TIME RESOLVED REFLECTIVITY STUDIES OF SOLID PHASE EPITAXY IN ION IMPLANTED GERMANIUM, SILICON AND THEIR ALLOYS

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TIME RESOLVED RAYLEIGH SCATTERING STUDIES OF SCOPC PHASE EUTAXY IN ION IMPLANTED GERMANIUM SI-ICON AND THEIR ALLIES
Declaration

All the work described in this thesis was carried out by the author during the candidature of the research program, except where otherwise stated. None of the material included in this thesis has been presented for any other degree or diploma.

Paul Gortmaker
Decision
Acknowledgments

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we would end up with a user base estimated in the millions? It has been fun being involved and sure has been amazing to watch it unfold.

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Abstract

This study examines the behaviour of solid phase epitaxy (SPE) in silicon and germanium, silicon-germanium alloys and implantation doped variations of these materials. Time Resolved Reflectivity (TRR) has been employed as the measurement technique. The primary focus has been on germanium since its potential as a valuable resource for SPE data has largely been neglected by the research community until now.

The SPE rate of self-implanted a-Ge on (100) Ge has been measured for five different substrates with different preparation conditions, suppliers and with n-type, p-type, and undoped compositions. The temperature range covered by these measurements is significantly greater than any other published a-Ge SPE data. A single set of growth parameters for intrinsic amorphous germanium was determined from these results.

The potential role of hydrogen contamination in causing reductions in the SPE rate has been investigated in self-implanted a-Ge layers in excess of 3 µm thick. Secondary Ion Mass Spectrometry (SIMS) measurements of the hydrogen content in partially annealed samples with and without hydrogen implants were performed in addition to SPE measurements. These measurements have indicated that the intrusion of hydrogen from the annealing environment into a-Ge does not occur to the same extent as observed in similar measurements for a-Si layers. However, once hydrogen is present in the a-Ge layer, the reduction in the SPE rate is similar to that observed for a-Si layers containing a comparable concentration of hydrogen.

The effect of electrically active dopants on the SPE rate of a-Ge was then investigated by the use of multiple ion-implantation steps to create constant concentration profiles of the dopants arsenic and aluminum in pre-amorphized a-Ge layers. Three
different constant concentrations for each dopant have been investigated by TRR and SPE rate enhancements have been observed. Compensation measurements involving overlapping n-type and p-type dopants have also been performed. The scope of these measurements is sufficient to allow insight into both the temperature and concentration dependence of the SPE enhancement for each dopant species. These results have been critically compared to previous measurements of dopant-enhanced SPE and to the present theories of SPE and significant limitations in these theories due to nondegenerate approximations have been recognized. Fully degenerate calculations have been performed, and based on these, modifications to some of the theory have been proposed.

Similar measurements of SPE rates in a-Si layers have also been performed. Long wavelength (1152 nm) TRR has been used to profile the SPE rates in a-Si layers up to 3 μm thick. Prior to investigating dopant effects, the SPE rate in thick intrinsic a-Si layers has been measured for normalization purposes and to compare with the recent report of retarded SPE rates due to hydrogen contamination. The use of constant concentration dopant profiles spanning significant depth ranges allows the enhanced SPE rate to be unambiguously assigned to a particular dopant concentration. Arsenic, aluminum and compensation measurements involving the simultaneous presence of both dopants have been performed, and high resolution crystalline-amorphous interface velocity profiles have been obtained. This data has also been compared to the dopant induced SPE enhancements predicted by present SPE theories, and also those modified to include degenerate doping.

Finally, the recent interest in silicon-germanium alloys has prompted a similar measurement of dopant-enhanced SPE rates in these materials. The intrinsic SPE rate has been measured for two strain-free Si_{x}Ge_{1-x} alloys of different composition grown on (100) Si substrates. Amorphized alloy layers were then implanted to give constant concentrations of arsenic as was performed for the germanium and silicon samples. These samples have provided the first reported measurements of arsenic-enhanced SPE in silicon-germanium alloys.
# Contents

Declaration iii  
Acknowledgments v  
Abstract vii  

## 1 Introduction

1.1 Background 2  
1.2 Solid Phase Epitaxy 3  
  1.2.1 What is it? 3  
  1.2.2 An Analogy of the SPE Process 3  
  1.2.3 Focus of This Work 4  
  1.2.4 Solid Phase Epitaxy in Germanium 5  
  1.2.5 Solid Phase Epitaxy in Silicon 6  
  1.2.6 Solid Phase Epitaxy in Silicon-Germanium Alloys 7  
1.3 Measurement of SPE Rates 10  

## 2 Review of Solid Phase Epitaxy

2.1 Introduction 14  
2.2 SPE Studies of Germanium 15  
  2.2.1 Partial Anneal/RBSC Measurements 15  
  2.2.2 Calorimetry Measurements 15  
  2.2.3 TRR Measurements 16  
2.3 SPE Studies of Silicon 17  
  2.3.1 The Csepregi Group 17  
  2.3.2 Other Dopant Related SPE Measurements 18
2.3.3 The Olson Group .................................................. 19
2.3.4 Diamond Anvil Cell Measurements ................................. 21
2.3.5 The Walser Group .................................................. 21
2.3.6 Hydrogen Retardation .............................................. 22
2.4 Models of the SPE Process ........................................... 24
  2.4.1 Transition State Theory ........................................... 24
  2.4.2 The Spaepen-Turnbull Dangling-Bond Model ...................... 26
  2.4.3 Saito and Ohdomari's Extension to Spaepen's Model .............. 27
  2.4.4 Kinetic Analysis of the Dangling Bond Model .................... 29
  2.4.5 General Semiconductor Parameters ............................... 30
  2.4.6 Vacancy Models .................................................. 40
  2.4.7 Bulk Defect Diffusion Models .................................... 44
  2.4.8 The Kink-Site Model ............................................... 47
  2.4.9 The Fractional Ionization Model .................................. 51
  2.4.10 Lattice Softening Models ........................................ 54
  2.4.11 The Generalized Fermi Level Shifting Model .................... 56
  2.4.12 Model Summary .................................................. 60
2.5 SPE Studies of Silicon-Germanium Alloys ............................. 61
  2.5.1 Strained vs. Unstrained Layers ................................... 61
  2.5.2 Buffered Layer Measurements .................................... 62
  2.5.3 Thick Layer Measurements ........................................ 63
2.6 SPE Studies Performed by TRR ........................................ 64
  2.6.1 Expression for the Reflectivity ................................... 66
  2.6.2 Reflectivity Dependence .......................................... 68
  2.6.3 Implications for TRR Measurements ............................... 68
  2.6.4 Systematic Errors in the Index of Refraction .................... 70
  2.6.5 Systematic Errors in Temperature Measurement .................. 71
  2.6.6 TRR Versus Partial Furnace Anneals ................................ 74
2.7 Summary ............................................................... 77

3 Experimental Techniques .................................................. 79
  3.1 Introduction ........................................................ 80
3.2 Time Resolved Reflectivity

3.2.1 Overview

3.2.2 General Layout of the System

3.2.3 Choice of TRR Laser Wavelength

3.2.4 Optical Components

3.2.5 Photodiode Detectors

3.2.6 Filters and Diffusers

3.2.7 Specimen Heater/Holder

3.2.8 Temperature Control

3.2.9 Temperature Calibration

3.2.10 Signal Processing Electronics and Data Acquisition

3.2.11 Data Analysis

3.3 Other Experimental Systems

3.3.1 Rutherford Backscattering Spectrometry System

3.3.2 Ion Implantation System

4 SPE of Amorphous Germanium

4.1 Introduction

4.2 Background Information

4.2.1 The First a-Ge SPE Measurement

4.2.2 Unexpected High Dose Implant Effects

4.2.3 The Calorimetry Based Measurement

4.2.4 The Diamond Anvil Cell Measurements

4.2.5 Recent a-Ge SPE Measurements

4.2.6 Possibility of Hydrogen Contamination Effects

4.2.7 Dopant Concentration SPE Effects in Germanium

4.2.8 Summary

4.3 Experimental Methods

4.3.1 Sample Preparation

4.3.2 TRR and Refractive Index Determination

4.4 SPE of Intrinsic a-Ge Layers

4.4.1 Measurement of SPE Rate on (100) Ge
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.2</td>
<td>Consideration of Past Results</td>
<td>154</td>
</tr>
<tr>
<td>4.5</td>
<td>Hydrogen Effects</td>
<td>157</td>
</tr>
<tr>
<td>4.5.1</td>
<td>TRR of Thick a-Ge Layers at 1.523 µm</td>
<td>157</td>
</tr>
<tr>
<td>4.5.2</td>
<td>SIMS Measurements of Hydrogen in a-Ge Layers</td>
<td>161</td>
</tr>
<tr>
<td>4.5.3</td>
<td>TRR of a-Ge Layers Implanted with Hydrogen</td>
<td>163</td>
</tr>
<tr>
<td>4.5.4</td>
<td>SIMS of a-Ge Layers Implanted with Hydrogen</td>
<td>167</td>
</tr>
<tr>
<td>4.6</td>
<td>Dopant Effects in Amorphous Germanium</td>
<td>170</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Doping with Arsenic</td>
<td>170</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Doping with Aluminum</td>
<td>177</td>
</tr>
<tr>
<td>4.6.3</td>
<td>Doping with Arsenic and Aluminum</td>
<td>181</td>
</tr>
<tr>
<td>4.7</td>
<td>Discussion</td>
<td>185</td>
</tr>
<tr>
<td>4.7.1</td>
<td>Undoped Germanium and the Kinetic Model</td>
<td>185</td>
</tr>
<tr>
<td>4.7.2</td>
<td>Hydrogen and SPE in Intrinsic a-Ge</td>
<td>186</td>
</tr>
<tr>
<td>4.7.3</td>
<td>Doped Ge as Extrinsic and Nondegenerate</td>
<td>187</td>
</tr>
<tr>
<td>4.7.4</td>
<td>Fermi Levels in Doped Germanium</td>
<td>189</td>
</tr>
<tr>
<td>4.7.5</td>
<td>Fractional Ionization in Doped Germanium</td>
<td>191</td>
</tr>
<tr>
<td>4.7.6</td>
<td>Dopant Enhanced SPE and Nondegenerate Models</td>
<td>195</td>
</tr>
<tr>
<td>4.7.7</td>
<td>SPE in Compensation Doped Germanium</td>
<td>201</td>
</tr>
<tr>
<td>4.8</td>
<td>Conclusions</td>
<td>205</td>
</tr>
</tbody>
</table>

5 SPE of Amorphous Si and Si-Ge Alloys | 209

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>210</td>
</tr>
<tr>
<td>5.2</td>
<td>Review</td>
<td>211</td>
</tr>
<tr>
<td>5.2.1</td>
<td>SPE of Undoped Silicon</td>
<td>211</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Hydrogen Effects</td>
<td>211</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Dopant Effects</td>
<td>212</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Silicon-Germanium Alloys</td>
<td>215</td>
</tr>
<tr>
<td>5.2.5</td>
<td>Summary</td>
<td>215</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental</td>
<td>218</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Formation of Undoped Samples</td>
<td>218</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Formation of Implantation Doped Samples</td>
<td>219</td>
</tr>
<tr>
<td>5.3.3</td>
<td>TRR Measurements and Index of Refraction Values</td>
<td>223</td>
</tr>
</tbody>
</table>
5.4 Intrinsic Growth Behaviour of Si
5.4.1 Measurement of the SPE Rate on (100) Si
5.4.2 SPE Rate Reduction Due to Hydrogen Contamination
5.5 Dopant Effects on the Growth Rate of Si
5.5.1 Doping with Arsenic
5.5.2 Doping with Aluminum
5.5.3 Doping with Arsenic and Aluminum
5.6 Measurements in Silicon-Germanium Alloys
5.6.1 Undoped Material
5.6.2 Arsenic Doped Material
5.7 Discussion
5.7.1 Hydrogen and SPE in a-Si
5.7.2 Doped Si as Extrinsic and Nondegenerate
5.7.3 Fermi Levels in Doped Silicon
5.7.4 Fractional Ionization in Doped Silicon
5.7.5 Dopant Enhanced SPE and Nondegenerate Models
5.7.6 SPE Measurements in Compensation Doped Silicon
5.7.7 SPE Measurements in Si$_x$Ge$_{1-x}$Alloys
5.8 Conclusions

6 Summary and Conclusions
6.1 Germanium
6.2 Silicon and Silicon-Germanium Alloys
6.3 Further Work

References
# List of Figures

2.1 Dangling Bond Induced Crystallization Events ........................................ 28  
2.2 Band Gap Width for Si and Ge ................................................................. 33  
2.3 Effective Density of States for Si and Ge .................................................. 36  
2.4 Intrinsic Carrier Concentration for Si and Ge ............................................. 38  
2.5 Kink Sites at a (100) $c/a$ Interface ......................................................... 48  
2.6 Simple Schematic of the TRR Method ......................................................... 65  
2.7 Simulated TRR Curve .................................................................................... 69  
2.8 Effect of Temperature Errors ....................................................................... 73  
3.1 Schematic of the Dual Beam TRR System ..................................................... 82  
3.2 Schematic of the TRR Detector Design ....................................................... 86  
3.3 Custom TRR Heater Stage Design ............................................................... 90  
4.1 SPE Rate in a-Si vs. Hydrogen Concentration ............................................ 111  
4.2 Implants of Arsenic into a-Ge by Suni et al. .............................................. 116  
4.3 Implants of Boron into a-Ge by Suni et al. .................................................. 118  
4.4 Implants of Boron and Arsenic into a-Ge by Suni et al. ............................... 118  
4.5 SIMS Calibration from H Implant Standard in Si ....................................... 126  
4.6 Hydrogen Implants into a-Ge ..................................................................... 126  
4.7 Arsenic Implants into a-Ge ........................................................................ 127  
4.8 Aluminum Implants into a-Ge .................................................................... 130  
4.9 SIMS Measurement of Aluminum in a-Ge ............................................... 132  
4.10 Dopant Compensation Implants into a-Ge .............................................. 133  
4.11 1.15 $\mu$m TRR Curve from Annealing of a-Ge ....................................... 136  
4.12 632.8nm TRR Curve from Annealing of a-Ge ......................................... 136
4.44 Fractional Ionization of Arsenic in Germanium .......... 194
4.45 Fractional Ionization of Aluminum in Germanium .......... 194
4.46 GFLS Fitting with a Variable Degeneracy .......... 198
4.47 GFLS Fitting with a Fixed Degeneracy .......... 198
4.48 Band Gap Structure for a p-n Junction .......... 200
4.49 Proposed Band Gap Structure for the c/a Interface .......... 200
4.50 Fermi Level in Compensation Doped Germanium .......... 203
4.51 Fractional Ionization in Compensation Doped Germanium .......... 203

5.1 Arsenic Implants into a-Si .......... 220
5.2 RBS Measurement of Arsenic Concentration in Silicon .......... 220
5.3 Aluminum Implants into a-Si .......... 222
5.4 Compensation Dopant Implants into a-Si .......... 222
5.5 Arsenic Implants into Si_{0.79}Ge_{0.21} .......... 224
5.6 Arsenic Implants into Si_{0.47}Ge_{0.53} .......... 224
5.7 TRR curve from Annealing of a 2 μm a-Si Layer .......... 228
5.8 SPE Rate in a-Si at 580 °C .......... 228
5.9 Arrhenius Behaviour of SPE Rates in a-Si .......... 230
5.10 Normalized SPE Behaviour of Hydrogen Contaminated a-Si .......... 230
5.11 TRR Curve from Annealing of Arsenic Implanted a-Si .......... 233
5.12 SPE Rates During Annealing of Arsenic Implanted a-Si .......... 233
5.13 SPE Rates in Arsenic Doped a-Si .......... 235
5.14 Arrhenius Behaviour of SPE Rates in Arsenic Implanted a-Si .......... 235
5.15 Hydrogen and Normalization of As Enhanced SPE Data .......... 239
5.16 Normalized Velocity Plot for Arsenic Implanted a-Si .......... 239
5.17 TRR Curve from Annealing of Aluminum Implanted a-Si .......... 241
5.18 SPE Rates During Annealing of Aluminum Implanted a-Si .......... 241
5.19 Arrhenius Behaviour of SPE Rates in Aluminum Implanted a-Si .......... 242
5.20 Normalized SPE Rates for Aluminum Implanted a-Si .......... 242
5.21 TRR Curve and Interface Location for Compensation Doped a-Si .......... 244
5.22 SPE Rates in Compensation Doped a-Si .......... 244
5.23 SPE Rates in Single Dopant and Compensation Doped a-Si .......... 246
List of Tables

2.1 Band Gap Parameters for Silicon and Germanium .......................... 32
2.2 Density of States Effective Masses for Silicon and Germanium ............. 34

4.1 Implants of Arsenic into a-Ge by Suni et al. ................................. 117
4.2 Implants for Formation of $\sim 1.5 \, \mu m$ a-Ge Samples .................. 122
4.3 Implants for Formation of Thick a-Ge Samples ............................... 122
4.4 Samples for Studying SPE Rates in a-Ge ...................................... 123
4.5 Implants for Doping a-Ge Samples with Arsenic ............................. 128
4.6 Implants for Doping a-Ge Samples with Aluminum ........................... 129
4.7 Layer Thickness vs. TRR of a-Ge at $1.5 \, \mu m$ ............................... 144
4.8 Activation Energies for Various a-Ge Samples ............................... 149
4.9 Activation Energies from Other a-Ge Studies ................................. 152
4.10 Activation Energies for Various Arsenic Doped a-Ge Samples ............. 174
4.11 SPE Enhancement Dose Dependence for Arsenic in Ge .................... 175
4.12 Activation Energies for Various Aluminum Doped a-Ge Samples .......... 179
4.13 Net Ionized Dopant Concentration in Ge .................................... 193

5.1 Implants for Creating a-Si Layers $3 \, \mu m$ Thick ............................ 219
5.2 SPE Rates in Thick a-Si Layers .................................................. 234
5.3 Activation Energies for Undoped a-Si ......................................... 236
5.4 Activation Energies for Various Arsenic Doped a-Si Samples ............. 237
5.5 SPE Enhancement Dose Dependence for Arsenic in Si ....................... 238
5.6 Activation Energies for Undoped $Si_x Ge_{1-x}$ Alloys ...................... 250
5.7 Net Ionized Dopant Concentration in Si ..................................... 258
5.8 Defect Energy Levels for Degenerate FLS Model ........................... 265
Chapter 1

Introduction

1.3 Solid Phase Epitaxy

Backgrond
1.1 Background

The research into semiconductor materials is driven primarily by the electronics industry which relentlessly strives for faster and smaller devices. The central processing units (CPUs) manufactured by Intel make a good example. Their first models (i4040, i8080) of the early 1970's contained on the order of 3000 transistors, and could operate at frequencies of a few hundred kHz. Now, the CPU of a typical home computer contains in excess of 3 million transistors and operates at frequencies above 100 MHz[1]. This endless quest for smaller and faster parts in turn requires a continual refinement of the understanding of the basic properties of the semiconductor materials that are exploited in the device manufacturing process. Growth of semiconductor materials by solid phase epitaxy (SPE) is one of these properties, as will be shown below.

It is a well known fact that the manufacture of an active semiconductor device requires the controlled introduction of electrically active impurities, typically group III or group IV elements such as boron or phosphorous and arsenic. Similarly, the use of ion implantation as a method for introduction of these impurities is now commonplace, where the manufacture of a reasonably complex device can involve on the order of 100 implantation steps. The use of ion-implanted dopants into semiconductor materials has been in use for more than twenty years to produce well controlled and custom dopant profiles in the host material[2]. It offers far greater control of dopant placement than typical diffusion based doping schemes.

A side effect of the implantation procedure is that each implanted ion leaves a trail of displaced atoms in the crystal along its trajectory. For a sufficiently high dose of incident ions, the regions of disorder overlap, at which point there is no long range order in the implanted layer, as compared to the periodically spaced atoms in the underlying crystalline material. To return this amorphous layer to a crystalline state, the material is usually given a thermal treatment at a temperature below the melting point, during which solid phase epitaxy (SPE) takes place[2,3].
1.2 Solid Phase Epitaxy

1.2.1 What is it?

The Oxford Dictionary[4] defines epitaxy as “the growth of a thin layer on a single crystal substrate that determines the lattice structure of the layer” with its origin based upon the Greek word for arrangement. Solid phase epitaxy is then just thin layer growth upon a single crystal that takes place within the solid phase. Of course these sorts of definitions are not particularly enlightening to those outside the field, but fortunately the general concept of SPE is within the grasp of even those without a scientific or mathematical background.

1.2.2 An Analogy of the SPE Process

As a simple analogy of the SPE process that is hopefully understandable by all, consider the common game ‘Chinese Checkers’ in which a board that has a symmetrical pattern of spherical indentations is used to hold marbles which are then played in a similar fashion to how Checkers is played on a common chess board. Imagine that the board in question has a small lip around each indentation so that a marble placed between any two indentations will not automatically fall into an indentation by itself. Now imagine that a quantity of marbles, equal to the number of indentations on the board, are poured onto the board. Most of these marbles will lie between the indentations on the board, if the indentation size is small as compared to the spacing between the indentations.

In terms of the physical system described above, where an amorphous or disordered layer lies on top of an ordered crystalline base, the board represents the ordered crystalline material, with the indentations on the board representing the pattern of the crystal and thus where the next building blocks of the crystal should go. Similarly, the marbles poured onto the board represent the amorphous layer, as they are the next set of building blocks to be used, currently at random locations between the indentations, rather than in the crystal sites represented by the indentations themselves.

This situation is stable, in that it will remain unchanged in the absence of any
external intervention. However, imagine that someone now lightly shakes the board with the marbles upon it so that the agitation is sufficient to get a marble over the lip around an indentation and into an indentation, but not sufficient to get a marble out of the depth of an indentation and back out onto the surface of the board. If this is continued for a long enough time, all the marbles will clearly end up lying inside the indentations, and hence will have formed another layer of the crystal. In terms of the analogy, the external agitation of the board represents the thermal vibrations caused by the external heating of the material.

Once this layer has reordered itself to match the crystal, it is indistinguishable from the rest of the crystal, and the process is ready to continue with the next layer of atoms in the amorphous material. The result is that the crystalline-amorphous (c/a) interface has moved forward one layer from its original position. As long as the heat remains applied, the amorphous material will continue to reorder itself to match the underlying crystal substrate and hence the c/a interface will progress through the amorphous layer until all the amorphous material is ‘consumed’. Experimental results have indicated that the rate at which this process takes place scales exponentially with temperature, with SPE rates on the order of one Å/s observed at temperatures around half of the melting point.

1.2.3 Focus of This Work

This study is concerned with the mechanism by which SPE takes place and how the addition of dopants effects the SPE rate. The SPE rates for germanium, silicon and silicon-germanium alloys are investigated. These results are then contrasted with those obtained when controlled amounts of dopant material have been introduced into the amorphous layer. The proposed theories for the SPE process and how it should be affected by dopant impurities are then reviewed in light of this data.
1.2.4 Solid Phase Epitaxy in Germanium

Motivation

The advent of metal oxide semiconductor (MOS) devices quickly helped silicon to overtake germanium as the semiconductor material of choice. The oxide of germanium is very unstable and difficult to work with, whereas the formation of an oxide layer on silicon is a trivial process, and the resulting layer is so stable that harsh acids are required to remove it. While germanium has all but been completely abandoned by those making typical device structures, it still is a useful vehicle for research into solid phase epitaxial regrowth that has yet to be fully exploited. When this work was initiated, there were only a few published journal articles\[5-8\] that considered the issue of SPE in germanium. Yet the similarities between Si and Ge make Ge a valuable resource for testing current SPE theories on a different but closely related system.

SPE Research

There is a significant amount of variance in the few data sets currently available in the literature for SPE in germanium. This makes it difficult to use the Ge data for the purposes of performing quantitative comparisons to the predictions of various SPE models. Furthermore, hydrogen contamination has been demonstrated to play an important role in SPE measurements in silicon, yet the issue of whether this also holds true for germanium has still not been treated in any of the various publications. With respect to how doping impurities effect SPE in germanium, there has only been one research group who have even touched on the subject, and currently there is no quantitative data of this sort available. The results currently in the literature pertaining to SPE in germanium are reviewed in Chapter 2.

