are considered. If the setup remains the same and the same injection level is used, this measurement should be repeatable and distinguishable between all four different growth methods.
As an indicator of defect density, etch pit density (EPD) measurements were taken for all four growth methods with 1-µm-thick Ge films. We used 1-µm-thick instead of 3-µm-thick Ge films because the defect density decays rapidly from the Ge/Si interface. Defect density virtually does not change after 400 nm from the interface. EPD was measured for Ge films grown on both heavily-doped, low-resistivity (HDLR) and low-doped, high-resistivity (LDHR) Si substrates. It was found that EPD is consistently higher on Ge films grown on LDHR Si substrates compared to Ge films grown on HDLR Si substrates of the same growth method. Table I lists the EPD of the four growth methods and various substrates they were grown on.
TABLE I. Etch pit density of Ge films grown on Si substrates with various resistivities.\textsuperscript{116}

*This measurement corresponds to threading dislocations only.

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>Substrate Resistivity (Ω-cm)</th>
<th>EPD (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Ge/Si (method 1)</td>
<td>0.003-0.005</td>
<td>7.3×10(^7)</td>
</tr>
<tr>
<td>Direct Ge/Si (method 1)</td>
<td>1000-4000</td>
<td>5.0×10(^8)</td>
</tr>
<tr>
<td>Sealed oxide and post-growth annealed (method 2)</td>
<td>0.003-0.005</td>
<td>3.4×10(^7)</td>
</tr>
<tr>
<td>Sealed oxide and post-growth annealed (method 2)</td>
<td>1000-4000</td>
<td>6.5×10(^7)</td>
</tr>
<tr>
<td>Unsealed oxide and post-growth annealed (method 3)</td>
<td>0.003-0.005</td>
<td>6.0×10(^7)</td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4)</td>
<td>0.003-0.005</td>
<td>1.6×10(^7)</td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4)</td>
<td>1000-4000</td>
<td>3.1-3.3×10(^7)</td>
</tr>
<tr>
<td>Touchdown\textsuperscript{26}</td>
<td>50</td>
<td>*&lt;2×10(^6)</td>
</tr>
<tr>
<td>Touchdown</td>
<td>1000-4000</td>
<td>2×10(^8)</td>
</tr>
</tbody>
</table>

The Ge ingot used for MBE Ge growth is 99.99% pure, therefore the main source of doping is not from the Ge ingot, but from the Si substrate whose concentration ranges
from $3.3 \times 10^{12}$ to $1.5 \times 10^{18}$ cm$^{-3}$. We speculate that boron diffuses into the Ge film during growth and the anneal steps. The activation barrier ($E_a$) for boron in Ge is 4.5 eV with an activated diffusion ($D$) of $1.3 \times 10^{-16}$ cm$^2$/sec at 1123 K.$^{125}$ Using these two values, the pre-exponential factor ($D_0$) can be calculated using the equation below:

$$D = D_0 \exp \left( -\frac{E_a}{k_B T} \right) \quad \text{(Eq. 5.1)}$$

where $k_B$ is the Boltzmann constant and $T$ is the growth or anneal temperature. The pre-exponential factor is calculated to be $2.0 \times 10^{-16}$ cm$^2$/sec. Using the calculated $D_0$, the activated diffusion at the growth temperature (873 K) is estimated to be $2.2 \times 10^{-22}$ cm$^2$/sec. Assuming that the Si substrates act as an infinite source of boron, the dopant concentration ($n$) can be estimated using a complementary error function:

$$n(x,t) = n_0 \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right) \quad \text{(Eq. 5.2)}$$

where $n_0$ is the initial boron concentration, $x$ is the distance away from the Ge/Si interface in centimeters, and $t$ is the growth or anneal time in seconds. Figure 5-3 plots boron concentration as a function of distance from the Ge/Si interface for Ge growth for six hours [Fig. 5-3(a)] and for anneal times of 30 minutes and 60 minutes [Fig. 5-3(b)].
Assuming that the Si substrate is an infinite source of boron, boron diffuses into Ge mostly during annealing steps.

Figure 5-2(a) shows that diffusion during growth is negligible. In comparison, after 30 minutes at 1123 K [● and ■ in Fig. 5-2(b)], the boron concentration at 20 nm from the Ge/Si interface is $1.1 \times 10^{10}$ and $5.2 \times 10^{15}$ cm$^{-3}$ for LDHR and HDLR Si substrates, respectively. The boron concentration increases to $1.2 \times 10^{11}$ and $5.8 \times 10^{16}$ cm$^{-3}$ after the second 30-minute anneal (60 minutes).

Boron in Ge will segregate along dislocation lines and immobilize dislocations.\textsuperscript{125, 126} In Ge, boron will also suppress dislocation formation and penetration into the Ge film.\textsuperscript{126} In other words, the higher the initial concentration of boron, the lower the dislocation density. We speculate that boron diffusion during the anneal step is sufficient in suppressing the nucleation of misfit dislocations due to the lattice mismatch between Ge and Si. A reduction in misfit dislocations results in a reduction in threading
dislocations. We suspect that the threading dislocations seen in the Ge film for growth method 3 and 4 are from Ge island coalescence.

5.3 Quasi-Steady-State PCD Lifetimes

All samples used in the QSSPCD study were grown on highly-doped, low-resistivity (LDHR) Si substrates. Each sample is polished after growth to produce a specular finish. Before each lifetime measurement, the samples are dipped in a diluted HF bath, rinsed, and blown-dry with an argon gun. All samples are measured with the Si substrate facing up due to the Ge film’s absorbing all of the light. This caused an issue since the Ge film by itself is too thin to produce a detectable change in photoconductance by the system. After each measurement, the samples are polished and measured until the Ge film is polished away.