The experiments performed as a part of this work address these shortcomings. The intrinsic SPE rate for germanium has been measured in a variety of different substrates and over a temperature range much wider than any of the previous measurements. The issue of whether hydrogen contamination is a significant factor during SPE of germanium is also treated in detail. Specially manufactured samples containing constant concentrations of the dopants arsenic and aluminum have been
used to provide the first qualitative measurements of doping effects on the SPE rate of germanium. These measurements are then used to address the validity of some of the basic assumptions present in the current SPE models. The results of the SPE studies in germanium from this work are presented in Chapter 4.

1.2.5 Solid Phase Epitaxy in Silicon

Motivation

While the number of SPE studies in silicon have continued to increase since the first detailed investigation[9] over twenty years ago, the complete picture is far from clear. The number of applications for silicon device technology and the subsequent demand for a better understanding of the properties of the material always seem to keep ahead of the current knowledge base assembled by the various researchers. The properties of SPE in silicon are included in this general rule of thumb. For example, various groups are now employing ‘lateral SPE’ as a part of device fabrication[10]. In this case, a small crystalline region is used to seed an amorphous film that is otherwise isolated from any crystalline growth sites, and growth spreads out laterally from the location of the original seed. These groups have then had to try and apply or extend the current models of planar or conventional SPE to this new regime. If the current understanding of conventional SPE is not sufficiently advanced then adaptations to more complex situations will be difficult at best.

SPE Research

Even though the quantity of silicon SPE data in the literature far surpasses that which exists for germanium, there are still cases where completely different models[11,12] predict similar quantitative results, and the available data[10,13,14] is not sufficient to distinguish between them. Furthermore, most of the early SPE experiments on both intrinsic[9,15] and doped[16–18] material used a cumbersome and time consuming partial anneal technique which provided insufficient data to clearly elucidate SPE behaviour.

While it is now known that hydrogen contamination[19–21] plays a significant
role in SPE measurements in silicon, the fact remains that nearly all of the SPE measurements published in the literature were performed before this fact was uncovered. The most recent set of experiments [12, 22–25] that investigated doping effects for SPE in silicon were reported at the same time as the hydrogen problem, and hence those measurements are also presumed to suffer from hydrogen contamination[20], yet what effect the simultaneous presence of hydrogen and doping impurities will have on the SPE rate, if any, is currently unknown.

Another concern with these dopant-enhanced SPE experiments is that they use a non-uniform dopant concentration profile. While it is unclear as to whether the gradient of the concentration profile will effect the SPE rate, the main problem is trying to assign a common depth scale between the SPE measurement and the concentration profile. In some cases, anomalous offsets between the two have been reported[23, 24], while for other dopants[22, 25] the two parameters appear to be synchronous with respect to depth.

The silicon SPE measurements presented in Chapter 5 were designed to clarify some of these unresolved issues. Firstly the SPE rate in intrinsic silicon was measured to set a baseline for the experimental apparatus and to compare with the reported hydrogen contamination effect. Then samples containing constant concentrations of selected dopants, similar to those created for the germanium study, were used to accurately measure the effect of doping impurities on the SPE rate. These results were then used to quantitatively review the currently accepted SPE models.

1.2.6 Solid Phase Epitaxy in Silicon-Germanium Alloys

Motivation

The recent interest in \( \text{Si}_x\text{Ge}_{1-x} \) alloys is once again fueled by the electronics industry's demand for faster components. The maximum switching speed for transistors has steadily increased with time primarily due to scaling. Scaling refers to the overall reduction in device size, and the resulting shorter electrical paths translate into an increase in device speed. However, it is clearly impossible to continue this trend \textit{ad infinitum} as the physical size of the constituent atoms themselves set a lower limit on the minimum device size, and so researchers have started to look elsewhere
CHAPTER 1. INTRODUCTION

for possible increases in device performance.

If it is not physically possible to further shorten the electrical paths in a device in an effort to reduce signal propagation time, then the other obvious option would be to try and increase the speed of the individual carriers that traverse these paths. Herbert Kroemer, known to many as the co-author of the common text ‘Thermal Physics’[26] is given credit for the original idea of combining different materials in device fabrication to achieve this goal. Heterojunction bipolar transistors created from a mating of silicon and a silicon-germanium alloy have an electric field on the order of 30 kV across the base, and this accelerates the carriers (i.e. enhanced mobility) so that the signal propagation time can be as low as half of that for a similar silicon-silicon homojunction device[27]. Hence Si_xGe_{1-x} materials are also of interest to the research community, and thus knowledge of the SPE behaviour in these materials will prove valuable.

SPE Research

Unlike silicon or germanium, for which the substrate materials are typically purchased in wafer form from a commercial supplier, the nature of manufacture for the silicon-germanium alloys becomes an important factor. The two main methods used for formation of Si_xGe_{1-x} alloys used in SPE studies have been high concentration ion implantation or a deposition technique such as molecular beam epitaxy (MBE) or chemical vapour deposition (CVD). Germanium has a natural lattice spacing that is 4% larger than that of silicon, and hence Si_xGe_{1-x} alloys will also have a larger lattice spacing than that of silicon, with the magnitude of the difference scaling with the germanium content. If a Si_xGe_{1-x} layer is epitaxially deposited onto a silicon substrate, as is usually the case, then the atoms of the Si_xGe_{1-x} material are compressed in the plane of the interface since they are constrained to match the underlying silicon lattice. The potential energy associated with this strain increases with the thickness of the alloy layer, and at some critical thickness, it becomes energetically favourable to form an extended defect such as an edge dislocation so that the strain is relieved. The case for samples formed by ion-implantation is similar, except that the cause of the strain is not localized at an abrupt interface, but spread
out according to the concentration gradient of the implanted alloying element.

Since the level of strain in the Si$_x$Ge$_{1-x}$ alloy is a direct result of how the alloy was created, the nature of how the sample was formed becomes particularly important. The addition of strain introduces another variable that the SPE rate will depend on, and the treatment of this is a separate issue in itself[28, 29]. Ideally one would like to investigate SPE in strain-free material prior to considering additional effects introduced by strain and subsequent defects. Fortunately a near strain-free environment can be achieved by growing layers that are much thicker than the critical thickness and/or by the use of compositionally graded buffer layers.

Most of the earlier SPE studies in Si$_x$Ge$_{1-x}$ were performed with strained deposited layers[30-32] and a few others have used implanted layers[33-35] also exhibiting strain. One exception is the measurements performed by Pai et al.[36] who used co-doping with boron to relieve strain, however the strain removal is then at the expense of introducing a dopant enhancement. It has only been in the last few years that an effort to perform SPE measurements in strain-free Si$_x$Ge$_{1-x}$ layers[37-40] has been reported in the literature.

Hong et al.[37] reported that unstrained alloys containing 10% Ge exhibited SPE rates 20% larger than that of pure silicon at 525 °C, whereas strained layers of the same compositional background had SPE rates 20% lower than that of pure silicon. Subsequently, Shiryaev et al.[38] measured the SPE rates in alloys containing 25% Ge, and found that the activation energy was the same (to within experimental error) as that observed for hydrogen-free silicon SPE data[19]. Kringhøj and Elliman[39] then performed experiments on relaxed alloys of varying composition and found that the activation energy for SPE did not vary monotonically with the Ge concentration. Haynes et al.[40] also did a similar set of experiments on relaxed alloys of varying composition, and found a similar behaviour for the activation energy dependence on the Ge content. More details on the results in the literature pertaining to SPE in Si$_x$Ge$_{1-x}$ alloys are reviewed in Chapter 2.

While these researchers have recently started to investigate the SPE dependence on the alloy composition, the consideration of doping effects on the SPE rate in Si$_x$Ge$_{1-x}$ alloys has only come up once in the literature[36]. In this work, the
CHAPTER 1. INTRODUCTION

SPE rates for two Si$_x$Ge$_{1-x}$ alloys of different composition have been measured. These values have served as a reference for identical samples that have subsequently been doped with constant concentrations of arsenic, thus presenting the first n-type dopant-enhanced SPE measurements in Si$_x$Ge$_{1-x}$. These results are presented in Chapter 5 in conjunction with the silicon research.

1.3 Measurement of SPE Rates

The measurement of the solid phase epitaxial regrowth rates used to be a very tedious process. The technique that was commonly used involved measuring the initial thickness of the amorphous layer, annealing the sample for a period of time, and then measuring the remaining amorphous layer thickness. From this, a mean SPE rate for the region of regrowth could be established. If the remaining thickness was non-zero, then this process could be repeated. Since the thickness measurements were performed via Rutherford Backscattering Spectrometry and Channeling (RBSC), this meant moving the sample from the annealing environment into the RBSC system and back again for each step, with up to five steps typically being performed on each sample. If the measurement was to be repeated at successive temperature intervals, then the difficulty of the task scaled accordingly. Furthermore, only mean SPE rates were obtained, and the samples in question would be subject to thermal cycling for each measurement step.

Fortunately there is now a much simpler technique to measure SPE rates, and it also gives real time information on the SPE rate while the anneal is in progress. The technique, called Time Resolved Reflectivity (TRR) by Olson et al.[41] when they first reported it in 1980, makes use of the basic interference properties of light reflected from layered structures. The essentials of the experimental apparatus can be reduced to a single laser and a detector, thus making it a very cost-effective technique. The duration of the measurement is simply the duration of the anneal, and no external involvement is required during the annealing process. By removing the workload associated with partial anneal/RBSC measurements, detailed SPE studies involving large temperature ranges and large numbers of samples had now become feasible.
1.3. **MEASUREMENT OF SPE RATES**

This work makes extensive use of the TRR technique to measure SPE rates in various germanium, silicon and silicon-germanium alloy samples. In excess of 250 TRR measurements of the SPE rate have been performed just for germanium alone as part of this study. Clearly the use of the partial anneal/RBSC technique would have been impractical for the same number of measurements. More information on the fundamentals of the TRR technique are documented in Chapter 2, and details of the particular experimental arrangement used here can be found in Chapter 3.
CHAPTER 1. INTRODUCTION
Chapter 2

Review of Solid Phase Epitaxy
2.1 Introduction

There is currently a reasonable amount of experimental data available on solid phase epitaxy (SPE) in various materials, and from that there have been several theories proposed to explain the observed behaviour. With the introduction of the Time Resolved Reflectivity (TRR) technique, the collection of SPE data has become a lot easier.

This chapter documents the experimental results of the past that are relevant to the studies being presented in this manuscript, in the order that they are dealt with in the later chapters. The TRR technique is also introduced and contrasted to earlier methods for measuring SPE rates. Sections 2.2 and 2.3 summarize the relevant experimental results for germanium and silicon that have led to the development of the various SPE models existing at present, including results for implantation doped materials. Section 2.4 details the various models that have been developed primarily from the Si and Ge SPE data. Section 2.5 outlines some of the pertinent Si$_x$Ge$_{1-x}$ alloy SPE measurements as a precursor to the implantation doped Si$_x$Ge$_{1-x}$ layers that are studied as a part of this work. The chapter concludes with Section 2.6, which reviews the TRR technique of measuring SPE rates, comparing it to the previously used partial-anneal/RBSC technique and noting its dependence on the various optical parameters of the material being studied.
2.2. SPE STUDIES OF GERMANIUM

2.2 SPE Studies of Germanium

By the time the interest in performing SPE measurements had become reasonably widespread, silicon had long since edged out germanium as the more important semiconductor. Due to this, SPE data for germanium is relatively sparse. Fortunately, the recent (i.e. since 1994) interest in Si$_x$Ge$_{1-x}$ alloys has caused a few more SPE studies to be undertaken with a-Ge being the logical 'x=0' end point of the alloy curve. Here, the results of all of these Ge SPE studies are summarised briefly to give context to the models that are described later in this chapter. More detailed considerations of these results are presented in a later chapter (section 4.2) and are reviewed critically (section 4.4.2) in light of the current Ge experiments of this study.

2.2.1 Partial Anneal/RBSC Measurements

The first reported SPE measurement for a-Ge was published by Csepregi et al.[5] in 1977. They used a furnace/RBSC technique as described in section 2.6.6 to study the SPE behaviour of 0.5 µm a-Ge layers on (100) Ge in the relatively narrow temperature range of ~310 °C to ~340 °C. They reported an essentially Arrhenius behaviour, with an activation energy of 2.0 eV.

In 1982, Suni et al.[7] implanted approximately $10^{20}$/cm$^3$ of $^{11}$B and $^{75}$As into separate a-Ge layers on (100) Ge, and by using the same technique as Csepregi, they measured the SPE rate in the doped region. They found that the SPE rate was considerably enhanced in the regions containing the dopants for both of the temperatures studied. The observed SPE rates were $\sim 1.5 \times$ and $\sim 2.5 \times$ that of the undoped material for As and B respectively. They also studied a sample containing both As and B, and determined that the SPE rate returned to a value close to that of the intrinsic material at depths where similar concentrations of both p-type and n-type dopants were present.

2.2.2 Calorimetry Measurements

Donovan et al.[6] used a calorimetry-based measurement of the heat of crystallization of a-Ge layers on (100) Ge in the approximate temperature range from 690 K
to 730 K. From a fit to the normalized power output of the calorimeter as a function of temperature they reported an Arrhenius behaviour of the SPE rate with an activation energy of 2.17 eV and a velocity prefactor of $4 \times 10^7$ m/s.

### 2.2.3 TRR Measurements

Lu *et al.* [8,11] measured the SPE rate of ~800 nm thick a-Ge layers on (100) Ge in the temperature range between 300 °C and 365 °C with a TRR based technique as part of their pressure dependence measurements. They reported an activation energy of 2.17 eV and a velocity prefactor of $1.2 \times 10^7$ m/s. As one of the recently reported SPE measurements of a-Ge on (100) Ge, in 1994 Olson and Roth [14] reported having measured an activation energy of 2.26 eV in the temperature range from 350 °C to 450 °C for a-Ge layers formed by Si+ implantation. In their measurements of Si$_x$Ge$_{1-x}$ alloys, Kringhei *et al.* [39] used TRR to measure the SPE rate of a-Ge on (100) Ge in the depth range from 900 Å to 2800 Å and reported an activation energy of 2.02 eV and a velocity prefactor of $6.1 \times 10^6$ m/s. The most recently reported measurement is that by Haynes *et al.* [40] who again were investigating Si$_x$Ge$_{1-x}$ alloys. They also used TRR to measure the SPE rate in a-Ge layers on (100) Ge in the near surface region (approximately 800 Å to 1600 Å) over the temperature range from 290 °C to 390 °C. From their analysis, they reported an activation energy of 2.19 eV and a velocity prefactor of $7 \times 10^7$ m/s.

So, in summary, the SPE rate in undoped germanium is known to follow an Arrhenius behaviour with an activation energy between 2.0 and 2.3 eV, and the velocity prefactor lies somewhere between $6.1 \times 10^6$ and $7 \times 10^7$ m/s. The results of these previous studies are compared and contrasted with those of the present work in Chapter 4. Qualitative data describing the effect on the SPE rate of the two common dopants, As and B, has been reported in the literature, but quantitative data is presently unavailable. This work also presents accurate quantitative data for dopant effects on the SPE rate in Chapter 4.
2.3 SPE Studies of Silicon

In contrast to germanium, the number of SPE studies involving silicon is relatively large. The results of the prominent studies that were used for a basis of developing the current SPE models are summarised here. The particulars of those measurements that are relevant to the silicon study of this work will be detailed later in section 5.2 along with the Si based results of this work.

2.3.1 The Csepregi Group

Even though the process of epitaxial reordering of a-Si layers on c-Si was reported a lot earlier[42], Csepregi et al.[9] were the first to report measurements on the kinetics of the process back in 1975. There they reported that the SPE rates in ~ 4600 Å thick self-ion implanted a-Si layers on (100) and (110) Si followed an Arrhenius behaviour with an activation energy of 2.3 ± 0.1 eV for both orientations. The overall growth velocity for the (110) samples was lower than that of the (100) samples. They also noted that an attempt to perform similar measurements on (111) samples resulted in non-linear growth rates and the regrown c-Si layer had a high level of residual defects. They continued their investigations into (111) Si[43] and then proceeded to map out the growth rate from (100) to (111) in 5° increments[15]. These last measurements indicated that the orientation dependence could be fitted reasonably well to the sine of the angle between the substrate orientation and the <100> direction, which has since been a heavily cited result.

The Csepregi group then turned their attention to a-Si layers that had been further implanted with the doping impurities phosphorous, arsenic and boron[17] which provided the first data on doping effects in SPE, back in 1977. They found that for these dopants, the SPE rate was considerably enhanced for concentrations approaching the order of ~ 1×10²⁰/cm³. Enhancements of six to 25 times that of the intrinsic SPE rate were reported. For the P case, it was found that the SPE rate was not strongly concentration dependent for levels above 2×10²⁰/cm³. They noted that the accurate determination of activation energies was not feasible since the dopant concentration varied considerably with depth. In addition, the As doped sample was only studied at one temperature. In a separate paper[44] they studied the effect of
common contaminants such as $^{12}$C, $^{16}$O, $^{14}$N and noble gases, and found that these typically had a rate retarding effect at concentrations above $\sim 0.5$ atomic percent.

### 2.3.2 Other Dopant Related SPE Measurements

In 1980, Williams and Elliman[45] also investigated SPE in (100) Si implanted with arsenic, but turned their attention to a higher concentration regime. They found that for a peak concentration of $\sim 4 \times 10^{20} / \text{cm}^3$ ($\sim 0.8$ at. %) SPE proceeded in a reasonably linear fashion, but for a peak concentration of $\sim 3 \times 10^{21} / \text{cm}^3$ ($\sim 6$ at. %) the SPE rate was severely retarded. However, even at the highest concentration, no As precipitation was observed, and more than 90% of the As was reported to be substitutional. The retardation at high As concentrations ($> 1$ at. %) was attributed to local stress caused by incorporating such a large quantity of As into the Si matrix.

In 1982, Suni et al.[7, 16] continued along the vein of the dopant studies performed by Csepregi et al.[17] by measuring SPE rates in $^{11}$B, $^{75}$As and $^{31}$P implanted a-Si layers. They were the first group to extend the investigation to overlapping dopant impurity profiles. In doing so they found that when both p-type ($^{11}$B) and n-type ($^{75}$As or $^{31}$P) dopants were present in similar concentrations, a compensating effect was observed where the SPE rate returned to a value close to that measured for intrinsic a-Si layers. Similarly, the combination of two n-type dopants ($^{75}$As and $^{31}$P) had an additive effect on the SPE rate.

Shortly after Suni et al. reported on their compensation measurements, Lietoila et al.[18] noted that both the dopant measurements of Csepregi et al.[17] and the compensating impurity measurements of Suni et al.[16] suffered from the same problem of varying dopant concentration which limited the ability to deduce quantitative activation energy values from the experiments. In light of this, they calculated custom implant profiles to give a constant concentration of $^{31}$P in one sample, and equal constant concentrations of both $^{31}$P and $^{11}$B in another sample to be used for compensation measurements. They also measured the SPE rate in intrinsic a-Si to allow direct comparison with the dopant implanted samples, and in doing so found an activation energy of 2.85 eV, in contrast to the 2.35 eV reported by Csepregi et al.[15] earlier. The sample containing $1.7 \times 10^{20} / \text{cm}^3$ of $^{31}$P exhibited
an activation energy of 2.5 eV, however, the authors noted that there was considerable uncertainty in that value since it was derived from only three measurements in a \( \sim 50 \, ^\circ\text{C} \) interval. On the other hand, the SPE rate in the compensated sample was measured at five temperatures in an \( \sim 100 \, ^\circ\text{C} \) interval, and the activation energy determined from that was 2.8 eV, which is nearly the same as that of the intrinsic material. The overall SPE rates for the compensated sample were between 10% and 30% higher than that of the intrinsic sample, but the authors attributed that to imperfect compensation, noting that an error of \( \pm 1\% \) in either dose could result in a net doping level of \( \sim 1 \times 10^{19} / \text{cm}^3 \).

In 1986, Licoppe and Nissim[124] performed TRR measurements on four silicon samples each containing a single arsenic implant. The concentrations reported for these samples ranged from from \( 2 \times 10^{19} \, \text{As/cm}^3 \) to \( 1.5 \times 10^{20} \, \text{As/cm}^3 \). They reported an activation energy of 2.7 eV for self-implanted samples, and a reduction in the activation energy as the arsenic concentration was increased. The activation energy reduction as a function of arsenic concentration was initially rapid, but then appeared to plateau at 2.35 eV for the two higher concentrations studied. An order of magnitude reduction in the velocity prefactor was also reported for the highest arsenic concentration.

### 2.3.3 The Olson Group

It is interesting to note that both the studies of Suni et al.[7,16] and Lietoila et al.[18] both employed partial furnace annealing combined with RBSC measurements to determine the SPE rate, similar to the method used by Csepregi et al.[9], even though the TRR technique was first reported by Olson et al.[41] a year or two earlier, in 1980. However, this initial report was aimed at applying TRR to cw-laser annealing, and without hindsight its application to conventional thermal annealing may not have been so obvious as it seems now. Later in 1983 the Olson group[13,46] reported TRR measurements performed on a-Si layers formed by Si\(^+\) implantation to measure the SPE rate over a much larger temperature range (\( \sim 550 \, ^\circ\text{C} \) to \( \sim 950 \, ^\circ\text{C} \)) and determined that the SPE process was still well described by an Arrhenius equation even
though the measured rates spanned approximately six orders of magnitude. They reported an activation energy of 2.68±0.05 eV and a velocity prefactor of 3.1×10^6 m/s for these measurements. In 1985 they extended this temperature range even further, reaching temperatures of ~ 1350 °C and interface velocities of ~ 1 cm/s for 1600 Å thick ion implanted a-Si layers[13,47]. The activation energy and velocity prefactor for these measurements, involving a-Si layers formed by low-dose As⁺ implantation, were reported to be 2.75±0.05 eV and 3.68×10^6 m/s respectively.

At about the same time, the Olson group[13, pp. 38-44] performed measurements on SPE in (100) Si with various doses of 220 keV arsenic, giving peak concentrations ranging from 3.5×10^{19} /cm³ to 1.4×10^{21} /cm³ at a depth of ~ 1300 Å. They reported a detailed and complex dependence of the SPE rate on the As concentration and the annealing temperature, in contrast to the boron and phosphorous systems for which the SPE rate appears to simply track the impurity concentration. Of particular interest was the fact that the maximum SPE rate was observed at a depth prior to the point where the c/a interface would intersect the expected peak As concentration, and this offset or 'hysteresis' tended to increase with increasing As dose.

Olson and Roth[13] then revisited the compensation issue in 1988, by applying the TRR technique to measure the SPE rates in boron and phosphorous systems. The samples used were similar to those used by Lietoila et al.[18] (B, P and B + P at 1.8×10^{20} /cm³), but the study involved a much larger temperature range ( ~ 550 °C to ~ 950 °C). From their measurements, they reported activation energies of 2.52 eV, 2.68 eV and 2.68 eV for the B, P and B + P systems respectively, and the B + P system exhibited essentially complete compensation. These results are all in reasonable agreement with the low temperature data of Lietoila et al. discussed previously. They also considered independent samples containing uniform concentrations of either B or P and measured the SPE rates as a function of concentration (0.1, 0.2, 0.5 and 1.0 at. %) for a fixed temperature (625 °C). The concentration dependence of the SPE rate was observed to be quite sharp initially, but quickly tapered off and appeared to plateau for concentrations near and above 1.0 at. %.
2.3.4 Diamond Anvil Cell Measurements

In 1989, Lu et al.[48] took a different approach to SPE measurements, investigating the effect of hydrostatic pressure at constant temperatures by annealing samples within a diamond anvil cell loaded with liquid argon. They found that the SPE rate in intrinsic Si was enhanced by pressure, and from Arrhenius fits of velocity versus pressure, (analogous to the more commonly observed velocity versus inverse temperature) they were able to assign an activation volume of $-0.28 \Omega_{Si}$ to the SPE process, where $\Omega_{Si}$ is defined as the crystalline atomic volume of Si.

Aziz et al.[29] then extended the initial hydrostatic measurement to the non-hydrostatic regime by the use of a three point bending device. In the generalization of the above to non-hydrostatic stress, the activation volume becomes an activation strain tensor for which the trace gives the activation volume in the hydrostatic limit. Based upon those measurements, they reported that the SPE rate is increased by uniaxial tension in the interface plane, and decreases with uniaxial compression in the interface plane.

2.3.5 The Walser Group

The Walser group was the next to direct considerable research effort to SPE in implantation doped a-Si layers, starting with boron[49] in 1988, arsenic[25] and phosphorous[24] in 1989, and then aluminum[22] and B + P compensation[23] in 1990. They found that the SPE rate increased monotonically with boron concentration at a fixed temperature, approaching a maximum rate at a boron concentration between $2 \times 10^{20}$/cm$^3$ and $3 \times 10^{20}$/cm$^3$.

More importantly, for boron concentrations below $\sim 5 \times 10^{19}$/cm$^3$, they could fit the ratio of the dopant-enhanced velocity to that of the intrinsic material as

$$\frac{v}{v_i} = 1 + \frac{N_B}{N_o} exp(\Delta E/kT)$$

Eq. 2.1

with $N_B$ being the boron concentration, and with $N_o$ and $\Delta E$ determined from the fit to be $1.9 \times 10^{21}$/cm$^3$ and 0.30 eV respectively. In the context of their description, they called the second term in Eq. 2.1 the ‘normalized’ boron concentration. They were also able to fit the results for arsenic and phosphorous implanted samples to this type
of equation, with \( N_o = 2.9 \times 10^{21} / \text{cm}^3 \), and \( \Delta E = 0.34 \text{ eV} \), and \( N_o = 2.7 \times 10^{21} / \text{cm}^3 \) and \( \Delta E = 0.26 \text{ eV} \) for As and P respectively. However, their study of aluminum implanted samples indicated that the SPE rate enhancement from Al did not fit the normalized equation (Eq. 2.1). Instead, they found that low doses \(( \leq 2.3 \times 10^{19} / \text{cm}^3)\) caused a decrease in the SPE rate, and doses considerably above that caused an increase in the SPE rate.

The Walser group's compensation sample consisted of a single implant of boron overlapping with a single implant of phosphorous. They found that the depth at which the SPE rate was equal to the intrinsic rate was about 250 Å to 290 Å closer to the surface than the point at which the B and P concentrations were expected to be equal (1630 Å). This was surprising, since \textit{a priori} one would have expected that the depth of minimum SPE and equal concentrations would have been coincident with each other.

### 2.3.6 Hydrogen Retardation

At about the same time as the last of the Walser group measurements were presented, Roth \textit{et al.} [19] uncovered an effect that had far reaching ramifications on essentially all of the previous SPE rate measurements in (100) Si, even including their own [13]. They used multiple MeV ion implants to create a-Si layers 4.3 \( \mu \text{m} \) thick, and then measured the SPE rate in these thick layers via TRR both in a vacuum and an air annealing ambient. The SPE rates for the two ambients were essentially equal until the \( c/a \) interface reached \( \sim 2 \mu \text{m} \), and then they observed a dramatic reduction (up to 40%) in the SPE rate of the air annealed sample until the \( c/a \) interface reached the surface.

The various measurements that were performed indicated that no impurities were present in the layer prior to annealing or after complete regrowth. But Secondary Ion Mass Spectrometry (SIMS) measurements of partially annealed samples indicated a high \(( \sim 1 \times 10^{19} / \text{cm}^3)\) concentration of hydrogen was present in the amorphous material during the last micron of SPE. The presence of H was sufficient to explain the SPE rate reduction, since it had already been demonstrated that H did retard the SPE rate in Si[50]. Roth \textit{et al.} [19] postulated that the source of the H was from
2.3. **SPE STUDIES OF SILICON**

the formation of a native oxide during the annealing process in the presence of water vapour. In light of this they noted that essentially all previous SPE measurements had been performed in a-Si layers less than 1 µm thick and hence they would have been measuring the H retarded rate unless special care had been taken to remove all water vapour from the annealing environment.

A subsequent report by Roth *et al.* [20] showed that 3400 Å thick a-Si layers that were partially annealed in a vacuum furnace at ~ $10^{-5}$ Torr were still found to be saturated with hydrogen to a constant level of about $\sim 1 \times 10^{19} / \text{cm}^3$. Hydrogen was still observed to be present in samples that were annealed in a vacuum furnace with a pressure less than $1 \times 10^{-7}$ Torr. In this case the total amount of hydrogen was limited to the amount contained in the pre-existing native oxide, and hence the surface of the sample did not act as an infinite diffusion source. Instead the hydrogen concentration profile was more uniform, with one sample containing $\sim 2 \times 10^{18} / \text{cm}^3$ to a depth of 2 µm. This indicated that the pre-existing hydrogen content in the native oxide would be sufficient to saturate thin ($\sim 4000$ Å or less) a-Si layers to a level of $1 \times 10^{19} / \text{cm}^3$ or more, even in UHV annealing conditions.

A recent measurement by McCallum [51] has further reinforced the evidence of the hydrogen intrusion problem. SPE measurements of both c/a interfaces of buried a-Si layers gave rates that were within 5% of the H-free thick layer data reported by Olson and Roth [14]. SIMS measurements of partially annealed samples indicated that the H concentration was at or below the detection limit of $\sim 10^{17} / \text{cm}^3$ within the a-Si material. Measurements of 2.2 µm thick a-Si surface layers that did not have a c-Si layer to prevent H penetration, exhibited SPE rates between 20 and 40% lower than the buried layer c/a interfaces, in agreement with the retardation reported by Roth *et al.* [19] for a-Si layers approximately twice as thick.


2.4 Models of the SPE Process

Even though the first report of solid phase epitaxial regrowth in silicon was published back in 1968[42], the main thrust of experiments involving SPE that led to the current models did not take place until the mid to late 1970’s. The majority of these first experiments were performed by the group led by Csepregi et al.[5,9,15,17,43]. Since then numerous other investigators have also become involved by measuring SPE data in various systems, or by contributing models of the SPE process.

As the amount of SPE data has accumulated, various review articles have been published to document the various models and how well they fit the experimental data. Some of the more prominent ones are ‘Solid Phase Epitaxial Growth of Si and Ge’ in 1980 by Lau et al.[52], ‘Solid Phase Recrystallization Processes in Silicon’ in 1983 by Williams[53], ‘Kinetics of Solid Phase Crystallization in Amorphous Silicon’ in 1988 by Olson and Roth[13], ‘Pressure Enhanced Crystallization Kinetics of Amorphous Si and Ge’ in 1991 by Lu et al.[11], ‘Solid Phase Epitaxy’ in 1994 by Olson and Roth[14], and ‘Topics in Solid Phase Epitaxy: Strain, Structure and Geometry’ in 1996 by Hellman[10]. Technically speaking, the article by Lu et al.[11] is not a review article, however it does consider each of the proposed SPE models in detail, and is thus an important work that should not be overlooked.

The following portion of this chapter aims to document the various models, with the emphasis being on dopant-enhanced SPE since that is the main focus of this study.

2.4.1 Transition State Theory

Most of the models that have been proposed to explain the experimental SPE data that currently exists have some sort of foundation in transition state theory, also known as reaction rate theory[54,55]. The three fundamental postulates of transition state theory are that:

(a) The unit step of the reaction consists of a continuous change of the configurational coordinate from the initial state to the final state.

(b) When considering the free energy as a function of the configurational coordinate, there is a region between the initial and final states that has has an energy associated
with it that is higher than either that associated with the initial or final state. This implies that an increase in free energy is required to overcome this energy barrier. 

(c) One of the intermediate steps or configurations that lead from the initial state to the final state has a configurational coordinate associated with the maximum of the energy barrier, and upon reaching this activated state, the process will be very likely to move to the final state.

From these postulates, it is possible to show that the rate of such a reaction taking place in a solid will be of the form

\[ k_f = C \nu \exp(-\epsilon/kT) \]  

(2.2)

with \( \epsilon \) being the activation energy, \( \nu \) being the reaction's characteristic vibration frequency and \( C \) being a constant related to the entropy change associated with the reaction. This is of course the well known Arrhenius equation.

However, as Christian\cite{54} points out, one must be careful to not blindly apply transition state theory to solid state processes without proper consideration of these postulates, since the original reaction rate theory was meant to describe gaseous and liquid solutions in which the particles involved behaved independently and ideally. Christian then details a treatment which involves adding the assumption that the atoms in both the initial and final states can have their motions described adequately as small simple harmonic vibrations. The resulting form of the reaction rate from this treatment can also be put in the form of Eq. 2.2, with a slight variation on the interpretation of the frequency and entropy terms.

A simple application of an Arrhenius type equation to the SPE process involves taking the experimental activation energy, and then writing the prefactor in terms of geometrical lattice parameters and an attempt frequency for atoms to go from the amorphous phase to the crystalline phase. However, when this is done, the calculated SPE rates are found to be at least an order of magnitude below the experimentally determined values\cite{10,52}.

Olson and Roth\cite{13,14} detail a slightly more complex treatment based upon transition state theory, in which they decompose the free energy terms into enthalpy and entropy terms. The resultant expression is

\[ v = v_o \exp(-E_a/kT) [1 - \exp(\Delta S_{ac}/k) \exp(-\Delta H_{ac}/kT)] \]  

(2.3)
with $\Delta S_{ac}$ and $\Delta H_{ac}$ being the entropy and enthalpy difference respectively between the amorphous and crystalline state, and $E_a$ being the measured activation energy. By doing this, the experimental data for SPE rates and $\Delta H_{ac}$ can be applied to Eq. 2.3 in such a way that the entropy terms can be estimated. In particular, they showed that a value of zero for $\Delta S_{ac}$ gives the best fit to the SPE data, and that the special case of $\Delta S_{ac} \sim 1k$ in Eq. 2.3 would predict a dramatic fall in the SPE rates as $T$ approaches the melting point of c-Si. However, the SPE rates have been measured to within about 60 °C of the melting point of c-Si and no such behaviour has been observed, and thus $\Delta S_{ac} \ll 1k$. This is in agreement with the recent measurement by Stolk et al.\[132\], in which they reported a value of $\Delta S_{ac} = 0.2k$.

### 2.4.2 The Spaepen-Turnbull Dangling-Bond Model

Spaepen first proposed a static model of the $c/a$ interface in (111) silicon or germanium by the physical construction of a model based on sensible phase-specific construction rules\[56\]. The model was started with two crystalline layers, and then the replacement of sixfold rings with combinations of five, six and sevenfold rings was used as a construction rule for the amorphous phase. In addition, they required that all bonds were satisfied, that a common nearest neighbour distance was maintained, and that the bond angle distortion was minimized. By applying these rules, an amorphous structure was created after the addition of two atomic layers. The resulting amorphous structure exhibited a radial distribution function (RDF) similar to that which is obtained for a continuous random network (CRN). Having no dangling bonds in the interface results in the lowest energy configuration (a 0 K representation), since the energy associated with a broken bond is 1.63 eV, which is much greater than the 0.10 eV/atom associated with the bond distortion at the interface\[56\]. This model was then proposed as a starting point for understanding the solid phase epitaxial regrowth process in terms of bond breaking and reconnection at elevated temperatures.

Following from this model of the $c/a$ interface, Spaepen and Turnbull\[57, 58\] proposed a system in which dangling bonds are generated at the interface, and these dangling bonds migrate along the interface allowing crystallization events to
take place. The dangling bond would continue to migrate until suitably trapped or until annihilated by another dangling bond. A schematic representation of this process is shown in Fig. 2.1 in which the dangling bond pair (DF) act to transfer atoms B and E into the crystal phase. There are still two dangling bonds left after the process, indicating that they have a catalyst type of role, and are free to continue adding atoms to the crystal until suitably trapped or annihilated. Since their original model of the c/a interface showed that an interface without any dangling bonds was preferred on the basis of a minimum energy argument, the process of crystallization would then have an activation energy associated with the formation of these dangling bonds.

2.4.3 Saito and Ohdomari’s Extension to Spaepen’s Model

In a similar fashion to the model of the (111) c/a interface built by Spaepen, Saito and Ohdomari[59] also built a model for the (100) c/a interface. In addition to relaxing the bond angles, as Spaepen did, they also allowed simultaneous relaxation in the bond lengths to minimize the elastic energy as given by a Keating potential. The amorphous layer depicted by this model also showed favourable comparisons to properties such as the RDF and the r.m.s. bond angle deviation as predicted for a bulk CRN. They then used this model to propose a nine step process in which three atoms are added to the crystal following the formation of a dangling bond pair[60].

While these models may not provide a direct mathematical treatment of the SPE process, they allow insight into the ‘efficiency’ of a dangling bond in converting atoms from the amorphous phase to the crystalline phase. Some of the mathematical models that have been proposed relate the SPE rate to the dangling bond efficiency. The value of three determined from this physical model provides a plausible result that can be used in the evaluation of these other models. In addition, both this model and that of Spaepen[56] give evidence that the interface can be essentially atomically flat, in agreement with the many RBS and TEM[61, 62] measurements that indicated a very sharp c/a interface.
CHAPTER 2. REVIEW OF SOLID PHASE EPITAXY

Figure 2.1: A schematic representation in which an initial dangling bond pair (DF) are shown to facilitate transfer of two atoms (B and E) to the crystal phase. The net effect is the movement of a [110] ledge along the (111) terrace. Two dangling bonds are still left free to further the process. (From Spaepen and Turnbull[57].)
2.4. MODELS OF THE SPE PROCESS

2.4.4 Kinetic Analysis of the Dangling Bond Model

Lu et al.[11] reconsidered the dangling-bond model of Spaepen and Turnbull, and performed a kinetic analysis on it beginning from transition-state theory[54] applied to the dangling bonds. They derived a more general expression for the growth velocity than the one proposed by Spaepen and Turnbull[57,58] by relaxing some of the simplifying assumptions that were overly restrictive. The functional form of the growth velocity as predicted by this extended model was

\[ v = 2\sin(\theta)v_s n_r e^{\frac{\Delta S_f + \Delta S_m}{k}} e^{\frac{-\left(\Delta H_f + \Delta H_m\right)}{kT}} \]  
(2.4)

where \( \theta \) is the misorientation from \{111\} (55° for the (100) surface), \( v_s \) is the speed of sound at the interface, \( n_r \) is the net number of jumps each dangling bond makes before it is annihilated, \( \Delta S_f \) and \( \Delta H_f \) are the entropy and enthalpy of formation of a dangling bond pair respectively, and \( \Delta S_m \) and \( \Delta H_m \) are the entropy and enthalpy of motion of the dangling bond at the interface respectively. By comparing this equation to the experimentally observed Arrhenius SPE behaviour, a velocity prefactor and an activation energy term can be immediately identified.

Using the velocity prefactors of Si and Ge that were available then, combined with the speed of sound in the amorphous material, they were able to determine a value for the product of \( n_r \) and the entropy exponential. The entropy term was then bounded between zero and the entropy of fusion, and the ratio of 9:3 for dangling bond jumps to crystallization events from Saito and Ohdomari was used to determine \( N_r \), the number of atoms crystallized per dangling bond pair formed. This resulted in \( 5 \leq N_r \leq 200 \) for Si, and \( 30 \leq N_r \leq 1200 \) for Ge, with an additional uncertainty of \( \sim 50 \% \) for the Ge value due to the large uncertainty in the Ge velocity prefactor.

The activation energy predicted by Eq. 2.4 is in keeping with the experimental values if a migration energy of 0.3 to 0.4 eV is assumed. According to Lu et al.[11], this magnitude of \( E_m \) is reasonable, given that it is comparable to the value that has been measured for ion-beam enhanced SPE measurements.

The model can also account for the observed hydrostatic pressure dependence of SPE[8,11], and the \( \sin(\theta) \) term accounts for the experimentally observed SPE orientation dependence reported by Csepregi et al.[15]. Furthermore, the results of the nonhydrostatic pressure measurement[29] discussed in section 2.3.4 were interpreted.
in terms of defining a general shape for the activated state. From this, it appears to be flattened out in the plane of the interface, akin to an oblate spheroid with its axis normal to the $c/a$ interface.

However, when the model is taken on its own, it is evident that no explicit doping dependence is predicted by Eq. 2.4. To account for dopant-enhanced SPE, the kinetic model must be taken in conjunction with another compatible model that makes predictions about the doping dependence without conflicting with any of the above results. Lu et al.[11] propose the Generalized Fermi Level Shifting (GFLS) model discussed later in this section as one possible model to fill this role.

Olson and Roth[14] note that this model, and in fact all dangling bond models, do not address the fact that the quantity of dangling bonds already present in the material as determined by Electron Spin Resonance (ESR) measurements is the same order of magnitude or even greater than the quantity of thermally generated ones assumed to control the SPE process. In order to avoid such an inconsistency, it can only be assumed that the defects which are already present are different in such a way that they play a much lesser role in the SPE process.

### 2.4.5 General Semiconductor Parameters

Some of the models for SPE use Fermi level shifting arguments, propose defect levels within the band gap, or use general semiconductor statistics to predict certain properties. In light of this, it is useful to consider the behaviour of some of these semiconductor parameters in Si and Ge for the temperature ranges that are of interest. In this way it will be clearer when certain models are no longer applicable due to a violation of any of their original assumptions. The following is intended only as a quick overview to allow introduction of the relevant equations describing semiconductor statistics, since a detailed treatment is given in many standard texts, such as those by Kittel[26,63].

Quantum Treatment of an Electron Gas

The quantum treatment of a three dimensional electron gas of $N$ particles results in a sphere in $k$ space with the surface of the sphere representing the state with
the k vector that has the largest magnitude that is populated at absolute zero. The energy associated with this state is called the Fermi energy \( E_f \), or the Fermi level. At non-zero temperatures, the probability of a state with energy \( E \) being populated is given by the Fermi-Dirac distribution:

\[
f(E) = \frac{1}{\exp\left(\frac{E - E_f}{kT}\right)}
\]

(2.5)

If \( (E - E_f) \gg kT \) then the exponential term dominates, and one has the classical Boltzmann distribution function. The other quantity of interest that comes from this treatment is the density of orbitals (or quantum states) for a given energy, i.e.

\[
D(E) = \frac{dN(E)}{dE} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}
\]

(2.6)

which is the concentration of states that lie in the shell of k space between \( E \) and \( E + \delta E \). In general, the carrier concentration in an energy interval between \( E_1 \) and \( E_2 \) is given by the integral of the product of the above two functions:

\[
n = \int_{E_1}^{E_2} f(E) D(E) \, dE
\]

(2.7)

The total carrier concentration is usually of interest, and in that case, the integration takes place over all energy space, so that the limits of the integral are zero and infinity. In this case the integral in Eq. 2.7 reduces to one of the form

\[
F_{1/2}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{1 + e^x(x - \eta)} \, dx
\]

(2.8)

Unfortunately this integral, known as the Fermi-Dirac integral, can not be written in closed form without making some sort of approximations. If the Boltzmann distribution is valid over the parameter space of interest, and it is used instead of the Fermi-Dirac distribution in the integrand of Eq. 2.7 then this problem is avoided.

**Band Gaps, Effective Mass and Density of States**

Expanding this treatment to electrons subject to a periodic potential (such as that created by a lattice of ions) results in energy gaps for which no wavelike solution exists. (The constant energy surface in k space is typically no longer a sphere but rather multiple volumes of revolution about various axes.) In intrinsic semiconductors at absolute zero, this energy band gap sits above the filled valence band.
and below the empty conduction band making the material an insulator. As the temperature is increased, electrons will be excited to the conduction band, leaving vacant valence band orbitals (holes) behind, and an intrinsic carrier concentration consisting of both electrons and holes results. Hence a smaller band gap will result in more intrinsic carriers for a given temperature. The band gap widths for both Si and Ge are shown in Fig. 2.2 as a function of temperature over the ranges of interest.

The values shown in Fig. 2.2 were determined from fitting the experimental data\[64\] to a Varshni equation of the form

\[ E_g = E_o + \frac{\alpha T^2}{T + \beta} \]  \hspace{1cm} (2.9)

with \(\alpha\) and \(\beta\) given as per Table 2.1. For both Si and Ge, the tabulated values were determined from fitting experimental data only up to 177 °C, however Thurmond\[64\] notes that they accurately predict the experimental values for both Si and Ge at temperatures just below the melting point and thus they are expected to be valid over the entire temperature range. For convenience, the energy of the upper valence band edge \((E_v)\) is typically referenced to zero, which then makes the energy of the lower conduction band edge \((E_c)\) equal to the width of the band gap \((E_g)\). Note that these band gap widths are for intrinsic or lightly doped material, since the band gap can be expected to become smaller for highly doped materials\[65\]. The treatment of band gap narrowing (BGN) due to high dopant concentrations is a complex problem in itself, for which there are some low temperature models\[66\], but the temperature dependence is unclear. Experimental measurements\[67\] for n-type silicon at room temperature indicate that the narrowing would be between \(\sim 50\) meV and \(\sim 100\) meV for the dopant range of \(10^{19}/\text{cm}^3\) to \(10^{20}/\text{cm}^3\), but it is unknown if similar magnitudes could be expected at typical SPE temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>(E_o)</th>
<th>(\alpha \times 10^{-4})</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>1.1700±0.001</td>
<td>4.730±0.25</td>
<td>636±50</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.7437±0.001</td>
<td>4.774±0.30</td>
<td>235±40</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters used to determine the magnitude of the band gap in eV for both silicon and germanium as a function of temperature. (After Sze\[65\].)
Figure 2.2: The magnitude of the band gap as a function of temperature for both intrinsic Si and Ge over the respective temperature ranges of interest. Values were derived from the fitting of experimental data as done by Thurmond[64].
Material & $m_e/m$ & $m_h/m$ \\ 
--- & --- & --- \\ 
Silicon & 1.06 & 0.58 \\ 
Germanium & 0.56 & 0.35 \\ 

Table 2.2: Density of states effective masses for holes and electrons for both silicon and germanium. Values are normalized to the true or free electron mass. (From Kittel and Kroemer[26].)

In addition to the introduction of band gaps, the application of a periodic potential also changes the equations of motion for the carriers. For a free electron, the energy is related to the magnitude of the wavevector through the equation $\epsilon = (h^2/2m)k^2$, and thus one can think of the quantity $1/m$ as dictating the curvature of the energy band. When the effect of a periodic potential is taken into account, an effective mass ($m_e$) is introduced, which is defined by

$$\frac{1}{m_e} = \frac{1}{\hbar^2} \frac{d^2 \epsilon}{dk^2}$$

(2.10)

Regions of the band that have a high degree of curvature correspond to an effective mass that is less than the true mass. Within this framework, the carrier in the periodic lattice accelerates under an applied electric or magnetic field as if it had a mass equal to its effective mass. The effective mass for electrons and holes in both silicon and germanium are listed in Table 2.2.

With the addition of the concept of effective mass to Eq. 2.6, the effective density of states corresponding respectively to the conduction and valence band edges (i.e. the band gap boundaries) are written as

$$N_c = 2 \left(\frac{m_e kT}{2\pi \hbar^2}\right)^{3/2}$$

(2.11)

$$N_v = 2 \left(\frac{m_h kT}{2\pi \hbar^2}\right)^{3/2}$$

(2.12)

where $m_e, m_h$ are the effective masses of electrons and holes respectively. The effective density of states as a function of temperature for both electrons and holes in Si and Ge are shown in Fig. 2.3 by substituting in the accepted values for the effective masses for each carrier in each material[26]. It should be noted that even though the
2.4. MODELS OF THE SPE PROCESS

effective masses are treated as constants, there has been a temperature dependence reported\[68\] for silicon. However the compiled data of Thurmond[64] indicates that the temperature dependence over the range covered by SPE measurements is slight, and hence the treatment as constant is valid.