5.3.1 Effective Lifetime Equation Derivation

A Sinton WCT-120 is used to measure the PCD and calculate the effective sample lifetime. To examine the carrier lifetime in our GoS heterostructures, an expression is derived for the effective lifetime representing this structure. For a bare Si substrate, the observed lifetime can be represented as:  

$$\frac{1}{\tau_{\text{measured}}} = \frac{1}{\tau_{\text{Si}}} + \frac{L_{\text{Si}}^2}{\pi^2 D} + \frac{L_{\text{Si}}}{2S_{\text{Si}}}$$  

(Eq. 5.3)
where \( \tau_{\text{measured}} \) is the measured lifetime, \( \tau_{\text{Si}} \) is the lifetime in bulk Si, \( L_{\text{Si}} \) is the thickness of the Si substrate, \( D \) is the minority-carrier diffusion coefficient, and \( S_{\text{Si}} \) is the Si surface recombination velocity (SRV) [Fig. 5-4(a)]. In our case, \( 2S_{\text{Si}}L_{\text{Si}}/\pi^2D \ll 1 \), so that Eq. 5.3 can be reduced to:

\[
\frac{1}{\tau_{\text{measured}}} = \frac{1}{\tau_{\text{Si}}} + \frac{2S_{\text{Si}}}{L_{\text{Si}}} \quad (\text{Eq. 5.4})
\]

Fig. 5-4 (a) Si substrate with the components of the observed lifetime equation shown. (b) Ge film on Si substrate with the components of the measured lifetime shown.

In order to extract the average electron minority carrier lifetime in Ge, a relationship between the electron concentration in Ge and in Si is needed. Since the electron diffusion length is long compared to the substrate thickness, the electrons have time to reach a quasi-equilibrium throughout the entire sample before recombination. Therefore, assuming that the Ge and Si have the same quasi-fermi level and a Boltzmann distribution, the Ge and Si electron concentrations \((n)\) can be related by a proportionality

94
factor, \(M\). The Ge and Si electron concentrations can be determined by the following equation:

\[
n = N_c \exp \left( \frac{E_F - E_c}{e k_B T} \right) \quad \text{(Eq. 5.5)}
\]

where \(N_c\) is the effective density of states of the conduction band, \(E'_F\) is the quasi-Fermi level, \(E_c\) is the conduction band, \(e\) is the charge energy, \(k_B\) is the Boltzmann constant, and \(T\) is the measurement temperature. Therefore,

\[
n_{Si} = N_{c, Si} \exp \left( \frac{E_F - E_{Si}}{e k_B T} \right) , \quad n_{Ge} = N_{c, Ge} \exp \left( \frac{E_F - E_{Ge}}{e k_B T} \right) \quad \text{(Eq. 5.6)}
\]

Solving for \(E'_F\),

\[
\frac{n_{Si,Ge}}{N_{c,Ge}} = \exp \left( \frac{E_F - E_{c,Ge}}{e k_B T} \right)
\]

\[
\ln \left( \frac{n_{Si,Ge}}{N_{c,Ge}} \right) = \frac{E'_F - E_{c,Ge}}{e k_B T}
\]

\[
E'_F = E_{c,Ge} + k_B T \ln \left( \frac{n_{Si}}{N_{c,Ge}} \right)
\]

To solve for \(n_{Ge}\), first let \(\Delta E_c = E_{c,Ge} - E_{c,Si}\)

\[
\Delta E_c = E_{c,Ge} - E_{c,Si} = k_B T \ln \left( \frac{n_{Ge}}{N_{c,Ge}} \right) - k_B T \ln \left( \frac{n_{Si}}{N_{c,Ge}} \right) = k_B T \ln \left( \frac{n_{Ge} N_{c,Ge}}{N_{c,Si} n_{Si}} \right)
\]

\[
\exp \left( \frac{\Delta E_c}{k_B T} \right) = \frac{n_{Ge} N_{c,Ge}}{N_{c,Si} n_{Si}} \quad \text{(Eq. 5.8)}
\]

\[
n_{Ge} = \frac{N_{c,Ge}}{N_{c,Si}} \exp \left( \frac{\Delta E_c}{k_B T} \right) \times n_{Si} = M n_{Si}
\]
Now solving for $M$ by inserting the following values:\textsuperscript{129}

\[ N_{Si} = 3.22 \times 10^{19} \text{ cm}^{-3}, \quad N_{Ge} = 1.03 \times 10^{19} \text{ cm}^{-3}, \]
\[ \Delta E_c = E_{cSi} - E_{cGe} = \chi_{Si} - \chi_{Ge} = 4.13 \text{ eV} - 4.05 \text{ eV} = 0.08 \text{ eV}, \]
\[ k_B T = 0.0257 \text{ eV} \]

$M = 6.94$. Now we need an equation to describe our measured lifetime.

The flash lamp generates carriers in a certain volume ($V$) of the sample before the carriers diffuse through the entire sample. The extra conductance ($\Delta \sigma$) produced by the generated carriers of the entire sample is directly related to the electron concentration in the bulk Si. Therefore, the measured lifetime ($\tau_{\text{measured}}$) of the photoconductance is the same as the measured lifetime of photoexcited electron concentration:

\[ \frac{d(\Delta \sigma)}{dt} \frac{\Delta \sigma(t)}{\tau_{\text{measured}}} \rightarrow \frac{dn_{Si}}{dt} = \frac{n_{Si}}{\tau_{\text{measured}}} \quad (\text{Eq. 5.9}) \]

For an GoS sample with $L$ is the Si substrate thickness and $W$ is the Ge film thickness, $S$ is a surface velocity, $A$ is area, and $V$ is volume where $V = A \times \text{film or substrate thickness}$,

\[ V_{Si} \frac{dn_{Si}}{dt} + V_{Ge} \frac{dn_{Ge}}{dt} = V_{Si} \frac{n_{Si}}{\tau_{Si}} + V_{Ge} \frac{n_{Ge}}{\tau_{Ge}} + AS_{Si} n_{Si} + AS_{Ge} n_{Ge} + AS_{I} n_{Ge} \quad (\text{Eq. 5.10}) \]

Notice that $S_I$ is multiplied by $n_{Ge}$ instead of $n_{Si}$ due to the electron density at the Ge/Si interface being less than the electron density in the bulk. Substituting Eq 5.8 and Eq 5.9 into Eq 5.10,

\[ V_{Si} \frac{n_{Si}}{\tau_{\text{measured}}} + V_{Ge} \frac{n_{Ge}}{\tau_{\text{measured}}} = V_{Si} \frac{n_{Si}}{\tau_{Si}} + V_{Ge} M \frac{n_{Si}}{\tau_{Ge}} + AS_{Si} n_{Si} + AS_{Ge} M n_{Si} + AS_{I} M n_{Si} \quad (\text{Eq. 5.11}) \]
Canceling out \( n_{Si} \) and dividing by \( A \) gives our measured lifetime equation

\[
\frac{L + MW}{\tau_{\text{measured}}} = \frac{L}{\tau_{Si}} + \frac{MW}{\tau_{Ge}} + S_{Si} + M \left( S_{Ge} + S_f \right) \quad \text{(Eq. 5.12)}
\]

TEM images in Fig. 5-1 show that the defect density in the Ge film is the highest at the Ge/Si interface and decreases rapidly from the interface for all four growth methods, inferring that the defects are inhomogeneously distributed within the Ge film. Therefore, \( \tau_{Ge} \) in Eq. 5.12 is a lifetime averaged over the entire Ge film. From here on, we will refer to \( \tau_{Ge} \) as the average bulk Ge lifetime, \( <\tau_{Ge}> \):

\[
\frac{L + MW}{\tau_{\text{measured}}} = \frac{L}{\tau_{Si}} + \frac{MW}{\langle \tau_{Ge} \rangle} + S_{Si} + M \left( S_{Ge} + S_f \right) \quad \text{(Eq. 5.13)}
\]

The average bulk Ge lifetime can be calculated by integrating \( \tau_{Ge} \) over the Ge film thickness (\( W \)) and dividing by \( W \):

\[
\langle \tau_{Ge} \rangle = \frac{1}{W} \int_{0}^{W} \tau_{Ge}(z) \, dz \quad \text{(Eq. 5.16)}
\]

Assuming that the defect density (\( \rho_D \)) is inversely proportional to the minority carrier lifetime and can be related to a proportionality constant, we can describe the defect density with the following equation:\(^{130}\)

\[
\rho_D(z) = \frac{C}{\tau_{Ge}(z)} \quad \text{(Eq. 5.17)}
\]

\[
\langle \tau_{Ge} \rangle = \frac{1}{W} \int_{0}^{W} \frac{C}{\rho_D(z)} \, dz
\]

where \( C \) is a proportionality constant, and \( \tau_{Ge}(z) \) is the bulk lifetime at a given distance from the Ge/Si interface. Using the TEM images in Fig. 5-1 and the corresponding EPD...
measurement, the defect density, $\rho_D(z)$, is estimated at various distances away from the Ge/Si interface (Fig. 5-6).

Fig. 5-6. Exponential decay fit to the defect density measured at various distances from the Ge-Si interface for all four growth methods: (a) direct heteroepitaxy (Method 1), (b) sealed oxide (Method 2), (c) unsealed oxide (Method 3), and (d) pre- and post-growth annealed (Method 4).
As an empirical estimation, we use an exponential decay fit to describe the observed defect density:

\[
\rho_d(z) = A \exp\left(-\frac{z}{z_0}\right) + y_0
\]

\[
\langle r_{Ge} \rangle = \frac{1}{W} \int_0^W \frac{C}{A \exp\left(-\frac{z}{z_0}\right) + y_0} \, dz \tag{Eq. 5.18}
\]

Table II lists the values for \(A\), \(z_0\), and \(y_0\) for each growth method.

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>(A) (cm(^{-2}))</th>
<th>(z_0) (cm)</th>
<th>(y_0) (cm(^{-2}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Ge/Si (method 1)</td>
<td>(4.6 \times 10^{10})</td>
<td>(2.1 \times 10^{-5})</td>
<td>(1.0 \times 10^8)</td>
<td>0.94</td>
</tr>
<tr>
<td>Sealed oxide and post-growth annealed</td>
<td>(1.2 \times 10^{11})</td>
<td>(1.1 \times 10^{-5})</td>
<td>(3.0 \times 10^7)</td>
<td>0.98</td>
</tr>
<tr>
<td>Unsealed oxide and post-growth annealed</td>
<td>(3.8 \times 10^{10})</td>
<td>(5.0 \times 10^{-6})</td>
<td>(6.0 \times 10^7)</td>
<td>0.95</td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed</td>
<td>(2.5 \times 10^{11})</td>
<td>(2.5 \times 10^{-6})</td>
<td>(1.6 \times 10^7)</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Solving Eq. 5.18, we get:

\[
\langle \tau_{Ge} \rangle = \frac{z_0}{y_0} \frac{C}{W} \left[ \ln \left( A + y_0 \exp \left( \frac{W}{z_0} \right) \right) + W - \ln \left( A + y_0 \right) \right]
\]  
(Eq. 5-19)

The final equation is:

\[
\frac{L + MW}{\tau_{measured}} = \frac{L}{\tau_{Si}} + \frac{MW}{\tau_{Si}} \frac{z_0}{y_0} C \left[ \ln \left( A + y_0 \exp \left( \frac{W}{z_0} \right) \right) + W - \ln \left( A + y_0 \right) \right] + S_{Si} + M \left( S_{Ge} + S_I \right)
\]  
(Eq. 5.20a)

\[
\frac{1}{\tau_{measured}} = \frac{1}{L + MW} \left[ \frac{L}{\tau_{Si}} + \frac{MW}{\tau_{Si}} \frac{z_0}{y_0} C \left[ \ln \left( A + y_0 \exp \left( \frac{W}{z_0} \right) \right) + W - \ln \left( A + y_0 \right) \right] + S_{Si} + M \left( S_{Ge} + S_I \right) \right]
\]  
(Eq. 5.20b)