Carrier Concentration, Mass Action and the Fermi Level

The carrier concentration as a function of temperature will be of interest in discussion of the following models, and also in discussion of the results of this work in later chapters. As mentioned earlier, the carrier concentration will be given by integrating the product of the Fermi-Dirac distribution and the density of states function as per Eq. 2.7. However this results in a Fermi-Dirac integral which can not be solved in closed form, and so a Boltzmann distribution is typically used in the integrand whenever possible. The Boltzmann approximation to the Fermi-Dirac distribution is valid as long as the Fermi level is several $kT$ away from the energy at which it is being evaluated at. In this case, the energies of interest are $E_e$ and $E_v$, and a semiconductor is considered nondegenerate when the Fermi level is several $kT$ away from both band gap boundaries, so that the Boltzmann approximation can be applied. By using the Boltzmann approximation to Eq. 2.5 the concentration integral in Eq. 2.7 can be solved analytically. In the case of conduction electrons, the limits of integration are from $E_e$ to $+\infty$, and for holes, the limits are from $-\infty$ to zero. With those in place, the nondegenerate expressions for electron and hole concentration become

$$N_e = N_e \exp[-(E_e - E_f)/kT]$$  \hspace{1cm} (2.13)  

$$N_h = N_v \exp[-(E_f - E_v)/kT]$$  \hspace{1cm} (2.14)  

The intrinsic carrier concentration ($N_i$) is obtained simply by taking the square root of the product of these two equations ($N_i = \sqrt{N_e N_h}$), since the crystal is electrically neutral as a whole, and there is an equal number of holes and electrons acting as carriers (i.e. $N_e = N_h$) due to the fact that intrinsic carriers are thermally generated in pairs. In addition to giving the intrinsic carrier concentration, the
Figure 2.3: The effective density of states for electrons and holes as a function of temperature for both Si and Ge over the respective temperature ranges of interest. Symbols $N_e$ and $N_v$ represent the density of states for the conduction and valence bands respectively.
product of these two equations also gives the useful law of mass action for nondegenerate semiconductors:

\[
N_e N_h = N_c N_v \exp \left( \frac{-E_g}{kT} \right) = 4 \left( \frac{kT}{2\pi\hbar} \right)^3 (m_e m_h)^{3/2} \exp \left( \frac{-E_g}{kT} \right) \tag{2.15}
\]

which holds for doped material as well, since equations 2.13 and 2.14 are not specific to intrinsic material only. The intrinsic carrier concentrations for both Si and Ge, as determined from the square root of Eq. 2.15 are shown in Fig. 2.4. For a given temperature, germanium has a significantly higher intrinsic carrier concentration owing to the smaller band gap. Also, it is worth noting that the reduction of the band gap with increasing temperature as shown in Fig. 2.2 implicitly appears here inside the exponential term via \(E_g\). If one equates equations 2.13 and 2.14 instead of taking the product of them, then the immediate result is that \(E_f \simeq E_g/2\), indicating that the Fermi level is essentially in the middle of the band gap for intrinsic semiconductors.

For doped semiconductors, the Fermi level can be obtained by simply solving Eq. 2.13 (or Eq. 2.14) for \(E_f\) to obtain

\[
E_f = E_c - kT \ln \left( \frac{N_c}{N_e} \right) = E_v + kT \ln \left( \frac{N_v}{N_h} \right) \tag{2.16}
\]

which is valid for nondegenerate semiconductors. This equation allows one to get a feel for how the Fermi level will respond to doping. In the case of zero or insignificant doping, the previous paragraph indicates that the second term in this equation must approach \(E_g/2\). For example, as n-type dopants are added, \(N_c\) will increase, and as \(N_e\) approaches the magnitude of \(N_c\), the second term tends to zero and hence the Fermi level will move towards the conduction band. As the temperature is increased, the magnitude of the second term will increase (from both the \(kT\) factor and the \(T^{3/2}\) dependence of \(N_c\)) and hence the Fermi level will be pushed back towards mid-gap for a fixed doping level.

### Fractional Ionization of Impurity Atoms in Crystalline Material

Consider what happens when an n-type or donor impurity such as arsenic is incorporated into a silicon lattice. One electron is left over and is not involved in the bonding to the other atoms of the lattice. The arsenic ion is left with a positive
Figure 2.4: The intrinsic carrier concentration as a function of temperature for both Si and Ge over the respective temperature ranges of interest. Germanium has a much higher value than silicon at a given temperature due to the narrower band gap.
charge, balanced by the negative charge of the ‘free’ electron it has donated. The simplest treatment of this system involves a basic adaptation of the Bohr model of the hydrogen atom, taking into account the effective mass of the electron, and the dielectric constant of the medium. This will give an idea as to the order of the binding energy between the two. Performing the calculation for silicon[63,65], results in a binding energy on the order of 20 meV, indicating that the electron is lightly bound to the ion. This value turns out to be in reasonable agreement with the measured values, as for arsenic in silicon, the experimental value is 49 meV[63].

From a simple classical point of view, one might be tempted to think that all the dopant impurities are fully ionized at SPE temperatures. For example, the energy level of the As donor state in Si has been measured to be 49 meV, and $kT$ at 600 °C is about 75 meV and since $kT \gg \Delta E_d$ nearly all of the donors should be ionized. However this leads to the wrong conclusion. The reason this is misleading is because the measured donor energy level ($\Delta E_d$) is actually the energy at which the level sits below the conduction band, i.e. $\Delta E_d = E_c - E_d$. Thus the population of this donor energy level (i.e. fraction of non-ionized donors) will be determined by comparing the chemical potential or Fermi level of the electrons with the donor energy level, and the significance of the difference will be determined by normalizing to the thermal energy. Expressed as an equation, the quantity of interest will be

$$\eta_d = \frac{E_d - E_f}{kT}$$

(2.17)

This immediately allows one to make general predictions about the expected behaviour of the fractional ionization as a function of the Fermi level. When the Fermi level is well below the energy level of the donor state (i.e $\eta_d \gg 1$), there will be very few electrons populating that state, and hence the fraction of non-ionized donors will be low (i.e. full ionization approximation). As the Fermi level or chemical potential of the electrons reaches the energy level of the donor state (i.e. $\eta_d \approx 0$), it would be expected that a significant fraction (say 50% or so) of the donor states would be populated. When the Fermi level exceeds the level of the donor state (i.e $\eta_d \ll -1$), the remaining unpopulated donor levels would be expected to fill in rather quickly, and hence the number of ionized donors would rapidly tail off to zero.

The actual expression for the fraction of donors that are ionized as given by
Fermi-Dirac statistics can be written as

$$f_d^+ = \frac{N_d^+}{N_d} = 1 - \frac{1}{1 + \frac{1}{g} \exp\left(\frac{E_d - E_f}{kT}\right)} = \frac{1}{1 + \frac{1}{g} \exp\left(\frac{E_f - E_d}{kT}\right)}$$  \hspace{1cm} (2.18)$$

with $g$ being the degeneracy of the dopant level associated with $E_d$, which is two for donors and four for acceptor levels[65]. It can be shown that this has the characteristics that were deduced earlier. In particular, for $\eta_d \gg 1$, one has $\exp(-\eta) \ll 1$ and thus

$$f_d^+ \simeq 1 - \frac{1}{g} \exp\left(\frac{E_d - E_f}{kT}\right) \sim 0$$  \hspace{1cm} (2.19)$$

For $\eta_d \sim 0$, the fraction of ionized dopants is simply $1/(1 + g)$, which only differs from the previous ‘guess’ of $1/2$ because the degeneracy of the level was not taken into account. Finally, for $\eta_d \ll -1$, then $\exp(-\eta) \gg 1$ and hence

$$f_d^+ \simeq \frac{1}{g} \exp\left(\frac{E_f - E_d}{kT}\right) \sim 1$$  \hspace{1cm} (2.20)$$

which tails off rapidly towards zero as expected.

### 2.4.6 Vacancy Models

Csepregi et al.[5] proposed that ‘the epitaxial growth from the amorphous phase is governed by generation of broken bonds or vacancies.’ Evidence for this argument was the similarity in the activation energy for SPE and the energy associated with formation of a vacancy in both Si and Ge.

Suni et al.[7] extended this argument by proposing that the rate limiting step in SPE was the formation and migration of such vacancies at the c/a interface. In addition, they considered neutral, positively charged and negatively charged vacancies, with the number of charged vacancies of each type being exponentially dependent on the difference between the Fermi level and the energy level of the respective charged vacancy. Addition of dopants would then shift the Fermi level from mid-gap towards the conduction band or the valence band, depending on whether an n-type or p-type impurity was used. This Fermi level shift would then lead to an exponential increase in the number of charged vacancies of that particular type, and thus an increase in the SPE rate.
To put things a bit more mathematically, Suni et al.[7] used the following expression for the concentration of neutral vacancies:

\[ N^x = N^\circ \exp \left( \frac{\Delta E}{kT} \right) \]  

(2.21)

where \( \Delta E \) was the energy of formation of a neutral vacancy and \( N^\circ \) was taken as the density of lattice sites. Note that \( N^x \) is only a function of temperature and does not depend on the doping level. The concentration of negatively and positively charged vacancies does depend on the doping level by way of the Fermi level and hence the concentrations are given by Fermi-Dirac statistics as

\[ N^- = N^x \exp \left( \frac{E_f - E^-}{kT} \right) \]  

(2.22)

\[ N^+ = N^x \exp \left( \frac{E^+ - E_f}{kT} \right) \]  

(2.23)

These expressions both appear to be missing a constant fraction of one half, associated with the degeneracy of the vacancy level as reported by Van Vechten and Thurmond[69], but for the purposes of this discussion it is not overly significant. The significant point is that Suni et al. stated that the SPE rate is controlled by the concentration of point defects (vacancies) at the c/a interface, and that the concentration of the charged defects is enhanced by the Fermi level shift according to Fermi-Dirac statistics. Expressed mathematically, the general expression for the SPE rates based upon the development by Suni et al.[7] is given by

\[ V = C(N^x + N^- + N^+) \]  

(2.24)

where \( C \) is some constant. In the case of doped material that is significantly p-type or n-type, only one of \( N^- \) or \( N^+ \) will contribute significantly to the sum in Eq. 2.24. Unfortunately Suni et al.[7] did not take the extra step to combine the velocity and charged defect equations to get an expression for the velocity ratio. As will be seen later, these expressions for the SPE rate and for the concentrations of charged defects that control the SPE rate are essentially identical to the starting points for the kink site model (Section 2.4.8) and the generalized Fermi level shifting (GFLS) model (Section 2.4.11).

The Walser group[49] interpreted the model of Suni et al.[7] to simply state that the change in the activation energy for SPE was equal to the change in the
Fermi level caused by the introduction of doping impurities. In relation to models in which the SPE enhancement is solely due to this activation energy change, the Walser group wrote the velocity enhancement ratio as

\[ \frac{V}{V_i} = \exp \left( \frac{|E_F^e - E_F^i|}{kT} \right) = \frac{\Delta N}{2n_i} \left\{ 1 + \left[ 1 + \frac{(2n_i/\Delta N)^2}{1} \right]^{1/2} \right\} \]  

(2.25)

where \( E_F^e \) and \( E_F^i \) are the extrinsic and intrinsic Fermi levels respectively, and \( \Delta N \) is the difference between the concentration of donor and acceptor impurities. Although it is not stated explicitly, the assumption that only the activation energy is reduced by an amount equal to the Fermi level shift implies that the left hand side of Eq. 2.25 was arrived at by the simple ratio of two Arrhenius expressions such as

\[ \frac{V}{V_i} = \frac{V_a \exp\left(\frac{-E_a^c}{kT}\right)}{V_a \exp\left(\frac{-E_a^c}{kT}\right)} = \exp\left(\frac{E_a^i - E_a^c}{kT}\right) = \exp\left(\frac{|E_F^e - E_F^i|}{kT}\right) \]  

(2.26)

with \( E_a^e \) and \( E_a^i \) being respectively the extrinsic and intrinsic activation energies. The right hand side of Eq. 2.25 follows directly from the expression for the Fermi level (Eq. 2.16), and the roots of a quadratic equation (Eq. 2.42) based upon charge neutrality and mass action, however as will be shown, it is the origin of the left hand side of Eq. 2.25 that is important.

The Walser group then note the sensible requirement that dopant enhancement models must have the limiting case of

\[ \lim_{\Delta N \to 0} \left( \frac{V}{V_i} \right) = 1 \]  

(2.27)

i.e. a model must predict that the SPE rate approaches the intrinsic rate as the net number of dopants (\( \Delta N \)) tends to zero. However, for Eq. 2.25, the extrapolation of the velocity ratio versus dopant concentration ends up passing through the origin instead, and so it is clearly unsatisfactory.

While it is true that any sensible model must predict zero enhancement for zero doping level, it is felt that the mathematical description (Eq. 2.25) put forward by the Walser group is not an accurate representation of the model put forth by Suni et al.[7] and furthermore it is not a valid description of all Fermi level shifting (FLS) models, as claimed by the authors[49]. In particular, it is based upon the premise that a shift in the Fermi level will only show up as a direct shift in the activation energy of the SPE process, which does not appear to have any a priori
2.4. MODELS OF THE SPE PROCESS

justification. In the description by Suni et al.[7], an activation energy change related to the Fermi level shift is mentioned, but it is not treated as being the only effect. The consideration of the FLS model of Suni et al.[7] by the Walser group[49] neglects to treat the variation in the charged defect population associated with the Fermi level shift, which in turn results in an incorrect equation of the form of Eq. 2.25. Furthermore, the FLS model of Williams and Elliman[70, 71] had been published several years before the Walser group[49] claimed that Eq. 2.25 was representative of all FLS models. Yet, Williams and Elliman do not make any claims as to how the activation energy will change, as they only speak of velocity ratios, and the expression given for the velocity ratio (Eq. 2.35) by their model bears no resemblance to Eq. 2.25.

Lu et al.[11] have assumed that the functional form of Eq. 2.25 as provided by the Walser group[49] was an accurate representation of the FLS model from Suni et al.[7]. Based upon this, Lu et al. criticize the Suni FLS model since the derivation of Eq. 2.25 requires the implicit assumption that only the charged defects contribute to the SPE process, and that the neutral defects make no contribution regardless of concentration, which has no a priori justification. This assertion by Lu et al. arises from deriving the left hand side of Eq. 2.25 with Fermi-Dirac statistics instead of the simplistic approach detailed in Eq. 2.26. In particular, if the neutral defects play no role, and for example, if n-type material is considered, then the velocity ratio as per application of Eq. 2.24 and 2.22 will be simply

\[
\frac{V}{V_i} = \frac{C(N^-)}{C(N_i^-)} = \frac{N^x \exp\left(\frac{E_F - E^-}{kT}\right)}{N^x \exp\left(\frac{E_F - E_i^-}{kT}\right)} = \exp\left(\frac{E_F - E_i^F}{kT}\right) \tag{2.28}
\]

and for p-type material, the placement of \(E_F^p\) and \(E_i^p\) would be reversed, thus always resulting in a positive argument to the exponential. Removing the issue of ordering \(E_F^p\) and \(E_F^i\) by use of the absolute value of the difference results in the same expression as Eq. 2.26. However, the Suni FLS model does in fact include the contribution of neutral defects as per Eq. 2.24. In another paper[36] still published several years prior to the Walser group formulation, Suni explicitly states that “…in the presence of group III and IV impurities, the total vacancy concentration (neutral and charged vacancies) is enhanced due to shifts of the Fermi level.” Hence the criticism of Lu et al. should be taken against the mathematical interpretation provided by
the Walser group, and not against the Suni FLS model itself.

Lu et al.[11] also put the vacancy theory of Suni et al. in with the other bulk diffusion models. In particular, Lu et al. state that “Suni et al. adopted...and proposed that the rate-limiting step is the formation and migration of lattice vacancies to the c/a interface.” However, this does not appear to be evident from either of the two relevant papers from the Suni group. In the first paper from Suni et al.[16], it is stated that “For an interface between two different phases of a single element, no large scale transport is required and the recrystallization occurs primarily through a bond rearrangement at the interface.” Also in the same paper, while discussing SPE enhancements due to doping, Suni et al. state that “If the regrowth rate of the amorphous silicon is controlled by atomic diffusion at the amorphous-crystalline interface, it should be strongly dependent on the local doping level.” Furthermore, in the second of the papers from Suni et al.[7], they state that “…the rate is controlled by the formation of point defects at the amorphous-crystalline interface”. Similar wording regarding the Suni FLS model can also be found in two other papers[36,72] for which Suni is a co-author. Hence it is felt that this model should not be grouped with the other bulk diffusion models.

2.4.7 Bulk Defect Diffusion Models

Diffusion of Vacancies

Lu et al.[11] noted several key points against bulk diffusion models, and some additional ones specifically against the charged vacancy model from Suni et al.[7]. While it is felt that these arguments are not directly applicable to the model of Suni et al. since it does not explicitly require bulk diffusion, the arguments themselves are valid criticisms against any proposal requiring bulk diffusion, and hence are summarised here.

In general, any mechanism that involves generation of defects in the bulk and subsequent transport to the interface as the rate limiting step, would in turn require a complex and counter-intuitive bulk diffusion model to explain the fact that the SPE rates are observed to be essentially constant over depth ranges of several microns. In addition, tracer diffusion measurements in c-Ge, where diffusion is
only believed to occur by a vacancy mechanism, have revealed positive activation volumes, which is in contrast to the negative activation volume for SPE in Ge as measured by Lu et al.[8,11]. However, Mitha et al.[73] question whether the diffusion is completely controlled by vacancies, due to their recent result indicating a negative activation volume for As diffusion in Ge. To reconcile this result with vacancy mediated diffusion would require either the vacancy formation volume or the vacancy migration energy to be unrealistic. Lu et al.[11] also note that diffusion rates are substantially lower in relaxed amorphous material than they are in relaxed material, whereas relaxation does not have any significant effect on the SPE rate[11], which also tends to indicate that the defect which limits diffusion rates is not the same as that which limits SPE rates. If the defect which limits the SPE rate undergoes isotropic diffusion, then the origin of the orientation dependence is also unclear.

There are two points that could be taken to favour bulk models within certain constraints. The first is the measurement of the activation energy for diffusion of low concentrations of H in a-Si as performed by Roth et al.[21]. They found that the activation energy for diffusion was the same to within experimental error as that for the SPE process, and proposed that the diffusion takes place via H moving from one dangling bond to the next. From this, they suggest that the formation and migration energies of dangling bonds are the rate limiting step for both H diffusion and SPE. The second point giving bulk models plausibility is brought forward by Aziz[28] in which he shows that a rate limiting step associated with the bulk can be reconciled with the data, as long as it is taken in conjunction with an additional interfacial rate limiting step that is of comparable magnitude (i.e. of comparable activation energy), and thus the overall rate is determined by the two steps taken in series. Based upon this, Aziz shows that under certain circumstances, the activation energies of the two steps could be different by up to ~ 0.5 eV before the result differs significantly from the strict Arrhenius dependence experimentally observed in silicon[13]. As an example, Aziz considers the hydrogen data of Roth et al., in which it is possible that the migration energy of a dangling bond in the bulk differs from the migration energy along the interface by only a tenth of an eV or so.
Self-Interstitials

The model of Narayan[74] has diffusion of self-interstitials from the amorphous phase to the c/a interface as the rate limiting step for the SPE process. This results in the SPE rate being written in terms of the diffusivity of the self-interstitials from the amorphous phase to the c/a interface. Since it again relies on diffusion from the bulk to the interface, it can be ruled out based on the same arguments as listed previously.

However, Narayan also presents structural arguments to determine the geometry factor in his model that gives the SPE rate dependence on the substrate orientation. These structural arguments consist of determining the required bonding sequence of additional atoms for the three common orientations, (100), (110) and (111). Since the geometrical factor only describes the fraction of sites that are available for crystal growth, this part of the model can be taken independently of the diffusion portion of the model (which is used to predict absolute SPE rates) and it can then be used to predict velocity ratios for the different combinations of the three main orientations. The resulting velocity ratios as reported by Narayan seem to fit the experimental data reasonably well, and in addition it avoids the problem of predicting a zero growth rate for (111) material, which happens when a simple $sin(\theta)$ orientation dependence is used[15].

With respect to the orientation dependence, Custer[75] reported on a model that relates the substrate orientation to a difference in bond density between the a-Si and the c-Si. The difference in bond density was then correlated to the difficulty in breaking a bond across the interface and hence the SPE rate for that orientation. This model also fits the experimental data better than the $sin(\theta)$ model, but still predicts a zero growth rate for (111) material.

Charged Dangling Bonds

The Mosley group[76, 77] proposed a mechanism in which charged dangling bonds in the bulk amorphous material diffuse to the c/a interface, where they then stimulate atoms from the amorphous structure to adopt bonding configurations of the crystalline material. Dopant effects are explained in terms of charged dangling bonds (as opposed to the charged vacancies proposed by Suni et al.[7]) by assuming that the
electrons or holes are trapped on the dangling bond sites. A band bending argument, based on having the Fermi level at mid-gap in the amorphous material while at or near the conduction (n-type) or valence (p-type) band edge in the crystalline material, is used to establish the presence of an electric field at the c/a interface. This field is then responsible for attracting charged dangling bonds and thus enhancing the SPE rate over that of the undoped material.

The points made by Lu et al. [11] against bulk diffusion models mentioned previously also apply here. Furthermore, Lu et al. present additional arguments that indicate the rate enhancement predicted by this model is too small unless one is willing to accept unreasonably large values for the mean jump distance of a dangling bond.

2.4.8 The Kink-Site Model

In 1983, Williams and Elliman [53, 70, 71] reported on a model which combines structural aspects based upon that of Spaepen [56–58] with electronic effects needed to explain dopant enhancement and dopant compensation. The structural aspect consists of specifying the actual sites at the c/a interface where crystallization is expected to occur. The proposed sites are ‘kink’ sites on [110] ledges between {111} terraces, as shown schematically in Fig. 2.5.

In this figure, the kinks BB1 are on the [110] ledges shown between {111} terraces. The c/a interface is shown as the solid line joining the lower atoms on the terraces. The direction of interface motion during SPE is shown by the smaller arrows. Note that the lines between the atoms are only as a guide to the eye, and not an indication of actual bonds. With respect to the upper terrace, reordering takes place at the two kink sites, which then move towards each other along the ledge as indicated by the arrows showing kink motion, until the extending ledge is incorporated into the crystalline material. The concept of an immobile kink that has been pinned by an impurity atom is also shown.

The kink site is chosen as the preferred rearrangement site, since at that location, two of the four bonds would then be with other crystalline atoms, whereas other sites on the ledge, in the absence of a kink, only present one. More importantly
Figure 2.5: A schematic representation of kink sites at a (100) $c/a$ interface. Kinks $BB'$ propagate along [110] ledges $AA'$ which lie between $\{111\}$ terraces to facilitate SPE. The possibility of an immobile kink that has been pinned by an impurity atom is also shown. The lines between the atoms on the ledges are a guide to the eye only, and should not be interpreted as the actual bonding configuration. Crystalline material is on the upper half of the figure, with amorphous material on the lower half. The (100) $c/a$ interface propagates in the direction indicated by the smaller arrows during SPE. (From Williams[2].)
however, the kink site is used as a basis upon which the electrical aspect of the model can be presented. The electronic aspect of this model is based on a similar model for dislocations proposed by Hirsch [78]. Hirsch introduced a theory based on charged kinks to explain the fact that electrically active impurities alter dislocation velocities in Si and Ge. The dislocation velocity changes that resulted from doping were explained in terms of an altered charged kink concentration and the possibility of a different kink mobility with respect to their neutral counterparts. In the Hirsch treatment, the charged kinks have energy levels within the gap, and the charged kink concentration is given via Fermi-Dirac statistics.

Williams and Elliman [70] follow this development, by noting that the bond breaking mechanism required for SPE is expected to be quite similar to that which occurs during dislocation motion. The SPE rate is written as being proportional to the number of kink sites, which is the sum of both neutral and charged kinks, both being considered equally effective at facilitating a crystallization event. (In the context of the dislocation analogy, this is equivalent to assigning equal mobilities to both charged and neutral kinks.) Thus the SPE rates in the doped material and the intrinsic material are written as

$$ v = A(C_o + C_n) = AC_o(1 + C_n/C_o) \quad (2.29) $$

$$ v_i = A(C_o + C_i) = AC_o(1 + C_i/C_o) \quad (2.30) $$

where $C_o$ is the concentration of neutral kink sites, assumed to be independent of doping, $C_n$ and $C_i$ are the concentration of charged kink sites in the doped and intrinsic material respectively, and $A$ is a constant. The ratio of charged kink sites to neutral kink sites for both intrinsic and doped material are given by Fermi-Dirac statistics as was done by Hirsch, and is thus given (for $n$-type material) by

$$ \frac{C_n}{C_o} = g \exp \left( \frac{E_f - E_k}{kT} \right) \quad (2.31) $$

where $E_k$ is the donor level introduced by the charged kink, and $g$ is the degeneracy of the level. Note the similarity between these three equations and those used by Suni et al. [7] for the vacancy model as detailed in Section 2.4.6. For the intrinsic case, the ratio $C_i/C_o$ is given by the same expression but with $E_f$ being replaced with $E_{fi}$, the intrinsic Fermi level.
At this point, Williams and Elliman use the expression for the Fermi level in an extrinsic nondegenerate semiconductor to eliminate $E_f$ from Eq. 2.31. However, as will be seen later, it is useful to explicitly write the expression for the velocity ratio prior to making the substitution for $E_f$. Substituting Eq. 2.31 into the ratio of 2.29 and 2.30 results in
\[
\frac{v}{v_i} = \frac{1 + g \exp \left( \frac{E_f - E_k}{kT} \right)}{1 + g \exp \left( \frac{E_f - E_k}{kT} \right)}
\]
with $E_{fi}$ being the Fermi level of the intrinsic material. This allows later considerations of this model without being constrained to nondegenerate material which is implicit upon the application of Eq. 2.16 to eliminate $E_f$.