**5.2.2 Data Fit and Analysis**

Table III lists the measured lifetime and Ge film thickness for each growth method. Only one sample was used for each growth method except for Method 4. A ~3.4-µm-thick Ge film was grown using Methods 1-3. After growth, each sample is polished using 50:1 deionized water to hydrogen peroxide mixture for 20 minutes followed by a diluted HF dip before FTIR film thickness measurement. Another diluted HF dip is done before each lifetime measurement. The same sample is then polished again with a new batch of diluted H₂O₂ mixture for 20 minutes, following the same
procedure described above. As for Method 4, multiple samples were grown with various Ge film thicknesses. Each sample received a 20 minute polish to smooth out the surface before sending to Dr. Steve Johnston at NREL for lifetime measurements. Each sample was dipped in HF prior to measurement. All samples are measured with the Si substrate backside up and facing the strobe lamp.

TABLE III. Measured Lifetime and Ge film thickness

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>W (cm)</th>
<th>( \tau_{measured} ) (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Ge/Si (method 1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8 \times 10^{-4}</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>2.3 \times 10^{-4}</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>1.7 \times 10^{-4}</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>1.2 \times 10^{-4}</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Sealed oxide and post-growth annealed (method 2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.9 \times 10^{-4}</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>2.8 \times 10^{-4}</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>2.4 \times 10^{-4}</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>1.8 \times 10^{-4}</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>1.4 \times 10^{-4}</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Unsealed oxide and post-growth annealed (method 3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 \times 10^{-4}</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>2.7 \times 10^{-4}</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>2.2 \times 10^{-4}</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>1.5 \times 10^{-4}</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>1.1 \times 10^{-4}</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4)</td>
<td>2.5 \times 10^{-5}</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2.0 \times 10^{-4}</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>1.2 \times 10^{-4}</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>5.2 \times 10^{-5}</td>
<td>0.59</td>
</tr>
</tbody>
</table>
The measured lifetimes for all four growth methods show very little variation. This may be due to either the Si/Ge interface being the dominant contributor to the measured lifetime. Another possibility is that the Si substrate is the dominant contributor since it is much thicker than the Ge film.

Since samples are dipped in 100:1 deionized water to hydrofluoric (HF) acid, or diluted HF (DHF) for two minutes before each measurement, we will assume the best times reported for $\tau_{Si}$ and $S_{Si}$ which are 4 ms and 0.4 cm/sec, respectively.\textsuperscript{61} The Si substrate thickness is approximately 0.03 cm. Recall $M$ is calculated to be 6.94. Figure 5-7 shows the Origin model fit for each growth method and are shown as solid lines with the surface recombination velocities at the interface and the Ge surface, $S_I + S_{Ge}$, and the proportionality constant, $C$, as fitting parameters. If $S_{Ge}$ can be assumed to be approximately 150 cm/sec based on values reported from literature,\textsuperscript{131} $S_I$ can be estimated. Table IV lists $C$, $S_I + S_{Ge}$, $S_I$, and the adjusted root-mean-square ($R^2$) values, representing the goodness of fit for each growth method.

From eqn. 5-17, it is expected that the larger the value of $C$, the longer the Ge film lifetime. Looking at Table IV, the values for $C$ were found to be 260, 19, 270, and 10 for Methods 1-4, respectively. Figure 5-8 plots the Ge film lifetime versus the distance from the Ge/Si interface. At about 2 µm away from the Ge/Si interface, the Ge film minority carrier lifetimes are 2.6 µs, 0.65 µs, 4.5 µs, and 0.63 µs for Methods 1-4, respectively. This is not realistic since TEM images clearly show that Method 1 has a higher density of defects than Method 2 and Method 4. An unpassivated $n$-type Ge substrate has been reported to have a minority carrier lifetime of 5-10 µs.\textsuperscript{132} Therefore, an extracted lifetime of 2.6 µs or 4.5 µs is unrealistic. Several possibilities for the errors include: 1) non-
planar Si backside surface from polishing that may also vary from sample to sample, 2) variation in Ge surface planarity due to multiple polishes, and 3) inputting imprecise minority carrier densities. To help reduce the number of components in the measured lifetime, MWPCD was used discussed in the next few sections.
Fig. 5-7. Model fit for each growth method and are shown as solid lines with the surface recombination velocities at the interface and the Ge surface, $S_I + S_{Ge}$ and the proportionality constant, $C$, as fitting parameters for all four growth methods: (a) Method 1, (b) Method 2, (c) Method 3, and (d) Method 4.
<table>
<thead>
<tr>
<th>Growth Method</th>
<th>( C ) (sec/cm(^2))</th>
<th>( S_I + S_{Ge} ) (cm/sec)</th>
<th>( S_I ) (cm/sec)</th>
<th>( \overline{R^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Ge/Si (method 1)</td>
<td>260</td>
<td>1500</td>
<td>1350</td>
<td>0.89</td>
</tr>
<tr>
<td>Sealed oxide and post-growth annealed (method 2)</td>
<td>19</td>
<td>600</td>
<td>450</td>
<td>-0.27</td>
</tr>
<tr>
<td>Unsealed oxide and post-growth annealed (method 3)</td>
<td>270</td>
<td>2200</td>
<td>2050</td>
<td>-0.28</td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4)</td>
<td>10</td>
<td>(1.4 \times 10^4)</td>
<td>(1.4 \times 10^4)</td>
<td>-0.51</td>
</tr>
</tbody>
</table>
Fig. 5-8. Ge bulk lifetime as a function of distance from the Ge/Si interface for all four growth methods: (a) Method 1, (b) Method 2, (c) Method 3, and (d) Method 4.
5.3 Microwave PCD Lifetime