Now, continuing with the elimination of $E_f$ in Eq. 2.31 by using the expression for the Fermi level in an extrinsic nondegenerate semiconductor (Eq. 2.16), then
\[
\frac{C_n}{C_o} = g \exp \left[ \frac{E_c - kT \ln \left( \frac{N_d}{N_c} \right) - E_k}{kT} \right] = \left( \frac{N_d}{N_c} \right) g \exp \left[ \frac{E_c - E_k}{kT} \right]
\]
where the concentration of donors ($N_d$) has been substituted for $N_e$ in Eq. 2.16 by assuming that full donor ionization takes place. It is important to keep this assumption in mind in light of the behaviour of the fractional ionization level as discussed in section 2.4.5. Substituting this result into Eq. 2.29 gives the following expression for the SPE rate as a function of doping level and temperature:
\[
v = AC_o \left\{ 1 + g \left( \frac{N_d}{N_c} \right) \exp \left( \frac{E_g - E_k}{kT} \right) \right\}
\]
where $N_c$ is the effective density of states in the conduction band, and $E_g$ is the energy gap, which is equal to $E_c$ when the valence band edge is referenced to zero. By using this expression, the ratio of the doped SPE rate to intrinsic SPE becomes
\[
\frac{v}{v_i} = \frac{1 + g \left( \frac{N_d}{N_c} \right) \exp \left( \frac{E_g - E_k}{kT} \right)}{1 + g \exp \left( \frac{E_g - E_k}{kT} \right)}
\]
For $N_d$ and $T$ values of interest and with plausible values for $E_k$, the second term in the numerator will be $\gg 1$, and hence Eq. 2.35 can be written in the form of
\[
\frac{v}{v_i} = N_d \cdot \mathcal{F}(T)
\]
\[\text{\textsuperscript{1}Williams and Elliman chose instead to write it as } \ln \left( \frac{v}{v_i} \right) = \ln N_d + \text{constant}\]
where \( F(T) \) is some function of temperature, and does not depend on \( N_d \). The function \( F(T) \) can even be taken to include implicit temperature dependencies such as the band gap shrinkage with increasing temperature. So the net result is a predicted linear increase in the SPE rate with increasing dopant concentration. A similar treatment for p-type material leads to a similar result.

Elliman \textit{et al.}[71] noted that this mathematical treatment uses properties of the band structure of the crystalline material and hence does not account for the expected band bending that occurs at the interface due to the pinning of the Fermi level at mid-gap on the a-Si side of the c/a interface. In addition, they noted the difficulty associated with providing experimental evidence of the existence and the magnitude of the kink related energy levels. In light of this they postulated that further measurements of SPE enhancement under conditions of external stress or external bombardment with electrons or ions could prove useful.

Lu \textit{et al.}[11] note that for kink motion to occur, bond rearrangement must take place, and this will most likely occur by the breaking of bonds spanning the c/a interface, local rearrangement and then recombination of the dangling bonds. In light of this they consider the kink site model to be a special case of the dangling bond model (section 2.4.4) for which the dangling bonds are annihilated locally and quickly, rather than taking a large number \( (n_r) \) of jumps prior to annihilation. As for the electronic aspects of the model, Lu \textit{et al.} found enough merit in it to rework it in more detail, while noting that the model requires a defect state in the band gap, and that this could just as easily be due to a dangling bond as opposed to a kink. Their reanalysis of the electronic portion of the model results in the Generalized Fermi Level Shifting (GFLS) model which is discussed in section 2.4.11.

2.4.9 The Fractional Ionization Model

As mentioned earlier, in section 2.3.5, the Walser group[49] found that the velocity enhancement of the SPE rate in extrinsic material as compared to the intrinsic rate could be written as

\[
\frac{v}{v_i} = 1 + \frac{N_d}{N_i}
\]

\[
N_i = N_o \exp(-E_o/kT)
\]
with $N_d$ being the implanted concentration, and where $N_o$ and $E_o$ were determined from fitting Eqn. 2.37 to the experimental data. The expression was found to be valid for $N_d$ up to low $10^{19}$/cm$^3$ concentrations, with $N_o \sim 10^{21}$/cm$^3$ and $E_o \sim 0.3$ eV for boron, phosphorous and arsenic doped silicon[12,24,25,49].

The Walser group[12] then reported on a model designed to predict this type of behaviour. The model is based upon the assumption that there are charged defects in addition to the neutral defects that control the intrinsic SPE behaviour. The defects are presumed to be dangling bonds as per the Spaepen and Turnbull model[57,58] described in section 2.4.2, and the model involves a consideration of how the dangling bond density is expected to change with doping. The charged dangling bonds have an activation energy that is $E_o$ lower than that of the neutral dangling bonds, and it is the band structure of the amorphous phase which controls the overall concentration of these dangling bonds. Since the Fermi level is assumed to be pinned at mid-gap in the amorphous phase, Fermi level shifting does not enter into the picture. The model of Bourgoin and Germain[79] in which electron-hole recombination at the $c/a$ interface induces a structural change based upon the change in charge state is cited as the basis for the enhanced mobility of the charged defects.

However there is some confusion over the exact specifics of the model, since the paper that was to disclose the full details of the model, as cited in other papers by the Walser group[24,25] appears to have never been published. A clue to what happened is given by Lu et al.[11, p. 5340] who note that there was an error in their original derivation of the model which results in a $N_d^{1/2}$ dependence, rather than the reported $N_d$ dependence, and apparently the Walser group acknowledged the error via private communication. The $N_d^{1/2}$ dependence as cited by Lu et al. comes from the result of Street[80] who reported that the dangling bond density scaled as the square root of the gas phase doping concentration in a-Si:H. An additional result from Street’s work that Lu et al. did not note was the relation between the gas phase doping concentration and the resulting dopant concentration in the a-Si layer that was grown. In the case of phosphorous, Street reported a linear relation between the two, and hence the objection by Lu et al. is still valid. Yet for arsenic doping,
the concentration in the resulting a-Si layer scaled as the the square root of the gas phase doping concentration, and so the two powers of one half cancel each other out, leaving the original \( N_d \) dependence for the dangling bond density as required by the Walser group’s formulation.

Nevertheless, the concentration of charged reconstruction sites as per the Walser group theory is simply taken as the product of the fractional ionization \((\alpha)\) of that impurity in a-Si and the total concentration of implanted impurities. It is assumed for low doping levels that both the fractional ionization \((\alpha)\) and the number of neutral defects \((N_N)\) will remain independent of the doping concentration \((N_D)\). From this, the Walser group write the SPE enhancement ratio as

\[
\frac{v}{v_i} = 1 + \frac{\alpha N_D}{N_N} \exp(E_o)
\]  

(2.39)

By comparing this equation with the empirically determined behaviour (Eq. 2.37) one can immediately identify the experimentally determined quantities with those predicted by the model. The \( N_o \) value is associated with the ratio of the concentration of neutral dangling bonds \(([D^0])\) to the fraction of ionized dopants \((\alpha)\) in the amorphous material.

In their discussion of the Walser model, Lu et al.[11] noted that in the silicon case, a direct correlation could be made between \([D^0]\) and values for the unpaired electron density obtained from ESR measurements, and they determined that a value of \(\alpha \approx 0.4\%\) was required to fit the SPE data. They noted that this value was reasonable given the estimated value of 0.2\% to 1.0\% based upon photoconductivity measurements. However, Lu et al. went on to point out that the basic assumption that the fractional ionization is independent of the doping concentration has no prior justification, and it goes against the law of mass action as well. From this they noted that without the law of mass action, it was difficult for the model to explain the impurity compensation effect observed in SPE rates.

The boron and phosphorous doped compensation sample used by the Walser group[23] exhibited the intrinsic rate at an offset from the point at which the B and P concentrations were expected to be equal. In the context of their model, they then assumed that the fractional ionization of the boron was equal to that of the phosphorous \((\alpha_B = \alpha_P)\) at the depth where the SPE rate was equal to the
intrinsic rate.

The Walser group\cite{22} also found that Al retarded the SPE rate for concentrations up to $\sim 2 \times 10^{19}$ /cm$^3$, and then enhancement took over for higher concentrations. In a similar fashion to the compensation treatment, they assume that the minimum SPE rate corresponds to complete compensation for which there are essentially no charged dangling bonds. By assuming that the fractional ionization would be on the order of $\sim 0.01$ or less, they expect that there would be on the order of $10^{17}$/cm$^3$ positively charged dangling bonds resulting from the implanted Al. In light of this, Walser et al.\cite{22} introduce a rather ad hoc pre-existing concentration of $10^{17}$/cm$^3$ negatively charged dangling bonds present in the intrinsic material. In this way SPE rate reduction is observed up until the intrinsic concentration of negatively charged dangling bonds is fully compensated by the addition of p-type impurities. This, of course, begs the question as to why they did not observe the same effect in their boron implanted samples\cite{49}.

2.4.10 Lattice Softening Models

The Electronic Excitation Model

Wautelet et al.\cite{81, 82} proposed a very general theory based upon local electronic excitation, either induced by laser light or by doping. The general idea comes from associating filled valence orbitals with bonding states, and electrons in the conduction band with antibonding sites. Thus the hole resulting from an electron excited up into the conduction band represents a local ‘softening’ of the lattice due to the missing bond. The energy of formation of other states is then assumed to decrease linearly with the reduction in local bonds, which is reflected in an increase in the local electronic concentration. They use this theory to attempt to explain a wide range of processes, including oxidation, defect migration, and SPE.

In the case of SPE, Wautelet discusses the treatment in slightly more detail in a separate paper\cite{83} with a consideration of doping. The SPE rate of extrinsic material is written as the sum of two Arrhenius terms, one describing the portion effected by ionized impurities, and the other applying the intrinsic behaviour to the portion for which the impurities are not ionized. The activation energy of the
Arrhenius term associated with the ionized dopants will be less than that of the intrinsic term based upon this lattice softening argument.

The model is further developed by writing a velocity ratio in terms of this description, and then the number of ionized donors is replaced with a classical \( \exp(-E_d/kT) \) expression, which allows the velocity ratio to eventually be written in the form of Eq. 2.37. Furthermore, the author claims that the model explains why the dopant activation energy term in Eq. 2.38 is not equal to the Fermi level shift, simply because \( E_f \) does not appear in the expression for the velocity ratio as predicted by the model.

Herein lies the fundamental problem with the treatment of this model as presented by Wautelet. The number of ionized donors is not correctly described by such a classical expression, as detailed in section 2.4.5. The correct expression (Eq. 2.18) relies on the location of the introduced dopant level \( E_d \) with respect to the Fermi level, and once this is put in place, the model no longer immediately reduces to a form like that of Eq. 2.38, nor is it independent of the Fermi level, or any shifting of it caused by doping. A further problem of the electronic excitation model is the lack of a photoionization effect on the SPE rate as determined by the Walser group[84]. They found that the SPE rate increase that was observed while samples were under continuous laser irradiation was within the expected increase associated with the temperature rise due to laser heating.

The Bond Strength Reduction Model

Park[85] recently reported a qualitative model for dopant-enhanced SPE that also employs a similar argument to that used by Wautelet[83]. It is based upon the reduction of the strength of bonds across the interface, due to the presence of carriers. As a dopant atom is incorporated into the crystalline material, it goes from being fully coordinated and electrically inactive, to having tetrahedral bonds and a resulting carrier that is lightly bound. Park notes that the wavefunction of the bound carrier extends up to 30 Å, and so dopant atoms in the crystalline phase that are within this distance to the c/a interface can have their respective carrier in the amorphous phase. The difference in the Fermi levels of the amorphous and the
crystalline phase is given as a reason for these carriers to reside at the c/a interface, and hence reduce the strength of the bonds across the interface that need to be broken for SPE to occur. Compensation is then explained by not having any excess carriers present at the c/a interface.

Park also notes that the presence of the carriers at the interface predicted by the model may also play a role in the rearrangement process once a dangling bond has been formed, but has yet to present a quantitative mathematical treatment of this or of what SPE enhancements that the model would predict. However, the reason for considering the carriers as bound is unclear when one considers that most of the dopant atoms are expected to be ionized during SPE as per the fractional ionization treatment in section 2.4.5. In addition, the band bending that takes place across the interface should also enhance the fractional ionization near the interface as compared to the bulk crystalline value.

2.4.11 The Generalized Fermi Level Shifting Model

As mentioned in section 2.4.8, Lu et al. [11] reconsidered the Fermi level shifting description provided by Williams and Elliman [70, 71]. In Appendix A of the paper by Lu et al. [11], they develop what they call the Generalized Fermi Level Shifting Model. The basic premise for this model is that the SPE process is controlled by some unspecified interfacial defect, and its charged counterpart. They treat the negative defect case, with the positive charge state defect case being a reasonably straightforward extension. For simplicity, they assume that both the neutral and the charged defect have equal probabilities or efficiencies for causing SPE events at the interface and then later describe the effect on the resultant expression when non-equal mobilities are considered. The derivation closely follows that detailed in section 2.4.8, with the SPE rate being written as

\[ v = C ([D^0] + [D^-]) \]  

(2.40)

where C is some constant, and the other terms are the respective concentrations of the neutral and negatively charged defects. They then assign a functional form to both \([D^0]\) and \([D^-]\) and write an expression for the ratio of the doped to undoped SPE rates in the same fashion as was done by Williams and Elliman (section 2.4.8).
2.4. MODELS OF THE SPE PROCESS

This results in an expression[11, eqn. A6] identical to that derived in Eq. 2.32. However, it is at this point that the two treatments diverge. The difference in the two arises in the method used to eliminate the Fermi level of the doped material from the expression for the charged defect concentration (as given by Eq. 2.31), and thus the velocity ratio as well.

Instead of using Eq. 2.16 to eliminate $E_f$ as Williams and Elliman did, Lu et al. used a different approach, stating that they had used charge neutrality and the law of mass action for a nondegenerate semiconductor (Eq. 2.15) to get an expression for $E_f$, so that it could be eliminated from Eq. 2.32. However, there is an implicit assumption in their expression[11, eqn. A7] derived from charge neutrality that is not immediately obvious, unless one looks into what it is based on. Consider an n-type semiconductor with a concentration of $N_d$ donor atoms, for which some portion of those will be ionized, giving an ionized donor concentration of $N_d^+$. Electrical neutrality for this system requires that the net positive charge is equal to the net negative charge (i.e. $N_d^+ + N_h = N_e$). Following the methodology of Kittel and Kroemer[26], the law of mass action allows the elimination of $N_h$ from this expression, since it states that $N_e N_h = N_d^+$, which results in the following quadratic equation in $N_e$:

$$N_e^2 - N_d^+ N_e - N_i^2 = 0 \quad (2.41)$$

that has the following roots:

$$N_e = \frac{N_d^+}{2} \pm \sqrt{\left(\frac{N_d^+}{2}\right)^2 + 4N_i^2} = \frac{N_d^+}{2} + \left[\left(\frac{N_d^+}{2}\right)^2 + N_i^2\right]^{1/2} \quad (2.42)$$

where the positive root is taken in the final expression, since $N_e > 0$. Equation 2.13 can now be used to eliminate both $N_e$ and $N_i$ by noting that $N_e$ evaluated at $E = E_{Fi}$ is equal to $N_i$. When this is done one obtains

$$N_e \exp\left(\frac{E_f - E_c}{kT}\right) = \frac{N_d^+}{2} + \left[\left(\frac{N_d^+}{2}\right)^2 + \left\{N_e \exp\left(\frac{E_{Fi} - E_c}{kT}\right)\right\}^2\right]^{1/2} \quad (2.43)$$

which is the result derived from applying the neutrality condition in the same form as Lu et al. have written it[11, eqn. A7]. Herein lies the implicit assumption. In this development, the term $N_d^+$ has been used to make it clear that it is the ionized donor concentration that appears in the final expression. In the treatment by Lu et al.
the parameter appears as $N_d$ and it is listed as the concentration of donor dopant atoms, meaning that it is implicitly assumed that all the donors are ionized at the temperatures and doping levels used during the SPE measurements. This is a common assumption that is made for low to moderate doping levels and relatively elevated temperatures\[65\]. However, being aware that this assumption is implicitly present in the GFLS model will become important in the discussion that follows later in this work.

The use of this result to eliminate $E_f$ in the general velocity ratio equation (2.32) is best done by first dividing the neutrality condition by $N_c$ and then eliminating the $(E_f - E_k)/kT$ term in the numerator of the velocity ratio by making the following identification:

$$e^{\frac{E_f - E_k}{kT}} = e^{\frac{E_f - E_k + E_c - E_c}{kT}} = e^{\frac{E_c - E_k}{kT}} e^{\frac{E_f - E_c}{kT}}$$

where the use of $E_k$ has been maintained to indicate the energy level associated with the defect, even though it can be an unspecified defect instead of the kink site dealt with in section 2.4.8. By substituting the neutrality expression (2.43) into the left hand side of the above, and then putting the resulting expression back into the velocity ratio (2.32) then:

$$\frac{v}{v_i} = \frac{1 + g e^{\frac{E_f - E_k}{kT}} \left\{ \frac{N_d^+}{2N_c} + \sqrt{\frac{N_d^+}{2N_c}}^2 + \left[ e^{\frac{E_f - E_c}{kT}} \right]^2 \right\}}{1 + g e^{\frac{E_f - E_k}{kT}}}$$

Lu et al. make some simplifying approximations to this expression for the doping levels and temperatures of interest which appear to be based upon the following arguments. Since the intrinsic Fermi level is essentially mid-gap, the second term in the square root can be replaced with $e^{\exp(-E_0/kT)}$, which from Fig. 2.2 will be $\sim 10^{-5}$ for Si at 660 °C, whereas from Fig. 2.3 the first term will be on the order of 0.1 to 1 for typical doping levels and temperatures, and hence the second term can be neglected. Similarly, if $E_k$ is not a deep level, then a similar argument holds for the energy term in the exponential of the denominator. For example, with $E_k = 0.8E_g$, the exponential is $\sim 0.03$ at 660 °C. With these approximations
In place, the result collapses into the more manageable form, given by

\[
\frac{v}{v_i} \simeq 1 + g \frac{N_d^+}{N_c} e^{\left(\frac{E_c - E_k}{kT}\right)} = 1 + \frac{N_d^+}{N_c} e^{\left(\frac{E_k - E_c}{kT}\right)}
\]

which appears to be of the same form as the experimentally observed behaviour documented by the Walser group, but it is important to note that there is an implicit temperature dependence in Eqn. 2.46 due to the \(T^{3/2}\) that appears in the expression for \(N_c\) (Eq. 2.11) and an undetermined temperature dependence in the energy term of the exponential.

In comparing this to the experimental arsenic data from the Walser group[25], Lu et al. left \(N_c\) as a free parameter, and then considered the various ways in which the controlling defect could follow the band gap edges as a function of temperature, to see which defect behaviour was best able to match the actual value of \(N_c\) for c-Si as shown in Fig. 2.3. There are three plausible ways to describe the defect behaviour in the band gap: (1) the defect level remains at a constant energy from the valence band edge \(([E_k - E_v] = \text{constant})\), or (2) the defect level remains at a constant energy from the conduction band edge, \(([E_c - E_k] = \text{constant})\), or (3) the defect remains at some constant fraction of the band gap \(([E_k - E_v]/E_g = \text{constant})\). Lu et al. solved for the energy term and \(N_c\) as a ratio \((R)\) to the actual value as per Eq. 2.11 for all three cases, while including a \(T^{3/2}\) term and the temperature dependence of the band gap as per Eq. 2.9. From this they found the following: (1) leads to \([E_k - E_v] = 1.03\ \text{eV}\) and \(R = 0.13\), (2) leads to \([E_c - E_k] = 0.23\ \text{eV}\) and \(R = 5\), and finally (3) leads to \([E_k - E_v]/E_g = 0.82\) with \(R = 2.3\). Ideally, the model should be compared to the raw data, rather than to the parameters reported by Walser et al. since at that point, the data has already been represented by a strict Arrhenius form as per Eq. 2.38, whereas the prediction of the model is not strictly Arrhenius due to the two implicit temperature dependencies mentioned earlier. However, based upon this treatment the model can match the experimental value of \(N_o\) in Eq. 2.38 to within a factor of two.

In the case of unequal mobilities between charged and neutral defects, the ratio of the mobility prefactors and the difference between their migration energies appears in Eq. 2.46. This allows the value of \(N_c\) to be matched exactly, but as Lu et al. point out, this isn’t of great value, since then there are too many free parameters and thus
their values cannot be independently solved for based upon the experimental data.

Another interesting point is that the pressure dependence of the band gap is of different sign for Si and Ge[65], yet the SPE rates of both are enhanced by pressure[8, 48]. However, the magnitude of the effect is reasonably small, with \( \frac{dE_g}{dP} \approx 2 \times 10^{-2} \text{ eV/GPa} \) for Si[3], and thus it is reasonable to expect that the SPE behaviour with respect to pressure is dominated by how the controlling defect responds to pressure.

### 2.4.12 Model Summary

The dangling bond model in the form presented by Lu et al.[11] in section 2.4.4 gives reasonable qualitative predictions for the general properties of SPE in intrinsic material. However, it does suffer from predicting a zero SPE rate for (111) orientation material, although one way to overcome this would be to try to adapt a functional form to the orientation dependence as described by Narayan in section 2.4.7. Helman[10] does not think that the theoretical prediction of a zero growth rate is a problem, since he expects that “the intrinsic non-flatness of the amorphous-crystal interface... provide an intrinsic number of ledges, even at the (111) orientation”.

It is clear that modeling of dopant effects on the SPE rate must rely on electronic effects to explain the observed compensation effects. Yet, it is unclear as to whether it is the properties of the crystalline material or the amorphous material that control the process. Fermi level treatments of the bulk crystalline material can semi-quantitatively account for the observed behaviour, but the behaviour of the band gap with respect to the Fermi level precisely at the interface is in question. Models such as the fractional ionization model are more difficult to comment on since they rely on properties of the amorphous phase, which are presently not as well understood as the crystalline phase. This in turn makes formulating qualitative predictions based on the fractional ionization model considerably difficult.


2.5. SPE STUDIES OF SILICON-GERMANIUM ALLOYS

2.5 SPE Studies of Silicon-Germanium Alloys

The studies of solid phase epitaxial regrowth in $\text{Si}_x\text{Ge}_{1-x}$ alloys have not played a significant role in shaping the SPE models discussed previously since nearly all the $\text{Si}_x\text{Ge}_{1-x}$ SPE studies have taken place after 1990. Those measurements that were performed before this time were typically based on strained layers, and the effect of strain on the SPE rate is a sufficiently complex problem in itself to warrant a separate treatment[28,29].

2.5.1 Strained vs. Unstrained Layers

Pai et al.[36] were one of the first groups to consider SPE in $\text{Si}_x\text{Ge}_{1-x}$ alloys, and they also considered the issue of strain. In particular they used co-doping with up to 0.34 at. % boron to compensate for the strain in CVD grown $\text{Si}_x\text{Ge}_{1-x}$ alloys. However, the introduction of boron causes an enhancement in the SPE rate, and hence the intrinsic rate associated with a strain-free intrinsic alloy of the same composition is unknown. In particular, they measured the SPE rates in boron doped $\text{Si}_x\text{Ge}_{1-x}$ alloys containing between one and four atomic percent germanium, and their data tends to indicate that the SPE rate was dominated by the boron concentration and was essentially independent of the Ge concentration within this regime.