MWPCD samples were grown on either highly-doped, low resistivity (LDHR) or low-doped, high resistivity (LDHR) Si substrates. Because Method 4 yields the longest minority carrier lifetime amongst the four growth methods, Ge films grown by Method 4 are used to establish the correlation between minority carrier lifetime and defect density. That is, we have used Method 4 to grow a 3-µm-thick Ge film on a 2-inch-diameter Si substrate, diced the Ge-on-Si wafer into 1 cm x 1 cm samples, profiled the defect density in a representative sample as a function of distance from the Ge/Si interface, polished the remaining Ge-on-Si samples down to varying thicknesses, and measured the minority carrier lifetime. Samples grown using Methods 1-3 with Ge film thicknesses less than 3 µm yielded effective lifetimes less than what the MWPCD system can reliability measure (< 5ns).

5.3.1 Measured Lifetime Equation Derivation

The microwave photoconductance decay (MWPCD) setup ran by Dr. Steve Johnston at the National Renewable Energy Lab (NREL) uses a laser to excite carriers. This is advantageous because the laser can be tuned to not excite carriers in the Si substrate. Starting from Eq. 5.4, adding a Ge film layer to one of the Si surfaces [Fig. 5-9 (b)] introduces a recombination velocity at the defective Ge/Si interface ($S_I$), a Ge bulk lifetime ($\tau_{Ge}$), and a Ge SRV ($S_{Ge}$):

$$\frac{1}{\tau_{measured}} = \frac{1}{\tau_{Si}} + \frac{S_{Si}}{L_{Si}} + \frac{1}{\tau_{Ge}} + \frac{S_{Ge} + S_I}{W} \quad \text{(Eq. 5.21)}$$
where $W$ is the Ge film thickness. Since the laser used in MWPCD measurements can be tuned not to excite carriers in the Si substrate, the Si components in Eq. 5.21 can be neglected [Fig. 5-9(c)], and Eq. 5.21 can be reduced to:

$$\frac{1}{\tau_{\text{measured}}} \approx \frac{1}{\tau_{\text{Ge}}} + \frac{S_{\text{Ge}} + S_I}{W} \approx \frac{1}{\tau_{\text{Ge}}} + \frac{S}{W}$$  \hspace{1cm} (Eq. 5.22)

where $S$ is the effective recombination velocity combining both Ge surface and Ge/Si interface. It has been reported that the SRV on unpassivated Ge substrates can be in the range of $\sim$150-200 cm/sec. Since the Ge surface is polished until specular, we used the lower end of the range ($S_{\text{Ge}} = 150$ cm/sec).

![Fig. 5-9](image)

Fig. 5-9. (a) Si substrate with components that contribute to the minority carrier lifetime. (b) Ge film on Si substrate with components that contribute to the minority carrier lifetime. (c) The MWPCD laser is tuned not to generate carriers in the Si substrate, removing the Si substrate components from the effective lifetime.

Once again, TEM images in Fig. 5-1 show that the defect density in the Ge film is the highest at the Ge/Si interface and decreases rapidly from the interface for all four growth methods, inferring that the defects are inhomogeneously distributed within the Ge
film. Therefore, \( \tau_{Ge} \) in Eq. 5-14 is a lifetime averaged over the entire Ge film. From here on, we will refer to \( \tau_{Ge} \) as the average bulk Ge lifetime, \( <\tau_{Ge}> \), changing Eq. 5.22 to:

\[
\frac{1}{\tau_{measured}} = \frac{1}{<\tau_{Ge}>} + \frac{S}{W} \quad (\text{Eq. 5.23})
\]

The derivation for \( <\tau_{Ge}> \) remains the same as described in the QSSPCD section. Therefore, the final MWPCD measured lifetime equation is:

\[
\frac{1}{\tau_{measured}} = \frac{z_0}{y_0 W} \left( \ln \left( A + y_0 \exp \left( \frac{W}{z_0} \right) \right) + W - \ln \left( A + y_0 \right) \right) + \frac{S}{W} \quad (\text{Eq. 5.24})
\]

5.3.2 Data Fit and Analysis

Figure 5-10 shows the inverse lifetime measured by MWPCD for varying thicknesses of Ge grown on HDLR and LDHR Si substrates by the unsealed oxide and pre/post-growth annealing method [Method 4 in Fig. 1(d)]. We observe that the minority carrier lifetime in Ge films grown on HDLR Si substrates is greater than that in Ge films grown on LDHR Si substrates. These lifetimes consistently reflect the corresponding EPD measurements (1.57×10^7 vs. 3.3×10^7 cm\(^{-2}\)) on Ge films grown on HDLR Si substrates versus LDHR Si substrates. The model fits are shown as solid and dotted lines for LDHR and HDLR Si substrates, respectively with \( S \) and \( C \) as fitting parameters. The parameter values can be found in Table IV. The adjusted root-mean-square (\( R^2 \)) values, representing the goodness of fit, are 0.49 for LDHR and 0.97 for HDLR Si substrates. The proportionality constant, \( C \), and the effective SRV, \( S \), for unsealed oxide and pre/post-growth annealed Ge films on LDHR are 0.17 sec/cm\(^2\) and 370 cm/sec,
respectively. For HDLR Si substrates, $C$ and $S$ are found to be 0.22 sec/cm$^2$ and 250 cm/sec, respectively. If $S_{Ge}$ can be assumed to be approximately 150 cm/sec based on values reported from literature,$^{131}$ then $S_I$ is 220 and 100 cm/sec for LDHR and HDLR samples, respectively.