In 1992, Hong et al.[37] studied SPE in 3500 Å thick MBE grown $\text{Si}_x\text{Ge}_{1-x}$ layers on (100) Si with a Ge content between four and twelve percent. The layers were grown at 550 °C, and thus some of the samples were then annealed at 950 °C to relax the strain created during growth. The amorphization conditions were chosen such that there would be at least 1000 Å of crystalline alloy material remaining, and hence the strain would not be grown back in for the relaxed samples. A silicon wafer was similarly amorphized to act as a reference point for the SPE rates. For alloy samples with 10 at. % Ge they found that the SPE rate was 20% greater than Si for the relaxed samples and 20% less than Si for the strained samples. Furthermore, the strained samples only exhibited about 300 Å of quality regrowth before large quantities of threading dislocations started to form. Their work clearly demonstrated the need for measurements in relaxed alloy samples.
2.5.2 Buffered Layer Measurements

Shiryaev et al. [38] recognized this requirement, and in 1993 measured the SPE rates in MBE grown \( \text{Si}_x\text{Ge}_{1-x} \) alloy samples with 25 at. % Ge between 471 °C and 506 °C. Rather than use a heat treatment as employed by Hong et al. [37] to obtain a stress free layer, Shiryaev et al. used buffer layers in which the Ge content was linearly increased from near zero to the desired Ge content over several microns of material. The final alloy layer was then grown on top of this buffer layer to a thickness of 2 \( \mu \text{m} \). Implantation of germanium was then used to create an amorphous layer approximately 3400 Å thick in the alloy layer. To verify that the layers were indeed strain free, a sample was also given a heat treatment at 1050 °C prior to amorphization, and no difference in the SPE rate was observed when compared to the as-grown samples. From their measurements, they reported an activation energy of 2.76 ± 0.15 eV and a velocity prefactor of \( 6.7 \times 10^7 \) m/s, noting that only the prefactor differed significantly from the values associated with a pure Si sample. In the context of the kinetic model by Lu et al. [11] described in section 2.4.4, they took this as evidence that the addition of Ge only changes the number of atoms placed into the crystalline phase per dangling bond event, without altering the kinetics of interfacial bond breaking.

Kringhøj and Elliman [39] were the next to investigate SPE in strain-free \( \text{Si}_x\text{Ge}_{1-x} \) alloys. In 1994 they measured the SPE rates for six different alloys of varying composition that were grown on buffer layers with the germanium content ranging from 11 at. % to 53 at. %. In a similar fashion to Shiryaev et al. [38], some samples were given a high temperature anneal prior to amorphization, and these samples exhibited SPE rates identical to the as-grown material, indicating that the measured SPE rate was free from strain effects. For the alloys with between 11 at. % and 31 at. % they found that the activation energy was higher than the value they measured for pure Si. This was an unexpected result, since a priori one would expect that the activation energy would monotonically decrease towards the pure Ge value for increasing Ge content. Based upon this, they concluded that the activation energy increase was due to an increase in the migration energy of the defect that controls SPE.
2.5.3 Thick Layer Measurements

The most recent measurement of SPE rates in unstrained Si$_x$Ge$_{1-x}$ alloys was performed by Haynes et al.[40] in 1995. To obtain strain-free layers, they grew very thick (6-8 µm) alloy layers with CVD. Cross-sectional transmission electron microscopy (XTEM) was used to verify that relaxation was accommodated by a large density of threading dislocations near the silicon-Si$_x$Ge$_{1-x}$ alloy interface. In total, eight different alloy compositions were studied, ranging from 2 at. % Ge to 87 at. % Ge. They also found that the activation energy for alloys containing between 2 at. % Ge and 34 at. % Ge was higher than that of pure Si, with the difference being slightly larger than that reported by Kringhøj and Elliman[39].
2.6 SPE Studies Performed by TRR

The development of the Time Resolved Reflectivity (TRR) technique has enabled the real time measurement of SPE rates with an accuracy that was previously unobtainable. Widespread acceptance of the technique as a viable method is generally attributed to the detailed description of the process given by Olson and Roth[13] in 1988, although Olson et al. had previously described the process[41] in 1980 in a letter documenting SPE measurements during cw-laser annealing of a-Si.

The TRR technique in its most basic form is simply an application of a thin film interference. It involves the interference of monochromatic light reflected from a thin film on a semi-infinite substrate, which is essentially an undergraduate level physics problem. In this case, the thin film is the amorphous layer, and the semi-infinite substrate is the underlying crystalline material. A simplified schematic of a TRR system is shown in Fig. 2.6.

In this figure, a laser is directed at the sample surface, with the light reflected from the sample being measured by the detector and subsequently logged as a function of time on some sort of recording device. The incident beam marked as (a) undergoes partial reflection and partial transmission at the ambient/sample interface to create (b) and (c) respectively. The transmitted beam (c) then gets split in a similar fashion at the c/a interface due to the difference in the optical parameters of a-Si and c-Si. The transmitted portion (d) continues on into the semi-infinite bulk c-Si, while the reflected portion (e) traverses back out of the a-Si layer. At this point the two reflected beams (b) and (e) will undergo interference and the resulting beam is measured by the detector. The interference will be constructive or destructive, depending on the thickness of the amorphous layer, indicated as $\Delta x$. When the sample is heated and SPE takes place, the thickness of the amorphous layer decreases, causing a change in magnitude of the overall reflected beam as seen by the detector. For a sufficiently thick layer, oscillations are logged on the recording device as $\Delta x$ passes through values associated with successive interference maxima and minima.

So, in essence, the TRR apparatus shown in Fig. 2.6 records the reflectivity of the sample as a function of time while SPE takes place. The mathematical treatment
Figure 2.6: Simple schematic of a TRR system used to measure SPE rates. Incident beam (a) is partially reflected (b) at the surface of the sample, and partially transmitted (c) into the amorphous layer. The optical properties of c-Si and a-Si are sufficiently different to cause the c/a interface to appear as an optical interface to (c) which is then partially transmitted (d) into the c-Si and partially reflected (e) back out of the amorphous layer. Beams (b) and (e) exhibit constructive or destructive interference, depending on the amorphous layer thickness ($\Delta x$). When SPE takes place, $\Delta x$ decreases as the c/a interface moves in the direction of the arrow, and the detector observes oscillations in signal amplitude associated with the interference maxima and minima.
of the problem as detailed below gives the expected reflectivity as a function of \( c/a \) interface depth. The combination of the two and subsequent elimination of the reflectivity as the common variable leaves one with a data set describing the interface depth as a function of time. The SPE rate at any given depth is then obtained by simply taking the derivative of the resulting curve.

### 2.6.1 Expression for the Reflectivity

For the purpose of simplicity, Fig. 2.6 and the above description only indicate one ray emerging from the a-Si layer, whereas in fact there will be an infinite number of internal reflections in the amorphous layer, with each one transmitting some portion of its energy into the bulk and out into the ambient respectively. In terms of the diagram of Fig. 2.6, the internal reflection indicated by ray (f) will undergo the same division as for ray (c), which will then continue to create even more internal reflections. The amount that is reflected and the amount that is transmitted at each interface is dictated by the Fresnel reflection and transmission coefficients for each interface, the phase change incurred upon traversal of the layer, and the amount of absorption per traversal of the layer. All of these in turn rely on the complex index of refraction \( N \) for each layer, which is broken down into real and imaginary parts as

\[
N = n - ik
\]

with \( n \) being the index of refraction and \( k \) being the extinction coefficient. Since nearly all TRR measurements are performed at or near normal incidence, it is worthwhile to limit the treatment to normal incidence. The phase change for crossing a layer of thickness \( \Delta x \) with complex index \( N \) at normal incidence is given by

\[
\beta = 2\pi N \left( \frac{\Delta x}{\lambda} \right)
\]

where \( \lambda \) is the free space wavelength of the laser being used in the TRR measurement. The Fresnel reflection coefficients are usually denoted as \( r_{ij} \) for the interface between the \( i \)th and \( j \)th layer. For normal incidence, they are given by

\[
r_{ij} = \frac{N_j - N_i}{N_j + N_i}
\]
With these, the complex reflectivity can be written as an infinite series corresponding to the infinite reflections documented above, for which the sum is given by\[86\]

$$R = \frac{r_{01} + r_{12} e^{-i2\beta}}{1 + r_{01}r_{12} e^{-i2\beta}}$$  \hspace{1cm} (2.50)

The reflectivity that is being monitored by a TRR system is the magnitude of this expression, and is given by

$$\mathcal{R} = RR^* = |R|^2$$  \hspace{1cm} (2.51)

This expression permits the calculation of the reflectivity of a sample as a function of depth, as long as the index of refraction of both the crystalline material and the amorphous material are known. Alternative treatments of the problem of reflection from a thin film on a substrate, or the more general case of multiple thin films on a substrate are also documented in many other standard texts\[87, 88\].

It is possible to get an idea of how the expected result should look without having to plot the above. For a sufficiently thick film, the reflections from the \(c/a\) interface will have suffered strong absorption from traversing the amorphous layer, and thus the interference term will be negligible. Hence the measured reflectivity will be dominated by the initial surface reflection, which is equivalent to measuring the reflectivity of an infinitely thick amorphous layer (\(\mathcal{R}_a\)). As the \(c/a\) interface moves towards the surface, the amount of absorption will decrease, causing the interference term to become more significant with respect to the initial surface reflection, which will then be observed as sinusoidal oscillations about the \(\mathcal{R}_a\) baseline value. These oscillations will increase in magnitude as the absorption of the interference term continues to decrease. As the interface nears the surface, the absorption of the interference term will tend to zero, and so the maximum amplitude of the oscillations will simply be proportional to the difference between the reflectivities of the crystalline (\(\mathcal{R}_c\)) and the amorphous material. Finally, upon completion of the process, when the \(c/a\) interface reaches the surface of the sample, all that remains is a bulk crystalline sample, and therefore the reflectivity must finish up at \(\mathcal{R}_c\). Olson and Roth\[13\] give an approximation to Eq. 2.51, valid for \(\Delta x > \lambda/4n\), as

$$\mathcal{R} = \mathcal{R}_a + (\mathcal{R}_c - \mathcal{R}_a) \cos \left( \frac{4\pi n}{\lambda} \Delta x \right) e^{-\left( \frac{4\pi n}{\lambda} \right) \Delta x}$$  \hspace{1cm} (2.52)
where \( n \) and \( k \) are the index of refraction and extinction coefficient respectively for the amorphous layer. When written in this fashion, it is easy to see the base value, the maximum amplitude of oscillation, the exponential absorption envelope, and the sinusoidal term as deduced earlier. Finally, Fig. 2.7 shows a typical simulated TRR curve, based upon Eq. 2.51 in which these behavioural aspects are evident.

### 2.6.2 Reflectivity Dependence

The form of Eq. 2.52 makes it quite clear what the reflectivity will look like as a function of depth. It also makes it obvious how the reflectivity will depend on the real and imaginary parts of the index of refraction for the amorphous and crystalline phases respectively. First of all, and most importantly, the period of the interference oscillations is given by \( \lambda/2n \) and thus depends solely on the incident wavelength and the index of refraction of the amorphous layer. Secondly, the rate of decay of the exponential envelope is dictated by the level of absorption for the amorphous material. And finally, it can be seen that the properties of the crystalline material only play a role in the amplitude of the TRR curve. In addition, it is only the index of refraction of the crystalline material \( (n_c) \) that appears in this value. Since the reflected beam that contributes to the measurement never traverses any crystalline material, the crystalline extinction coefficient \( (k_c) \) plays no role.

### 2.6.3 Implications for TRR Measurements

As mentioned in the introduction, obtaining the \( c/a \) interface location as a function of time involves a mapping of the theoretically determined reflectivity as a function of the \( c/a \) interface location to the experimentally observed reflectivity as a function of time. Given that there are usually multiple stages of amplification applied to the raw TRR signal, the absolute magnitude of the measured reflectivity is not really known. However, it is not of any real significance to these types of measurements, since the theoretical or measured reflectivity curve can simply be scaled by a constant factor in the mapping process. This leaves the index of refraction and the extinction coefficient as the two remaining quantities required for the creation of an accurate theoretical curve to be used in the mapping process.
2.6. SPE STUDIES PERFORMED BY TRR

Figure 2.7: Simulated TRR curve, indicating the typical type and form of TRR spectra used to compare with those collected experimentally. Absolute magnitudes of the reflected signal intensity are not required to extract interface location data from the curve.
From Fig. 2.7 and Eq. 2.52, it is evident that most of the depth information is contained in the periodicity of the TRR curve, with some additional depth information implicitly contained in the rate of decay of the exponential envelope. With the periodicity given as \(\lambda/2n_2\), the immediate ramification is that to accurately quantify any TRR measurements, the index of refraction value for the amorphous material being studied must be precisely known for that particular TRR probe wavelength. In addition, one has to consider any temperature related variations in the index of refraction, since TRR studies usually cover a considerable temperature range.

Unfortunately, the properties of amorphous Si and Ge are not nearly as well documented as they are for their crystalline counterparts. In the case of Ge, there is also only a fraction of data in the literature when compared to the extensively studied Si. There are a few publications that list these properties for amorphous Ge[89], based on reflectivity measurements, however, they are typically based on sputter deposited layers, and hence suffer from density variations and relatively high oxygen content, as compared to pure amorphous material such as those produced by ion-implantation methods. The index of refraction values used in this work and the reasons for their selection are given in sections 4.3.2 and 5.3.3 for germanium and silicon respectively.

### 2.6.4 Systematic Errors in the Index of Refraction

Given the direct dependence on the index of refraction, it is worthwhile to consider how some typical causes of error in the index of refraction will effect the SPE data and subsequent Arrhenius-type fits to it. One common case is where the value used for the index of refraction is a constant factor \(C\) different from the 'true' value (i.e. \(n = C \cdot n_{true}\)). In a simple treatment, a depth scale can be assigned to an experimental TRR curve by associating each interference cycle with a \(c/a\) interface location change of \(\lambda/2n\). Thus the true depth scale will also be divided by this same factor, and so interface velocities that are determined from that depth scale will also incorporate this constant factor. For sake of argument, consider \(C < 1\), in which case the depth scale will be expanded, and thus velocities will be underestimated. Hence, when using these SPE rates to determine an Arrhenius form for the data, as
per Eq. 2.2, the velocity prefactor will be multiplied by the same constant, but the activation energy determined from the temperature dependence of the SPE rates will remain unchanged.

Another useful case to consider is when the index of refraction actually changes with temperature, but is assumed to be constant \( n_o \) for the purpose of assigning a depth scale at each temperature. For a linear variation, this can be expressed as 
\[ n = n_o + \Delta n \Delta T \]
where \( n_o \) is the constant value used, assumed to be correct for some given temperature, \( \Delta T \) is the difference between the temperature for which \( n_o \) is correct and the temperature of the measurement, and \( \Delta n \) is the linear variation with temperature, assumed to be \( \ll 1 \). Furthermore, the value of \( n_o \) that was used in the calculation will most likely have been determined experimentally at a temperature corresponding to near mid-range of the temperatures spanned by the SPE study. In this case, the ratio of the calculated velocity to the true velocity can be written as
\[
\frac{v}{v_{true}} = \frac{n_o}{n_o + \Delta n \Delta T} \approx 1 - \left( \frac{\Delta n}{n_o} \right) \Delta T
\]
For a-Si, \( n_o \sim 4.8 \) at typical SPE temperatures and \( \Delta n \sim 5 \times 10^{-4} \). With those values in the above equation, a maximum of \( \pm 1\% \) error is introduced into the above ratio for SPE measurements spanning a \( 200 \) \(^\circ\)C range.

### 2.6.5 Systematic Errors in Temperature Measurement

Often the actual temperature \( (T_a) \) of a TRR system is calibrated to the indicated temperature \( (T_i) \) in a linear form such as 
\[ T_a = \alpha T_i + \beta \]
where \( \alpha \) is a constant very near unity and \( \beta \) is an offset term. Similarly, the relation between the 'true' temperature and what is believed to be the correct temperature can be written in the same way. Due to the fact that the temperature appears within the exponential term of the Arrhenius equation, it is expected that the activation energy and velocity prefactor determined from SPE data would be very sensitive to the accuracy of the temperature assigned to each velocity measurement, and hence \( \alpha \) and \( \beta \). Indeed this is the case, and the relative sensitivity is best viewed by considering normalized velocity plots of hypothetical data sets with known introduced errors. Normalized velocity plots are more suited to observing small differences than are Arrhenius plots, due to the linear versus log scale. By substituting the above temperature
transformation into an Arrhenius equation, it is then possible to calculate theoretical SPE rates as a function of temperature with non-zero $\alpha$ or $\beta$ values introduced and observe the effect.

For the baseline hypothetical data set, consider velocity values generated by substituting the original activation energy and velocity prefactor as determined by Olson and Roth[13] for silicon (2.68 eV and $3.1 \times 10^6$ m/s respectively) into the Arrhenius equation for the temperatures of interest. This will represent the SPE rates for $\alpha = \beta = 0$ and will be what all other curves will be normalized against. On a normalized velocity plot, such as that shown in Fig. 2.8, the reference data set represents the line $v/v_o = 1$ (not shown). An increase in the velocity prefactor by a constant factor results in a horizontal shift upwards by the same factor on a normalized velocity plot.

The first two cases of systematic temperature error considered here are multiplicative transformations with $\alpha = 1 \pm 0.005$. A change of only 0.5% in the temperature calibration factor is sufficient to reconcile SPE rates that differ by as much as $\sim 20\%$. The other two cases shown represent an additive transformation with $\beta = \pm 2^\circ$. For the absolute temperature range shown, this represents a temperature difference of only 0.21% to 0.27%. Yet this is sufficient to reconcile SPE rates differing by 7% to 10%. For comparison, the normalization curve is shown with the activation energy changed by $\pm 0.01$ eV.

In section 2.6.4, it was demonstrated that neglecting the temperature dependence of the index of refraction would introduce an error on the order of 1% on the $v/v_o$ ratio. On the other hand, the above indicates that temperature calibration errors on the order of 0.5% can correspond to a 20% difference in the $v/v_o$ ratio. It is clearly evident that particular attention must be paid to obtaining an accurate and thorough temperature calibration of the system being used to measure SPE rates. This of course applies to any system used to measure SPE rates, and not just TRR systems.
Figure 2.8: Normalized velocity plots indicating shifts due to additive and multiplicative temperature errors on a hypothetical data set of SPE rates in Si. Curves are obtained by considering a transformation of the form $T' = aT + \beta$ substituted into an Arrhenius equation giving SPE rates for Si as a function of temperature. For reference, curves corresponding to an activation energy difference of $\pm 0.01$ eV are also shown. A shift in the velocity prefactor results in a horizontal shift on such a plot. The line $v/v_0 = 1$ (not shown) represents the data against which all the other curves have been normalized.
2.6.6 TRR Versus Partial Furnace Anneals

Prior to the introduction of TRR as a tool for measuring solid phase epitaxial regrowth rates, such measurements were performed by a three stage process. The first step of this process involved measuring the initial thickness of the amorphous layer by Rutherford Backscattering Spectrometry and Channeling (RBSC). Then the sample would be annealed in a furnace for an amount of time that had previously been observed to allow significant yet incomplete regrowth. A second RBSC measurement would then be performed to determine the remaining amorphous layer thickness, and hence the amount of solid phase epitaxial regrowth. Combining this result with the amount of annealing time, an average interface velocity could be calculated for that temperature range and over that depth range. Provided there was enough remaining amorphous material, the sample could be returned to the furnace for a subsequent anneal and RBSC measurement.

This combined partial-anneal/RBSC technique is only accurate for temperatures below which the sample loading time is negligible in comparison to the annealing time, which will in turn be a function of the sample material. A reasonable but arbitrary limit could be proposed as the temperature for which SPE rates exceed 5 Å/s. For temperatures above this point, a considerable amount of regrowth can occur during the time it takes for the sample to reach a steady state temperature, and thus the temperature at which the SPE measurement was taken becomes uncertain. Some of the other serious limitations of this technique as compared to TRR are summarised below.

**Maximum Layer Thickness:**

*Furnace:* The maximum allowable thickness of the layer being studied is determined by the maximum depth at which the initial RBSC measurement can still delineate the $c/a$ interface boundary. For a typical RBS analysis beam of 2 MeV He, the detection of a $c/a$ interface in Si or Ge at depths beyond 1 µm becomes extremely difficult.

*TRR:* The maximum allowable thickness is determined by the amount of absorption of the laser probe upon traversing the amorphous layer. If this becomes a limiting factor, a laser with a wavelength corresponding to a lower absorption can be used.
in the TRR system which will allow essentially unlimited depth probing.

Temperature Calibration:

*Furnace*: It is difficult to accurately (i.e. $\pm 1$ °C) determine the actual sample temperature inside the furnace. A vacuum furnace makes it even more difficult.

*TRR*: Accurate melting point standards can be placed upon the heater stage and the laser beam(s) can be used to determine the transition point, thus allowing an accurate temperature calibration of the system.

SPE Velocity Profiles:

*Furnace*: Only an average SPE velocity is determined for a given depth range. A velocity versus depth profile would require many anneal/RBSC steps and in general would be too tedious to perform.

*TRR*: SPE data is collected in real time, and from that the interface location is known as a function of time for all times. A differentiation of this gives a continuous velocity profile versus interface depth.

Annealing Sequence:

*Furnace*: The sample is annealed in multiple stages, and hence is subjected to additional thermal cycling that may introduce additional complications.

*TRR*: The sample is annealed in one continuous process without any intervening thermal cycling. In addition, should partial anneals be desired, one is essentially guaranteed that the sample has reached the desired annealing temperature in less than half a second after loading, and that the sample has cooled almost as quickly upon removal.

Annealing Duration:

*Furnace*: Determining an appropriate anneal duration is done by trial and error until there is sufficient data to form an estimate of the SPE rate of the material for that specific temperature.

*TRR*: A real time display of the TRR data allows an immediate observation of how fast the anneal is progressing, and the exact time upon which it has completed.
CHAPTER 2. REVIEW OF SOLID PHASE EPITAXY

SPE Rates:

Furnace: Measurements are limited to the regime where the interface motion is a few angstroms per second or less, otherwise considerable SPE can take place during the time taken to load and unload the sample.

TRR: Measurements of SPE rates in excess of 2 μm/s have been recorded in this study, with the primary limitation being when the total anneal time becomes comparable to the time taken for a sample to reach steady state temperature (∼ 0.5 s).

Near Surface Measurements:

Furnace: It is very difficult to determine the interface behaviour in the very near surface region (i.e. ≤ 500 Å) since stopping the anneal just prior to completion is required.

TRR: The TRR data curve continues to exhibit a non-zero slope as long as the c/a interface still exists and is still in motion. Hence the interface velocity as a function of depth can be determined right up to the point where it impacts the surface if so desired.

As indicated above, the use of a TRR system to monitor solid phase epitaxial regrowth offers many advantages over the combined partial anneal/RBSC technique used in past studies. SPE studies that would have otherwise been impractical with the partial anneal/RBSC method are now within reach by use of the TRR technique. However, the partial anneal/RBSC method is still useful to calibrate and verify SPE measurements performed with TRR, and has been employed to do so as part of this work.
2.7 Summary

With respect to solid phase epitaxial regrowth studies, germanium has not been extensively studied. At present, the few SPE measurements that have been performed on Ge are only enough to indicate that the regrowth and dopant behaviour in Ge are expected to be similar to those observed in silicon.

In contrast to Ge, there is considerable SPE data reported for silicon. SPE rates are observed to follow an Arrhenius dependence on temperature over many orders of magnitude in SPE velocity. The addition of small amounts (< 1 at. %) of electrically active dopants can cause large increases in the SPE rate as compared to the intrinsic material. However, the simultaneous addition of both n-type and p-type dopants in comparable concentrations leads to a compensating effect in which the SPE rate has been observed to return to a value close to that of intrinsic material.

Several models of the SPE process exist. In general they can be divided into two categories, kinetic models that delve into the physical aspects of how SPE takes place and electronic models that deal with SPE enhancements due to doping impurities. Models containing an electronic treatment appear to be required due to the observed dopant compensation effect mentioned above. Difficulties arise in determining whether it is the properties of the crystalline or the amorphous material that control SPE, or whether it is a combination of both.