![Graph](image-url)

Fig. 5-10. Plot of $1/\tau_{measured}$ vs. $L_{Ge}$ for Ge films grown on HDLR and LDHR Si substrates by the unsealed oxide and pre/post-growth annealing method.
TABLE IV. Model Fit Parameter Values for MWPCD

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>$C$ (sec/cm$^2$)</th>
<th>$S$ (cm/sec)</th>
<th>$S_I$ (cm/sec)</th>
<th>$\overline{R^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4) on LDHR Si substrates</td>
<td>0.17</td>
<td>370</td>
<td>220</td>
<td>0.49</td>
</tr>
<tr>
<td>Unsealed oxide and pre/post-growth annealed (method 4) on HDLR Si substrates</td>
<td>0.22</td>
<td>250</td>
<td>100</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Once again, we assume that the defect density ($\rho_D$) is inversely proportional to the minority carrier lifetime$^{133}$ and can be related to a proportionality constant, as describe by Eq. 5.17. Substituting the extracted $C$ into Eq. 5.17, Fig. 5-11 plots the minority carrier lifetime in bulk Ge film as a function of position from the Ge/Si interface for unsealed oxide and pre/post-growth annealed Ge films on LDHR and HDLR Si substrates. The lifetime is fairly uniform and constant in most of the Ge film, except that it precipitously drops near the Ge/Si interface at (~0.5 µm). As expected from the lower defect density, Ge film grown on HDLR Si substrates results in lifetimes higher than Ge film grown on LDHR Si substrates. At 1 µm away from the Ge/Si interface, $\tau_{Ge}$ is 8.2 ns and 11 ns for Ge films grown on LDHR and HDLR Si substrates, respectively. Literature values for bulk Ge lifetime range from 65 µs for $p$-type 1-3 $\Omega$-cm$^{134}$ to 1.17 ms for $p$-type 14-18 $\Omega$-cm Ge substrates.$^{131}$
Fig. 5-11.\textsuperscript{116} Ge bulk lifetime as a function of distance from the Ge/Si interface of unsealed-oxide and pre/post-growth annealed Ge films grown on LDHR and HDLR Si substrates.

This finding is important for practical device fabrication. When the minority carrier lifetime and its profile as a function of position can be estimated from the defect density by an empirical correlation, one can determine the distance from the Ge/Si interface, beyond which active devices can be fabricated without significantly sacrificing the device performance. For the carrier lifetime profile shown in Fig. 5-11, one could potentially fabricate high-mobility transistors approximately 0.5 to 1 µm away from the Ge/Si interface even with the high defect density and 2-3 orders of magnitude lower Ge bulk lifetimes since C-V measurements suggest mobilities of \(~1100\ \text{cm}^2/\text{V-s}\) and \(~1300\ \text{cm}^2/\text{V-s}\) for LDHR and HDLR, respectively.
Minority carrier lifetime is measured in Ge films grown on Si of varying dopant densities for different annealing strategies performed during and after Ge island coalescence, using the QSSPCD method and the MWPCD method. It was observed that the defect density in Ge decreases with increasing dopant density in Si substrates. In other words, Ge films grown on HDLR Si substrates showed to have a lower defect density than Ge films grown on LDHR Si substrates. This may likely be due dopants pinning defects near the Ge/Si interface. Etch pit density counts found that annealing steps introduced prior to and after full Ge island coalescence also reduce the defect density. A decrease in defect density in turn translates to an increase in lifetime.

In this work, we model the experimentally measured minority carrier lifetime ($\tau_{\text{measured}}$) as a function of surface recombination velocity on Ge film surface ($S_{\text{Ge}}$), average lifetime within Ge film ($<\tau_{\text{Ge}}>$), and recombination velocity at the Ge/Si interface ($S_I$). We further establish an empirical correlation between minority carrier lifetime ($\tau_{\text{Ge}}$) and defect density ($\rho_D$) within the Ge film as a function of distance from the Ge/Si interface: $\tau_{\text{Ge}} = C/\rho_D$, where $C$ is a proportionality constant and a fitting parameter.

QSSPCD was used to measure four Ge growth methods: (a) direct Ge/Si [Method 1], (b) sealed oxide and post-growth annealed [Method 2], (c) unsealed oxide and pre-growth annealed [Method 3], and (d) unsealed oxide and pre/post-growth annealed [Method 4]. Based on the model fit to the experimentally measured minority carrier
lifetime, it was determined that QSSPCD was not able to accurately measure the GoS heterostructure. The fitted parameters did not produce realistic values. Since measurements were taken with the Si substrate on top, there is a possibility that the Si substrate absorbed most of the flash, leading to a low concentration of generated carriers in the Ge film. Hence, the measured lifetime is dominated by the Si substrate lifetime and the Si/Ge interface SRV.

Since the MWPCD setup used has a tunable laser, the Si components in the derived measured lifetime equation were neglected. Also, MWPCD found that Ge films less than 3-µm thick grown using methods 1-3 produced Ge films with effective minority carrier lifetimes shorter than the laser decay time. Therefore, only Method 4 samples were used to establish the correlation between minority carrier lifetime and defect density. Based on the model fit to the experimentally measured minority carrier lifetime, we have determined $C$ and $S_I$: 0.17 sec/cm$^2$ and 370 cm/sec for LDHR Si substrates and 0.22 sec/cm$^2$ and 250 cm/sec for HDLR Si substrates, respectively. We further estimate the minority carrier lifetime within the Ge film as a function of distance from the Ge/Si interface, using our correlation. It was observe that the minority carrier lifetime reaches its maximum value approximately above 0.5 µm from the interface, where active devices can be fabricated without significantly sacrificing their performance.


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APPENDIX A

Temperature Dependent Characterization of Imbedded Quantum Dots Superlattice Solar Cell Structures by X-ray Diffraction

A.1 Introduction

In 1919, A.W. Hull wrote of X-ray diffraction (XRD): “Every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of others [1].” An atom diffracts X-ray waves, producing secondary circular waves. In a periodic structure, the diffracted waves are destructive in most directions. The remaining diffraction pattern is therefore unique for each crystal structure [2]. In this project, high resolution XRD (HRXRD) is used to characterize solar cell structures with quantum dots (QDs) imbedded in a superlattice (SL), a periodic construction of different semiconductor materials.

The insertion of nanostructured materials (such as quantum wells, wires, and dots) into the intrinsic region of p-i-n solar cells introduces an intermediate band within the bandgap of the host material [3]. It has been shown that this sub-bandgap, along with GaP strain compensation films, enhances the short circuit current as well as the overall efficiency of InAs quantum dots (QD) imbedded in GaAs superlattice (SL) solar cells [3]. In this case, indium arsenide (InAs) QDs are imbedded in a gallium arsenide (GaAs) host. XRD scattering profiles of SLs show profound periodic peaks caused by the total SL height, with the highest intensity at the central peak (SL0) and dimishing intensity at higher and lower angles. Fringe peaks can also be observed within the vicinity of the
central peaks, but are increasingly washed out with growing distance from SL0. The number of fringe peaks is equal to the number of repetitions of semiconductor materials. These fringe peaks are produced by reflections from the interfaces in the SL; the better the interface, the sharper the fringes [4]. This technical engineering memorandum will discuss the results of temperature dependent XRD scans of solar cell test structures grown by Seth Hubbard's group at the Rochester Institute of Technology.

A.2 Background/Experimental

For space applications, solar cells with a high power-to-weight ratio is desired, hence the need to increase power conversion efficiencies. One way to do so is through bandgap engineering with the insertion of multiple layers of quantum dots (QD) in the intrinsic region of p-i-n solar cells [3]. The QD layers form an isolated intermediate band within the bandgap of the host. Figure A-1 shows a cross-sectional band diagram of an InAs/GaAs QD solar cell structure with the QD structure repeated five times, with the QDs confined within the high electric field of the i-region. Photon absorption is believed to occur in two steps where incident photons with energies below the GaAs host bandgap result in absorption in the QD states. Secondary excitation causes carriers in the QD states to be excited into the conduction band where it is subsequently collected.

As a contender for space applications, it is necessary to subject these solar cell structures to temperatures it may encounter in the Low Earth Orbit (LEO), probing for any material degradation. Test structures with varying QD coverage, GaP strain compensation, and GaAs barrier coverage were analyzed at temperatures as high as
200°C using high resolution X-ray diffraction (HRXRD) for accelerated testing of thermal stability.

![Cross-sectional band-diagram of an InAs/GaAs QD solar cell structure](image)

**Fig. A-1.** A cross-sectional band-diagram of an InAs/GaAs QD solar cell structure [5].

Eleven QD enhanced GaAs solar cell test structures were selected for temperature dependent HRXRD studies. The 11 samples are classified into three groups: (1) InAs coverage for QD formation, (2) gallium phosphide (GaP) strain compensation coverage, and (3) GaAs barrier coverage. Structure growth conditions are described elsewhere [3, 6-8]. In group 1, various thicknesses (1.68 to 2.31 ML) of InAs films are grown at temperatures below the values typically associated with mass-transport limited growth (435-510°C) followed by a 60 sec growth interrupt step for coherent InAs QD formation. Varying the InAs coverage is one method for changing the quantum well width which
tunes state values to the desired transition energy. Increasing QD size and density track roughly with coverage value [6]. Figure A-2a shows a cross-sectional diagram of the film stack. The repeated films form the superlattice. Table A-I gives the film thicknesses of all 3 groups.

Fig. A-2 Cross-sectional diagram of the three QD enhanced GaAs solar cell test structures: (a) InAs coverage for QD formation, (b) gallium phosphide (GaP) strain compensation coverage, and (c) GaAs barrier coverage. The "X" denotes varying film thicknesses found in Table 1. "HT" stands for high temperature, and "LT" stands for low temperature.
Table A-I. Film thicknesses for the three QD enhanced GaAs solar cell test structures.

The structure of group 2 is shown in Fig. A-2b, where the thickness of the high temperature (HT) GaP layer is varied. The GaP layer is a strain balancing layer; the thickness of the first strain balancing layer determines the subsequent balancing layers [7]. InAs QDs in GaAs compressively strains the film. The proper GaP film thickness will shift the strain from compressive to tensile, capped with a second layer of HT GaAs to balance out the strain. Fig. A-2c shows the structure of group 3. This third set of samples have varying HT GaAs film thicknesses. The HT GaAs layers are part of a collective of layers (LT GaAs and HT GaP) which are barriers to the confined structures (QDs).

A Panalytical X'Pert Pro MRD system is used for the XRD scans. A 10 mm beam mask controls the width of the incident X-ray beam. A $\frac{1}{2}$° receiving slit is inserted on the detector side to reduce background and increase resolution. Two-theta-omega (2θ-ω)
rocking curves of the [004] plane at varying temperatures are performed at the following temperatures sequentially: 28°C, 50°C, 100°C, 150°C, 200°C, and after the sample is cooled back down to 28°C. In order to keep a constant focusing distance, the sample is rotated counter-clock-wise at an angle (θ) incident to the X-ray with the detector following at twice that angle (2θ) (see Fig. A-3). This focusing geometry is called the Bragg-Brentano parafocusing geometry. The 2θ angles range is from 62° to 70°, with a step sizes of 0.0005-6°, and an integration time of 1 second.