The TRR technique has been shown to be a relatively simple technique to understand, and its employment allows accurate real time monitoring of solid phase epitaxial regrowth. It holds many advantages over the partial-anneal/RBSC technique that was used exclusively prior to 1980. Many SPE studies that would have been too time consuming to be feasible are now easily achieved by the use of a TRR system.
CHAPTER 2. REVIEW OF SOLID PHASE EPITAXY

Summary

In this chapter, we will review the fundamentals of solid phase epitaxy (SPE), a technique used to grow high-quality epitaxial layers on substrates. SPE is particularly useful for growing GaAs and related materials, which are essential components in modern electronic devices. The process involves heating a substrate to a temperature just below its melting point, allowing the material to grow epitaxially on the substrate surface. SPE is widely used in the fabrication of semiconductor devices due to its ability to control the quality and composition of the grown layers. We will discuss the growing techniques, materials, and applications of SPE in the following sections.
Chapter 3

Experimental Techniques
3.1 Introduction

The primary research tool employed in the acquisition of the data presented in this work was the Time Resolved Reflectivity (TRR) technique that was introduced in section 2.6. Since TRR is a relatively new experimental technique, information regarding the construction of a TRR facility is still confined to publications in the various journals. Furthermore, these descriptions are typically very brief and only consist of a simplified schematic due to article length limitations. Hence, the construction of a quality TRR system able to collect TRR data with a high signal to noise ratio was not just a matter of following a recipe of components and assembly instructions. The majority of this chapter details the implementation of the TRR system that was constructed for these measurements.

The remainder of this chapter briefly describes the other secondary experimental techniques that were used during the research program. Techniques like Rutherford Backscattering Spectrometry and Channeling (RBSC) and ion implantation have been covered in detail in a large number of standard texts for quite some time now, and hence only the implementation specific details of these techniques are described here.
3.2 Time Resolved Reflectivity

While the bare essentials of a Time Resolved Reflectivity (TRR) system can be reduced to a single laser and a detector as schematically depicted earlier in Fig. 2.6, the actual implementation is considerably more complex and relies upon a lot more equipment. This section describes the components designed and used in construction of the TRR system, along with the particular details relating to assembly. A brief overview of the system is given, followed by a detailed discussion of the main components. The order in which the elements of the system are treated follows the order in which the analysis beam passes through the various elements of the system.

3.2.1 Overview

The TRR system designed and built was a dual beam apparatus, utilizing 1152 nm and 632.8 nm laser beams to monitor interface motion. The general design is similar to that described by Olson and Roth[13], except that this system employed two different wavelengths, and polarized lasers were used instead of external polarizers. The TRR system designed and used is schematically shown in Fig. 3.1. A sample is positioned on the heater stage, and the laser beams reflected from the sample surface provide the TRR data. Each beam is passed through a beam splitter which allows sampling of the raw laser output. The two signals are merged and later separated by the use of a visible light filter which reflects the 632.8 nm signal while letting the 1152 nm infrared signal pass through. The quarter wave plates alter the polarization of the signal so that the reflected beam ends up in the appropriate detector. The reflected signal is then divided by the reference signal to remove noise introduced by laser power fluctuations before being fed to the recording device.

3.2.2 General Layout of the System

Two separate optical rails were used along the two primary beam paths shown in Fig. 3.1 to hold the optical components. Rail mounts with sliding and locking capability were used. These mounts accepted standard sized optical posts which allowed independent adjustment of rotation and elevation. The optical rails were secured to
Figure 3.1: Schematic of the dual wavelength TRR system used to collect real-time TRR data. Two lasers are used to monitor SPE of a sample mounted to the heater stage, and a filter that is transparent to the infrared signal is used to merge the two signals. Beam splitters are used to sample the laser output as a reference, and quarter wave plates ($\lambda/4$) are used to alter the polarization so that the returning signal reflected off the sample ends up in the respective signal detector. A lens is used to minimize the size of the beam spots on the sample.
a vibration absorbing optical table top measuring approximately 1 m by 1.5 m. The optical post mounts used for the detectors had slotted holes to allow for position adjustment. The optical table top was mounted on pneumatic vibration isolators which were bolted to a heavy gauge steel frame. A shelf was fitted to the frame beneath the table top to house the laser power supplies and other electronic components. The computer used for data acquisition was not placed on or in contact with the steel frame since they are a considerable source of vibration through hard disk access and the operation of cooling fans. Considerable attention was directed towards obtaining a stable room temperature in the area and minimizing air currents, since both were found to significantly degrade laser output stability and signal quality.

3.2.3 Choice of TRR Laser Wavelength

The first component in any TRR system is the laser or lasers that provide the analysis beam(s). The main factor in choosing a laser for a TRR system is the determination of what wavelength will be best suited to the materials that will be studied. In keeping with many materials, the absorption coefficient of a-Si and a-Ge have a strong wavelength dependence. In the wavelength region of interest, the level of absorption increases with decreasing wavelength. It is this absorption coefficient which sets the maximum \( c/a \) interface depth that can be measured with the TRR system. Beyond this wavelength dependent depth, the amplitude of the interference term from the penetrating beam becomes insignificant in comparison to the amplitude of the surface reflection, and thus the TRR curve gives no meaningful information. It just indicates the signal level expected from an infinitely thick amorphous layer.

There is more to choosing a useful wavelength for TRR studies than just the maximum observable depth. One also has to consider the depth resolution of the instrument as well. The ability to resolve small amounts of interface movement or interface roughness will scale inversely with wavelength. In other words, it is desirable to obtain as many interference cycles as possible when annealing a given thickness of material.

Given this information it is evident that there is a significant tradeoff. Long
wavelength TRR probes give an ability to probe extended depths, but at the cost of poorer depth resolution. Shorter wavelength TRR probes can give enhanced depth resolution information, but at the cost of not being able to probe large depths of material. The TRR studies presented in this work were performed at wavelengths of 632.8 nm, 1152 nm and 1523 nm. The 1523 nm laser was installed at a later date on a separate system to facilitate extremely thick layer TRR measurements in a-Ge. The details of the depths which are accessible for each of these wavelengths in a-Ge are discussed in section 4.3.2. A similar discussion for a-Si and amorphous Si$_x$Ge$_{1-x}$ alloys can be found in section 5.3.3.

Both the 632.8 nm and the 1152 nm lasers were single-mode, polarized HeNe lasers with a power output on the order of 1.0 mW in a cylindrical housing requiring an external power supply. The laser tubes were supported by standard laser mounts consisting of two spatially separated rings, each with adjustable screws at 120° directed radially at the laser tube. These types of mounting devices are desirable since they allow many degrees of translational freedom, including laser tube rotation, while still permitting relatively small scale adjustments.

3.2.4 Optical Components

The polarizing beam splitter was used to direct a portion of the raw laser output into the reference detector which was used to monitor the laser output so that power fluctuations could be divided out of the TRR signal. The beam splitter cube was also responsible for directing the beam into the signal detector upon return of the reflected beam from the sample. In the case of the 1152 nm portion of the system, the beam splitter cube was a custom order part since it is not as common a wavelength as 632.8 nm. Both beam splitter cubes were mounted on small 8 cm diameter tables that accept optical rods at the centre on the underside. The beam splitter cubes were held firmly in place at the centre with a cross bar having a small rubber cushion to apply pressure to the top of the cube. The ratio of the laser output directed into the reference detector and the amount directly transmitted through the beam splitter cube was adjusted by rotation of the laser tube.

The quarter wave plates were mounted in standard 1 inch optical element holders
mounted on the optical posts. Upon passing through the quarter wave plate on the way to the sample, the beam is converted from linear polarization to elliptical (circular) polarization, and on the return path after being reflected from the sample, the beam is returned linear polarization but with the polarization angle rotated by 90°.

The infrared pass filter was oriented at 45° to both beams, with the coated surface oriented towards the 632.8 nm beam so that it would essentially behave as a front surface mirror to the shorter wavelength. Both the mirror shown in Fig 3.1 and the filter were mounted on precision drive mechanisms that allowed independent orthogonal tilts of up to approximately 5° to be achieved. These allowed the beams to be easily positioned at any point on the surface of the heater stage, and proved to be invaluable during initial alignment and configuration of the system. In addition, due to the design of the system as shown in Fig. 3.1, small adjustments of the filter orientation to position the 632.8 nm beam have little impact on the 1152 nm beam, allowing essentially independent alignment of each leg of the system.

### 3.2.5 Photodiode Detectors

Identical photodiodes were used for both the signal and reference detectors. For the 632.8 nm part of the system, silicon photodiodes with an active area of 100 mm² were used (Oriel[90] part number 7182). Since the spectral response of these photodiodes drops off rapidly above 900 nm they could not be used for the 1152 nm portion of the system. Instead germanium photodiodes (Oriel[90] part number 71152) with an active area of 9 mm² were used for the infrared part of the TRR system.

A detector system was required that allowed flexible placement of multiple standard 25.4 mm diameter optical components in front of the photodiode. Since none of the commercial offerings seemed to match these needs, custom designed cylindrical detector housings were designed and built according to the schematic shown in Fig. 3.2. This design allowed the placement of the optical components to be altered without disturbing the photodiode.

The raw material for each housing consisted of a 100 mm rod of opaque acetal plastic 40 mm in diameter. One side of the barrel was machined flat to accommodate an aluminum mounting bracket that would accept a standard optical post. Material
Figure 3.2: Schematic of detector housing design implemented for photodiode detectors. The photodiode is mounted to a disc to keep it on the central axis of the housing. A ‘C’ shaped spacer presses up against this disc to hold it in place once the rear plug is screwed in. Two flashed opal diffusers are spatially separated by an annular spacer and spread the incoming beam evenly over the active area of the photodiode. The diffusers and annular spacer are held in place by the front plug.
was milled out from both ends to create a 26.0 mm bore to depths of 65 mm and 30 mm respectively, leaving a dividing segment 5 mm thick closer to one end. The dividing segment was then drilled through (15 mm diameter) to allow full access to the active area of the photodiode. The length of the barrel between the dividing segment and the front plug was considerably longer than that shown schematically in Fig. 3.2.

Both bores were then threaded and matching plugs for the front and rear of the detector were machined from the same material. The plugs were fitted with two small holes ~ 4 mm deep to allow easy installation and removal with a custom tool. Two front plugs were created for each housing, with one being used to clamp any optical elements in place, and the second was placed at the very front of the barrel to act as an initial aperture. The combination of the spatially separated plugs each with an aperture 5 mm in diameter and 10 mm deep inhibited stray light from reaching the photodiode. The photodiode was mounted to a 25.4 mm disc to hold it in the centre of the barrel, and a ‘C’ shaped spacer was used to press against this while allowing room for the photodiode leads to attach to the internal side of a BNC connector. The rear plug then clamps the spacer and mounting disc against the dividing segment.

Annular rings of various thickness and with an outer diameter of 25.4 mm were created as an accessory to be used in the spatial positioning of optical elements in the front barrel. This overall detector design has proven to be very effective, and is currently employed on TRR systems at the Australian National University and at the University of Melbourne.

3.2.6 Filters and Diffusers

Narrow band ‘notch’ filters were fitted to the reflected signal and reference detectors, but it was found that this reduced the signal amplitude to the point where a higher amplifier gain was required, and signal quality was in fact reduced. The system was also tested with a single notch filter in each beam path after the beam splitter, to eliminate the possibility of cross-contamination of the two wavelengths, but again this gave no benefit to the overall signal quality.
Two flashed opal diffusers (Oriel part number 48010) were fitted in the detector barrels, separated by a spacer of approximately 5 mm. These were used to spread the incoming beam over the entire active area of the photodiode and thus reduce the noise associated with the position sensitivity of the photodiode. This had a dramatic effect on the signal quality. It was found that a single diffuser did not sufficiently spread the beam evenly over the active area of the photodiode. Further experimentation showed that when two diffusers were used together with a small spatial separation, the entire active area of the detector was illuminated. This also had the positive effect of significantly reducing the system’s sensitivity to sample orientation. Small differences in parallelism between the front and rear surfaces of the sample, or in the placement of the sample on the heater block would cause minor deflections in the path of the reflected beam. This in turn would put the reflected beam on a different part of the detector surface on a sample to sample basis, if it were not for the above diffusers. The use of the spatially separated diffusers provided excellent signal quality and very good run to run uniformity.

3.2.7 Specimen Heater/Holder

The heater stage of a TRR system is probably the most important component in the system. It has to provide a heat source capable of heating samples to temperatures approaching 700 °C, with a thermal stability on the order of 1 °C. Mechanical stability is also a crucial requirement, as vibrations of the heater stage will alter the return path of the beam and hence the signal level. The stable mounting of a metal block heated to these temperatures poses a significant challenge.

Original Heater Stage Design

Other TRR systems that were observed[91, 92] used an exposed metal block suspended on a tube of ~8 mm diameter. This tube was then clamped by some means to a stable post, and also served as a way to apply vacuum through a small hole in the centre of the block to hold the sample in place. The tube was generally clamped several centimetres back from the rear of the block, at a point where the
3.2. TIME RESOLVED REFLECTIVITY

temperature was significantly lower. A variation on this design was initially experimented with, where a flange was welded onto an 8 mm diameter inconel tube approximately 20 mm behind where it was inserted into a nickel cylinder 20 mm in diameter and 30 mm long. The nickel cylinder was fitted with a ring heater around its circumference. The flange was then bolted directly to a thick walled stainless steel shroud resembling an open can. The cylindrical area between the shroud and the ring heater was packed with ceramic fiber insulation to aid in thermal stability. The shroud was then bolted to a micrometer drive X–Y stage which allowed positioning of the stage with respect to the incoming beams.

While the addition of the ceramic fiber insulation and more rigid mounting made it a significant improvement over the other designs[91,92], it was felt that the heater stage was still the limiting factor in the observed signal quality and the level of reproducibility between runs. It was concluded that having the nickel block essentially ‘dangling’ on the end of a piece of pipe with a significant thermal gradient along it was a fundamental design flaw, since the distance from the flange to the surface of the heater stage was still at least 50 mm. In light of this, such design formats were completely abandoned.

Improved Heater Stage Design

The new heater stage was designed with complete rigidity in mind. Not only does it give excellent mechanical stability, but the design also incorporates all the required degrees of freedom for alignment purposes. A simplified schematic of the heater stage that was designed for TRR measurements is shown in Fig. 3.3.

To obtain the desired level of stability, 10 mm thick stainless steel was used for the mount plate, support plate, base plate, anchor plate and the two side supports. The side supports and the base plate had a 1 mm deep groove machined in them to allow a positive locking of the support plate. Four countersunk fasteners were affixed through the bottom of the base plate and up into each side support. The side supports in turn were also rigidly fastened to the support plate with two bolts each.

A piece of 10 mm stainless steel rod positioned between grooves in the base plate and the anchor plate acted as a pivot point and allowed adjustment of the reflected
Figure 3.3: Simplified two-dimensional representation of the TRR heater stage designed and manufactured for this study. The design incorporates angular adjustment in the $xy$ and the $yz$ planes, along with translational adjustment in both the $x$ and $z$ directions. All plates and supports are 10 mm thick stainless steel, and pivot points swivel on 10 mm stainless steel rod.
3.2. TIME RESOLVED REFLECTIVITY

beam direction in the $yz$ plane. Two bolts at each end of the base plate were screwed into the anchor plate to fix the final angular position. The holes in the base plate were slotted which also allowed translation in the $x$ direction. The anchor plate was bolted to a rail mount such as the Oriel 11628.

Four bolts through the support plate affixed the mount plate at each corner. Placed in the middle between the two plates were two short pieces of 10 mm stainless steel rod residing in grooves that acted as pivot points and allowed angular adjustment in the $xy$ plane. Small pins below each rod prevented them from dropping out during coarse adjustments. Furthermore, the holes in the support plate were slotted, which allowed $\pm 5$ mm of translation in the $z$ direction.

The core element of the heater stage was the nickel cylinder attached to the mount plate. To minimize thermal conduction to the mount plate, the cylinder had been machined out so that only a 3 mm thick annular ring was in contact with the mount plate. The mount plate had a matching annular groove machined into it to allow a positive lock between the two. The annular portion of the nickel cylinder also had a pattern of staggered 5 mm diameter radial holes drilled through it to further reduce the thermal conductivity to the base plate. Three countersunk fasteners placed at 120° pass through the mount plate and screw into the solid portion of the nickel cylinder. These fasteners had been axially drilled through similar to the method used in vacuum systems, only in this case the goal was again to reduce the thermal conductivity between the nickel cylinder and the mount plate. The fasteners were coated with a copper based anti-seizure compound prior to installation.

The only other items in direct contact with the nickel cylinder were a small (3 mm diameter) inconel tube to supply vacuum, a type K thermocouple and the heater ring itself. The heating element used was a Watlow ‘K-Ring’ heater[93], capable of delivering up to 600 W to the contained nickel cylinder, although 250 W has since proven to be sufficient for reaching the maximum temperatures required. A small hole (< 1mm diameter) was bored along the axis of the cylinder, to which a vacuum is applied for affixing samples. This hole was enlarged on the rear side to accommodate the inconel tubing. The type K thermocouple was mounted from the rear of the block through another bore such that the tip of the thermocouple
was within 1 mm of the face of the cylinder where the samples were mounted. The thermocouple and the heater ring were both coated with ‘Watlube’, an Al₂O₃-based thermal transfer agent[93], prior to installation onto the nickel cylinder. The maximum recommended operating temperature of the K-Ring heater was specified as 650 °C. The space between the nickel cylinder/heater was then filled with high temperature ceramic fibre insulation to aid in temperature stabilization.

Vacuum to the heater stage was supplied by a small diaphragm pump connected to a 3 litre reservoir fitted with a gauge. The pressure in the vessel was typically less than 50 kPa. A timer was used to periodically start the pump to replenish the vacuum lost during sample loading and unloading. A toggle valve mounted to the optical table base near the heater stage permitted the vacuum to the stage to be easily isolated during sample changing since the temperature stability was adversely affected by any air flow through the centre of the nickel cylinder.

This heater stage design has performed very well under continual use. Initial alignment was easily facilitated with the various adjustable parameters that were built in. Both beams were positioned on the surface of the nickel block to coincide with the location of the underlying thermocouple. Once alignment was achieved, the final position could be locked down with a permanence that far surpassed the typical locks available on X–Y translation stages. The rigidity literally allowed hundreds of samples to be easily removed and replaced without any intermediate alignment being required. The reproducibility of sample alignment obtained with this stage made TRR measurements of very short duration (≈ 2 s) possible. This design is now in use on the TRR systems at the Australian National University and at the University of Melbourne.

3.2.8 Temperature Control

Temperature control was provided by a Watlow 920 temperature controller unit with a type K input, and a standard 4-20 mA process control output. The Watlow 920 is a microprocessor based intelligent controller that has multiple software parameters to allow precise tuning of the controller to the attached thermal system. The Watlow 920 was ordered with a standard RS-232 serial port that allowed full control
3.2. TIME RESOLVED REFLECTIVITY

and monitoring to be performed through a computer.

The 4–20 mA process control was fed into a custom-built zero-cross triac assembly to decrease the time granularity and electrical noise usually associated with control done via mechanical relays. A comparator used the process control input signal and the output of a 555 based TTL ramp generator to gate the triac which then output a proportional integer number of 240 VAC half-cycles per ramp period to power the K-Ring heater element. At full power and with a 50 Hz line voltage, 100 half-cycles were output per ramp cycle, and hence the voltage pulse granularity was 1% of the full power output. The ramp generator was set to a frequency of 1 Hz, and since the input signal was not latched on a per ramp period basis, the response time was considerably better than a similar 1 Hz latched system.

3.2.9 Temperature Calibration

Initially the temperature calibration of the heater stage and controller combination was attempted with temperature indicating lacquers from the Omega Engineering Corporation. Small pieces of silicon were coated with lacquers of different transition temperatures. Since the coating of the material was not sufficiently reflective, the transition point had to be observed by eye and not by the use of the lasers and detectors. The accuracy and reproducibility of temperature calibrations based upon these lacquers proved to be unsatisfactory and hence they were abandoned.

Subsequently, temperature calibration of the heater stage was performed by using custom encapsulated layers of pure metals on a silicon substrate. These included indium, tin, and zinc evaporated layers, which were environmentally isolated by layers of SiO₂ above and below the metal layers. An aluminum sample was prepared in a similar fashion, with the only exception being that the buffer layers were Al₂O₃, instead of SiO₂. Both the infrared and visible lasers were used to monitor the temperature calibration samples. The temperature of the hot stage was varied through a range that included the melting point of the metal in question. The reflectivity variations caused by the liquid-solid phase change were visible in the reflected signals, giving a one-to-one correspondence between the reading of the thermocouple embedded in the hot stage and the surface temperature of the mounted samples.
Differential Scanning Calorimetry (DSC) was used to verify the melting points of some of the encapsulated layers against the equivalent pure metals. These showed no deviation of the transition temperature from that of their pure metal counterparts. The temperature calibration was also verified by determining the temperature from the observed SPE rate of hydrogen-free thick a-Si layers, which is now well known[14]. These values were in good agreement with those obtained from the thin metal films.

Periodic repolishing of the front surface of the nickel block was performed to remove any fine scratches and any oxide build up. Recalibration of the temperature was typically also performed at these times, and no significant drift in the temperature calibration over time was observed.

### 3.2.10 Signal Processing Electronics and Data Acquisition

The signals from the detectors were fed directly into current pre-amplifiers (Oriel[90] part number 70710) located within 30 cm of the detectors. These devices supply a voltage output with a selectable gain between $10^4$ and $10^8$ V/A and have BNC input/output connectors. They also have a bandwidth from DC levels up to 500 kHz which is more than adequate for TRR signals associated with conventional thermal annealing measurements.

The outputs from the four pre-amplifiers were routed into two individual custom designed divider devices. The heart of these devices relies on a Burr-Brown divider application-specific integrated circuit (ASIC) which does analog division of two inputs. The numerator input was the TRR signal and the denominator signal was the reference signal. Since the gain of the pre-amplifiers can only be set in powers of ten, the divider devices were built with a variable gain of between one and ten on the numerator and denominator signals prior to being input to the ASIC. An LCD voltage readout allowed adjustment of the numerator and denominator inputs to the ASIC and monitoring of the ASIC output level. A switch could be used to bypass the division step of the ASIC, in which case the numerator and denominator signals were passed directly through the unit after amplification. In pass-through mode, the numerator and denominator data could be collected individually, which
proven useful for monitoring laser stability and observing how laser power fluctuations manifested themselves in the reflected signal. If the division step was enabled, as per normal operation, the output of the divider ASIC was supplied to both the numerator and denominator outputs of the divider unit.

Clean electrical power to the laser supplies, pre-amplifiers, divider devices and the temperature controller was provided by a 2 kW active line conditioner. The data acquisition computer and triac heater driver assembly were not put onto the conditioner since they had no particular need for extremely clean power.

The two outputs from each divider device were attached to four input channels of an Analog Devices model RTI-800 16 channel, 12 bit analog to digital converter (ADC). The RTI-800 is a full length card requiring an 8 bit ISA slot in a standard IBM compatible personal computer. Access to control and read data from the card is performed with programmed input/output (PIO) instructions. The card was fitted to a 33 MHz 486 computer running the Linux [94] operating system. The no-cost nature of Linux, combined with complete source code availability makes it a good choice for university and research environments that typically need to make custom software and/or interface with the operating system.

A Linux character device driver\(^1\) was written for the Motorola MC146818 compatible real time clock (RTC) built into every IBM compatible personal computer. The driver allows the RTC to be programmed to generate interrupts on a per second basis or at frequencies between 2 Hz and 8192 Hz in steps of powers of two, and was included as part of the standard Linux kernel source during the development of kernel version 1.3. These interrupts are used to trigger an analog to digital conversion event. Interrupt based sampling is preferred to the usual DOS programming method of simply polling the clock through the standard `gettimeofday(2)` function in a loop, since the latter consumes 100% of the CPU resources. The standard RTC driver could be used to alert the program that it is time to sample the card, or a slightly modified RTC driver could be used to sample the card in the kernel interrupt handler and then pass the data back to the application program. For the former, a single call to `gettimeofday(2)` gave the exact time of sampling whereas for the latter method, the samples were assumed to be evenly spaced since

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\(^1\)Driver information is in `/usr/src/linux/Documentation/rtc.txt` on most Linux systems.
the sampling was not affected by any overhead associated with rescheduling of the application program. Use of the latter method was typically unnecessary in practice, unless the system was burdened with multiple other running tasks. Linux also supports enhanced scheduling options as documented in the on-line manual page for the `setscheduler(2)` function, which could be used to give the data collection application a higher priority above and beyond that which was available through the use of the standard `nice(2)` system call.