![Fig. A-3. The Bragg-Brentano parafocusing geometry: the X-ray tube is stationary, the sample moves by the angle THETA and the detector simultaneously moves by the angle 2-THETA.](image)

A ten minute delay is inserted after each temperature ramp up to ensure temperature equilibrium. After reducing the sample stage heater temperature to 28°C, a one hour delay is inserted to guarantee that the sample has cooled back down to room temperature before the measurement begins. Samples are enclosed in a graphite dome and subjected
to a 10x pump/purge routine. The enclosed space is pumped down to approximately -20 in. Hg, purged and pressurized to ~3.5 psi.

### A.3 Discussion

The goal of this study is to determine whether temperatures as high as 200°C will degrade the three QD enhanced GaAs solar cell test structures. A wide $2\theta-\omega$ angle range (62° to 70°) is used to determine whether the SL peaks shift with increasing temperature. Although no noticeable shifts in SL peaks are detected, some distortions in fringes and GaAs peaks are seen. The discussion section will be broken up into three sections, each describing the results and analysis of each QD enhanced GaAs solar cell test structures.

#### A.3.1 Varying GaP strain compensation

Long range HRXRD rocking curves of varying HT GaP thicknesses did not show any noticeable shifts in SL peak positions. Figure A-4a shows the long range HRXRD rocking curves of the 1.55 nm GaP strain compensated structure at different temperatures. A straight line can be drawn through the -3rd order SL peak [SL(-3)] for all of the different temperature measurements. We note that in this case, the zeroth order SL peak [SL(0)] is buried in the GaAs substrate peak, implying that this sample is strain compensated. Even with the worst case sample (0.75 nm HT GaP not shown), no noticeable shifts in SL peak positions were detected within the temperature range explored. Figure A-4b shows the calculated out-of-plain strain for these samples using the following equation [7]:

$$\text{[7]}$$
\[
\frac{\Delta a}{a} = (\theta_{\text{sub}} - \theta_{\text{SL}(0)}) \cot(\theta_{\text{sub}})
\]

where \( \theta_{\text{sub}} \) is the value of the substrate Bragg angle, \( \theta_{\text{SL}(0)} \) is the zeroth order SL peak, and \( \Delta a/a \) is the fractional lattice mismatch which represents the out-of-plane strain of the SL. The out-of-plane strain for all samples remains uniform at the different temperatures suggesting the absence of inter-mixing of films in the intrinsic layer. The slight variations in the 0.95 nm sample may be due to the sample shifting during HRXRD measurements. However, the variations are so small that they are negligible. Periodicity is taken as the thickness of each SL layer and is extracted by the following equation [8]:

\[
\text{Periodicity} = \frac{\lambda}{\theta_{\text{SL}(-1)} - \theta_{\text{SL}(0)}} \cot(\theta_{\text{sub}})
\]

where \( \lambda \) is the incident x-ray wavelength and \( \theta_{\text{SL}(-1)} \) is the -1\(^{st}\) order SL peak. Figure A-4c shows that the periodicity is also uniform at each temperature further indicating the absence of inter-diffusion within the SL layers. Figures A-4d-e shows the FWHM of SL(-1), SL(0), and SL(+1). Note that the scale is in arcsecs. Although there is a noticeable change in the 0.95 nm sample in the graphs, the difference between 160 arcsec and 180 arcsec is 0.006°, therefore making any variation in FWHM miniscule and negligible. Once again, the FWHM plots suggest an absence of inter-diffusion in the SL layers.
Fig. A-4. (a) Long range rocking curves for the 1.55 nm thick GaP sample. (b) Strain versus temperature. (c) Uniform periodicity. (d-e) The FWHM of SL(-1), SL(0), and SL(+1) are on the scale of arcsecs.

A.3.2 Varying GaAs barrier coverage

Similar to the varying GaP strain compensation samples, the varying GaAs barrier coverage samples also did not show any noticeable SL peak position shifts, once again inferring the absence of inter-diffusion within the intrinsic layer. Minimal variation in the calculated stress (Fig. A-5b) and strain (Fig. A-5c) and the FWHM of SL(-1), SL(0), and SL(+1) (Fig. A-5d-e) further affirms our conclusion.
A.3.3 Varying InAs quantum dots formation

Long range rocking curves of samples with varying InAs QD formation also did not display any noticeable shifts in SL peaks positions (Fig. A-6). However, there is noticeable degradation in the Pendellosung fringe resolution starting at 150°C suggesting minor inter-diffusion in the SL layers in the 1.68 ML sample (Fig. A-6a) suggesting some minor inter-diffusion at the SL interfaces. Fringes in the 2.31 ML sample are barely noticeable (Fig. A-6b) as reported by Bailey et. al. [6].
Fig. A-6. Long range rocking curves for (a) the 1.68 ML and (b) the 2.31 ML of InAs sample.

The strain plot of 2.31 ML of InAs (Fig. A-7a) sits below the 2.15 ML sample implies that the 2.31 ML sample has relaxed. Bailey et. al proposed that there is some relaxation in the SL for this sample reducing the lattice mismatch between the SL and the substrate, altering the Stranski-Krastanov growth mode [6]. Periodicity (Fig. A-7b) remains constant over all. Although the FWHM plots (Fig. A-7c-e) seem to have large variations, the difference between the variations are still minimal since the scale is in arcsecs.
Fig. A-7. (a) Strain versus temperature suggests relaxation in the 2.31 ML sample. (b) Uniform periodicity. (c-e) The FWHM of SL(-1), SL(0), and SL(+1) are on the scale of arcsecs.

A.4 Conclusions/Future Work

Three QD enhanced GaAs solar cell test structures are characterized at various temperatures using XRD. Looking just at long range HRXRD rocking curves did not show any noticeable shifts in the SL peak positions. However, further analysis of each samples' strain, periodicity and FWHM of SL(-1), SL(0), and SL(+1) affirms that minimal to no inter-diffusion occurred within the intrinsic layer. Future work includes rescanning samples that had shifted and increasing the stage heater to temperatures greater than the HT film growth temperature.
A.5 References