The custom software that was written to collect and store data from the card took multiple samples within a time period that was small in comparison to the sampling period requested by the user. These values were then internally averaged to further reduce the signal noise level. The time associated with the mid-point of the sampling burst and the calculated average value were then stored in memory or on disk as part of the TRR data. The software could also automatically determine whether the divider devices were operating in division mode or in pass-through mode by comparing the values on the respective pairs of channels to see if they were equal to within statistical fluctuations. A similar logic was employed to implement an autostart feature, where the program would immediately start collecting data at a high sampling rate (~ 1 kHz) upon detecting that a sample had been placed upon the stage. Since the reflectivity of the polished stage was still considerably less than that of a piece of Si or Ge, a threshold value was used to determine when a sample was present on the heater stage. This feature was used for the extremely fast TRR runs that were completed in only a few seconds.

On the other end of the scale, extremely long TRR experiments associated with low annealing temperatures created an opposite problem. A quick start of the data acquisition program was not required, but the ability to remotely stop data collection and remove power from the heater stage upon completion of the anneal was useful. Fortunately, this was also easily achieved with the use of Linux on the data acquisition computer, since secure remote network access is a standard feature. The experimenter could connect to the data acquisition computer from a remote location, regardless of whether it was through a modem from his/her home or from a computer at another university, and view the current TRR curve as annealing
was in progress. If the TRR data indicated that an anneal had completed, then the remote user could terminate the data collection program. The experimenter could also remotely turn off the supply of power to the sample heater stage, since the temperature controller was directly connected to the data acquisition computer through a standard serial communication link.

3.2.11 Data Analysis

The simplest technique of getting real-time a/c interface motion data from a TRR curve is by location of maxima and minima. As the amorphous layer thickness per half TRR interference cycle is known from the index of refraction as per section 2.6.1, the interface depth at any given maximum or minimum will be simply an integer multiple of that value. Before determining maxima and minima locations, the experimental TRR curve needs to be divided by a suitable function to remove the exponential envelope on the signal that is caused by the extinction coefficient. Failure to do this will result in a systematic error in the location of the maxima and minima. This simple method is useful in situations where it is known or expected that the c/a interface velocity will be relatively constant over a few complete interference cycles, since only a few depth versus time data points are determined in this fashion.

The most robust technique of getting real-time c/a interface motion data is by mapping the observed TRR curve onto a simulated curve for the same sample material. The simulated curve gives a mapping from the TRR signal level to the c/a interface depth, and the actual TRR data gives a mapping from the TRR signal level to the elapsed annealing time. Combining the two and eliminating the common TRR signal gives a measurement of the c/a interface depth versus time, which is easily transformed into a c/a interface velocity versus depth through differentiation. This method has the advantage of providing a continuous c/a interface depth versus time data set, whereas the simpler method of maxima and minima location only provides a few individual points. This advantage is particularly useful in situations where one expects the c/a interface velocity to vary over relatively short depth ranges.

The method involved in analysis of the TRR curves is similar to that outlined by
Olson and Roth[13]. In the implementation of the method used here, simulated TRR curves were created by using the full complex expression for the reflectivity (Eq. 2.50 and 2.51). The Octave[95] program, a freely available Matlab implementation that runs on nearly all Unix-like systems, was used to do the complex calculations. The Octave macro that performed the calculation read a small ASCII file containing the laser wavelength, the index of refraction for both the crystalline and amorphous materials and the layer thickness. The output was then written to a file in the desired format by using the C-language standard input/output functions supported directly by Octave.

Both the simulated curve and the real TRR data were then input to the Genplot[96] program. A Genplot macro was used to break the simulated curve into half cycles and archive this data. A second macro then does the same for the experimental data. It then retrieved a full cycle of the experimental data at a time and fitted a 10th order Chebyshev polynomial to that segment. This segment was then scaled to match the corresponding theory segment that was archived by the first macro. The theory segment was then traversed to find the \( y \) value matching each \( y \) value from the scaled experimental segment, and upon a match, the depth from the theory segment and the time from the experimental segment were recorded in an array. The mapping was only performed on the middle half of the full cycle since the Chebyshev fits are not as accurate at the end points of the segment. Hence the iteration step size is a half cycle and not a full cycle. Iteration over all segments then results in a continuous \( c/a \) interface location versus time data set.

As a consistency check for the accuracy of the mapping technique, the output was verified against the result obtained by maxima and minima determination for samples of constant SPE growth rate. Also, a simulated curve with some intentionally added noise was scaled to typical TRR amplitudes and fed back into the mapping procedure. Again, the mapping technique was able to accurately recover the expected interface depth versus time curve.
3.3 Other Experimental Systems

The following experimental systems are well documented and also considered standard apparatus for most material science facilities. Thus, only site specific details and details of particular importance to this work are documented here. References to comprehensive documentation sources are given where appropriate.

3.3.1 Rutherford Backscattering Spectrometry System


The RBSC system installed at the Australian National University utilised a 2 MV Van de Graff accelerator with a RF ion source. RBS analysis was performed with a 2 MeV helium beam at both glancing angle and near-170° geometries. A laser was installed at the straight-through port of the mass analysis magnet so that the laser beam would be coaxial with the ion beam and could be used for the precise location and angular positioning of samples prior to analysis. Sample manipulation was performed by a dual-translation, dual-tilt Hodges goniometer offering both manual and computer controlled operation. Data acquisition hardware and software were purchased from Canberra Instruments.

The measurement of arsenic in silicon to the desired depths required a higher beam energy than what was available on the Van de Graff system. These measurements were performed on the RBS facility at the Royal Melbourne Institute of Technology. A duoplasmatron source attached to a General Ionex Tandem accelerator provided a 3 MeV helium analysis beam. The goniometer was identical to the ANU system, with the exception that computer control was not implemented.

RBS data analysis was performed using the RUMP program written by Larry
Doolittle[101]. RUMP is currently being distributed as a part of the Genplot[96] software package, and makes use of the graphical support provided through Genplot. The Genplot package is now available for Unix-like systems that have the X Window System installed. Genplot and RUMP were compiled and installed on both Linux and Digital Unix platforms.

3.3.2 Ion Implantation System

The technique of ion implantation is also now a very common process that is described in standard texts such as ‘Surface Modification and Alloying by Laser, Ion, and Electron Beams’ edited by Poate, Föti, and Jacobson[102] and ‘Ion Implantation and Beam Processing’ edited by Williams and Poate[2] in 1984. There are also various review articles available, such as ‘Materials Modification with Ion Beams’ by Williams[103]. Hence, only the experimental aspects relating to the particular implants performed as part of this work are listed below.

Implantation was performed using a NEC Tandem accelerator. Given that the two stage acceleration tandem design involves performing a mass analysis of the beam, passing it through a charge stripping mechanism and then a subsequent mass analysis after that, extremely high beam purity is ensured. There is little chance of unintentional coimplantation of molecular species having the same mass as the intended implant species. Implants based on only a single acceleration stage can suffer from molecular beam contamination, with N2 in a 28Si beam being a common example. In addition, the pressure in the beam line after the secondary mass analysis was typically $10^{-7}$ to $10^{-8}$ Torr, which also reduces the probability of producing undesired charged and neutral species.

In most cases the implantation was performed at liquid nitrogen (LN$_2$) temperature. The nickel block of the sample stage had a hollow centre which could be filled with LN$_2$. The ion dose rates were sufficiently low (0.5 $\mu$A/cm$^2$ or less) to ensure any beam heating effects would be negligible. In addition, the substrates were fixed to the implant stage using a silver colloid conductive paste. By maintaining a low substrate temperature and a reasonably low beam current, the lattice damage caused by the implanted ions was frozen into the matrix, making these the preferred
conditions for amorphization implants. At higher temperatures and or higher ion flux, complications such as dynamic annealing and even ion beam induced epitaxial crystallization can occur, and hence higher doses would be needed to achieve amorphization. In turn, the use of a relatively higher dose can introduce other undesirable effects, such as the void formation that has been observed in germanium, which is discussed in section 4.2.2.

The initiation of sample stage cooling was not started until the implant chamber pressure was less than approximately $5 \times 10^{-7}$ Torr. In addition, the cold shield fitted to the implant chamber was always cooled to LN$_2$ temperature before cooling the sample stage. This minimized the possibility of condensation of impurities onto the surface of the samples, and thus reduced the probability of recoil implantation of surface impurities.

The implant stage was positioned to make an angle of approximately 7° between the wafer surface normal and the incoming ion beam to avoid axial channelling of the implanted ions. In addition, the wafers were rotated in the plane of the implant stage surface by a similar angle to prevent any remaining possibility of planar channeling of the implanted ions. There is evidence that a single tilt of 7° is not sufficient to stop inadvertent channeling of implanted MeV arsenic ions[104].
CHAPTER 3. EXPERIMENTAL TECHNIQUES

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Chapter 4

Solid Phase Epitaxial Regrowth of Amorphous Germanium
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

4.1 Introduction

The existence of germanium was predicted by Dmitry Mendeleyev in 1871 before it was actually discovered in 1886 by Clemens Winkler. Mendeleyev named his prediction 'ekasilicon' due to its location in the periodic table. In contrast to silicon, germanium is a rare element, only making up 1.5 ppm of the material in the Earth's crust, in the form of minerals such as argyrode, germanite and renierite[105]. The first widespread commercial use of germanium was instigated by the electronics industry when large scale manufacturing of solid state devices began in the early 1950's.

Since approximately the early 1970's, silicon has replaced germanium as the preferred semiconductor material for device fabrication. Some of the advantages silicon has to offer are availability of large volumes of the raw material at low cost, ease of purification and favourable behavioural characteristics. While these advantages are important for industrial production, they do not detract from the information that germanium can supply to those doing fundamental research measurements on elemental semiconductors. The availability of high quality germanium wafers make it an ideal candidate as an alternative group IV semiconductor for comparison of its solid phase epitaxial regrowth characteristics with those of Si. In doing so, the new data that is obtained may aid in the search for appropriate theoretical models that can accurately describe the solid phase epitaxial (SPE) regrowth process. Thus, the following chapter presents new results from a range of studies of solid phase epitaxial regrowth in a-Ge layers.

The existing results in the literature that are related to the work performed in this study are discussed first in section 4.2. Then, section 4.3 covers the sample preparation and experimental methods used for the SPE measurements, including the determination of the refractive index of a-Ge for the Time Resolved Reflectivity (TRR) studies. Section 4.4 presents the measurements of solid phase epitaxial regrowth in intrinsic amorphous germanium, with hydrogen effects being considered in section 4.5. The effect of some selected dopants on the SPE behaviour is presented in section 4.6 and the implications of these results are discussed in section 4.7. Finally, the conclusions drawn from these studies are summarised in section 4.8.
4.2 Background Information

An overview of the previous SPE studies in germanium was given in section 2.2. Those past studies that have relevance to the new work being presented in this chapter will be discussed in detail here. Previous solid phase epitaxial regrowth measurements in a-Ge will be reviewed, followed by considerations associated with hydrogen contamination, and finally what is currently known about dopant effects on solid phase epitaxial regrowth of a-Ge will be discussed. To put the relevance of this study into context with the past research into solid phase epitaxial regrowth measurements of amorphous germanium, it is best to review these important results of the past in chronological order.

4.2.1 The First a-Ge SPE Measurement

Csepregi et al.[5] were the first to report on the measurement of the rate of solid phase epitaxial regrowth of a-Ge on (100) Ge back in 1977. They performed their measurements in the limited temperature range of $\sim 310 \, ^\circ C$ to $\sim 340 \, ^\circ C$ by using partial furnace anneals as described in section 2.6.6. The anneals were performed at a pressure of $10^{-6}$ Torr, thus making an accurate determination of the sample temperature quite difficult. In addition, the amorphizations were performed with a rather high concentration of $^{28}$Si. The Si implants used for amorphization were performed in 50 keV steps from 50 to 250 keV, with respective doses of 1, 1.5, 2, 4 and $8 \times 10^{15}$/cm$^2$. This resulted in an amorphous layer 5000 Å thick. Silicon was chosen over Ge as an implant species due to the fact that the resulting amorphous layer for Ge implants in the available energy range was less than half the thickness, due to the reduced range of Ge ions relative to Si.

The interface motion for the Si implanted Ge was observed to be essentially linear until reaching within $\sim 2000$ Å of the surface, at which point the interface velocity was observed to slow down slightly. By taking the interface velocity from the linear portion of the curve, and performing similar measurements for five other temperature values, they found that the epitaxial regrowth rate followed a simple exponential dependence on temperature, with an activation energy of 2.0 eV.
They also briefly reported on solid phase epitaxial regrowth rates for Ge implanted Ge samples, and found that while the initial growth rate was similar, it tended to fall away from the Si implanted Ge rate as the interface approached the surface.

4.2.2 Expected High Dose Implant Effects

During 1982, further implantation studies of Ge uncovered an unexpected effect that had not been observed in silicon. In particular, both Appleton et al.[106] and Holland et al.[107] reported that high dose (>1 × 10^{15}/cm²) room temperature heavy ion implants into crystalline Ge were capable of producing a highly porous structure. The effect was observed even in self-ion implanted Ge. The reduction in the density of the affected area was sufficient to cause a significant reduction in the Ge yield of a typical RBS measurement.

The authors proposed that the mechanism for the formation of this damage structure is that of large scale vacancy clustering. It was also reported that if the same dose implantation is performed at liquid nitrogen temperature, then this damage structure did not form. In keeping with their vacancy clustering proposal, the lower temperature implant reduces the mobility of the vacancies to the point where clustering is prohibited.

In severe cases, the surface of the implanted region of the material becomes visibly blackened upon the formation of this honeycomb structure. It was also reported that this unique structure absorbs large quantities of oxygen and carbon impurities (up to ~ 50 impurities/ion in the worst cases) from the ambient. Attempts at annealing samples that exhibited this new damage structure indicated that the solid phase epitaxial regrowth was retarded in comparison to unaffected samples. In addition, this porous structure did not exhibit good quality solid phase epitaxial regrowth. This result had immediate implications upon the choice of the dose and temperature parameters chosen for the creation of a-Ge to be used in further solid phase epitaxial regrowth studies.
4.2.3 The Calorimetry Based Measurement

The calorimetry based measurement is interesting if for no other reason than the fact that the activation energy for the SPE process in a-Ge is determined by an entirely different process. In a calorimetric study primarily focussed upon relaxation of amorphous Si and Ge structures, Donovan et al.\cite{6} measured the heat release from a-Ge samples formed by implantation of noble gases into (100) Ge. They were able to discern the heat release associated with the relaxation of the amorphous structure from that released during the crystallization process, and found that for temperatures above 680 K the heat release was dominated by the heat of crystallization. With a knowledge of the heat of crystallization ($\Delta H_{ac}$) for germanium combined with the area of the sample in question, an interface velocity could be deduced for that specific temperature. An Arrhenius fit to their velocity data for temperatures above 680 K (407 °C) gave an activation energy $E_a=2.17$ eV and a velocity prefactor of $v_0=4 \times 10^7$ m/s.

4.2.4 The Diamond Anvil Cell Measurements

In an effort to determine the effect of an externally applied hydrostatic pressure on the solid phase epitaxial regrowth process, Lu et al.\cite{11} set up an elaborate diamond anvil cell (DAC) apparatus in conjunction with a heat source and a basic TRR system. In 1991, they reported on SPE rates for both (100) Si and (100) Ge under externally applied pressures as high as 5 GPa by using this mechanism. In the process of their measurements, they also did the default case of zero additional externally applied pressure for an 8000 Å layer of a-Ge on (100) Ge, which can be compared directly to the above result from Csepregi, and also to the results presented further on in this chapter. The solid phase epitaxial regrowth rate of these samples was measured for four different temperatures between 300 °C and 365 °C. The temperature in the DAC was calibrated by measuring the SPE rate in the cell at atmospheric pressure and comparing to SPE rates observed on a separate hot stage that had been calibrated using temperature indicating lacquers from the Omega Engineering Corporation. Using this method, they estimated the accuracy in the sample temperature determination to be ±5 °C. From these four a-Ge SPE
measurements, they reported an activation energy of $E_a=2.17\pm0.2$ eV, and a velocity prefactor $v_0=1.2\times10^7$ m/s.

### 4.2.5 Recent a-Ge SPE Measurements

Since the initiation of this study, three other measurements of SPE in a-Ge have been reported in the literature[14, 39, 40]. Two of these studies[39, 40] have resulted from interest in the SPE behaviour of silicon-germanium alloys. The SPE behaviour of pure Ge and pure Si are used as the endpoints of the mapping of SPE behaviour in $Si_xGe_{1-x}$ alloys for $0 < x < 1$.

In a recent book chapter from 1994 on solid phase epitaxy, Olson and Roth[14] report having measured an activation energy $E_a=2.26$ eV for a-Ge layers produced by Si implantation. As the result is presented as part of a review, the explicit details for this particular measurement are not documented. However, it is safe to assume that they used TRR based measurements similar to those described in detail in their previous review article[13] and also in their recent chapter[14]. The graphical data presented indicates that the activation energy for SPE of a-Ge reported above was derived from five solid phase epitaxial regrowth measurements performed at 25 °C intervals from 350 °C to 450 °C.

Also in 1994, Kringhøj et al.[39] measured the SPE rate of a-Ge at six temperatures ranging from 290 °C to 440 °C as part of their study of SPE in $Si_xGe_{1-x}$. The a-Ge layers used were created by a single implant of $1\times10^{15} / cm^2$ 200 keV Si. Temperature calibration was performed by comparing the observed SPE rate of a-Si samples to those originally reported by Olson and Roth[13]. The TRR measurement was performed with a 1.523 µm laser, and the SPE rate was determined over the depth range from 900 Å to 2800 Å. The index of refraction they used for a-Ge at this wavelength was not stated. They reported an activation energy of $E_a=2.02\pm0.015$ eV and a velocity prefactor of $6.1\times10^6$ m/s, noting that the quoted uncertainties were statistical only.

An even more recent $Si_xGe_{1-x}$ study by Haynes et al.[40] in 1995 also involved the study of SPE in pure Ge. Again a 1.523 µm TRR system was used for the Ge measurements. They used an index of refraction value of $n=4.80$ for all $Si_xGe_{1-x}$
samples for which $0.71 \leq x \leq 1$. This value was determined from an average of measurements similar to those described in section 4.3.2 on samples within the above composition range. A two-step Si implantation was used to create an amorphous layer approximately 3500 Å thick. The extracted velocity for a given temperature was determined from the division of the distance associated with a half interference cycle ($\lambda/4n$) from the time interval between the first maxima and the second minima from surface. Using their value of $n$ would imply that the SPE velocity reported for each temperature was taken as the mean value associated with the depth range from approximately 800 Å to 1600 Å. Six measurements were taken over the temperature range from 290 °C to 390 °C. From these measurements, they reported an activation energy of $E_a = 2.19 \pm 0.02$ eV and a velocity prefactor of $7 \times 10^7$ m/s.

4.2.6 Possibility of Hydrogen Contamination Effects

As mentioned in section 2.3.6, the presence of trace amounts of hydrogen in the annealing ambient can significantly reduce the rate of the solid phase epitaxial regrowth process in silicon samples[19, 20]. Due to the similarities between the silicon and germanium systems, it is of immediate concern to determine if this same behaviour occurs in germanium.

The interest in hydrogen effects is primarily due to the fact that the hydrogen appears to be absorbed into the amorphous material from the ambient when it is heated to the crystallization temperature. Once present in sufficient quantities, the hydrogen slows down the silicon SPE rate, in keeping with the previous measurements on hydrogen implanted silicon as reported Oberlin et al.[50]. The proposed mechanism[19] for the incorporation of the hydrogen into the amorphous layer is that the formation of a native oxide during annealing leaves H as a by-product of the dissociation of water vapour from the ambient and this H then diffuses into the amorphous layer.

The ramifications of this result is that all measurements of SPE in silicon that have been performed in an environment with any trace of water vapour will have been measuring the H retarded rate, and not the true intrinsic rate. Even samples annealed in a vacuum furnace at pressures of $10^{-5}$ Torr have been shown to contain
up to $\sim 1 \times 10^{19}$ /cm$^3$ of H after only a few hundred angstroms of SPE[14]. To determine whether germanium SPE studies are also suffering from a similar effect, it is useful to review the observations and techniques that Roth et al.[19] reported when they first observed this effect in silicon.

Thick Layer Measurements

The primary result that first demonstrated this effect was in fact TRR measurements of extremely thick layers of a-Si. As discussed in Section 3.2.3, longer wavelength TRR signals can probe thicker layers of amorphous material. Roth et al.[19, 20] made use of this by employing a 1.15 $\mu$m laser to measure the solid phase epitaxial regrowth rate of a-Si from depths of up to 5 $\mu$m. In doing so, they found that when the c/a interface of a sample annealed in air reached a depth of approximately 2 $\mu$m the SPE rate started to drop, and in some cases fell to about 60% of its original value. However, a similar sample that was annealed in a vacuum environment, in which extra precautions were taken to ensure that the ambient was free of water vapour, showed a constant SPE rate right to the very near surface region[19].

Roth et al.[20] then proceeded to do a detailed study of the hydrogen content of partially annealed samples via SIMS in conjunction with c/a interface velocity measurements performed by TRR, as shown in Fig. 4.1. They found that immediately after beginning the anneal, the sample contained a hydrogen profile resembling a diffusion profile that was being constantly fed from the surface, as shown in curve 1 of Fig. 4.1. This diffusion profile is consistent with the theory of constant liberation of H from ambient water vapour during the formation of a native oxide. In curve 2 of Fig. 4.1, it is evident that the diffusion profile has broadened, but the hydrogen content at the surface remains fixed at the initial value of approximately $1.2 \times 10^{19}$/cm$^3$, which is consistent with a constant diffusion source of H. As the c/a interface comes into contact with the indiffused hydrogen profile, the interface begins to collect the hydrogen as it encounters it. This segregation or zone-refinement of the hydrogen profile acts to rapidly enhance the hydrogen concentration at the c/a interface, as seen in curves three to seven in Fig. 4.1. In the last stages of growth (from curve 7 to the surface) the hydrogen level moves continuously from the segregation enhanced
Figure 4.1: A comparison of the solid phase epitaxial regrowth velocity, obtained via TRR measurements (top) versus the hydrogen content at the interface obtained via SIMS measurements of partially annealed samples (bottom). Initial a-Si layer was 4.2 µm thick, on (100) Si, annealed at 606 °C. (From Roth et al.[20].)
value to the surface concentration, due to the pinning of the hydrogen level at the
surface. By comparing the hydrogen concentration at the interface (arrows) with
the solid phase epitaxial regrowth rate shown in the top half of Fig. 4.1, Olson and
Roth[14] found that the SPE rate decreased linearly with increasing interfacial hy­
drogen concentration, up to approximately $3 \times 10^{19} \text{cm}^{-3}$ of hydrogen at the interface.
For concentrations above that, they reported a saturation effect, where the SPE rate
was not strongly affected by further increases in the amount of hydrogen present at
the interface. Oberlin et al.[50] also reported a similar saturation effect for the effect
of implanted hydrogen on the SPE rate in silicon, however their saturation value
was based on the implanted hydrogen profiles, and did not account for any enhanced
interfacial hydrogen concentration due to the segregation that is seen in Fig. 4.1.

Even at pressures of less than $10^{-7}$ Torr, Olson and Roth[20] still observed a
surface source based diffusion profile of H in the thick 4.3 µm samples, however in this
case the hydrogen level did not remain fixed at the surface as annealing progressed.
Instead the hydrogen concentration tended towards a flat profile in the a-Si layer,
consistent with a limited source surface-based diffusion process. This limited source
of hydrogen would be the hydrogen that remained trapped in the surface region of
the sample as its temperature was raised to that of the annealing process.

Thin Layer Measurements

Since most of the SPE studies to date had been performed on thin layers, where the
amorphous overlayer was typically less than 1 µm thick, it is important to determine
what effect the undetected automatic intrusion of hydrogen has had on these past
results. By performing similar SIMS experiments on a-Si layers only 3400 Å thick,
Roth et al.[20] found that the hydrogen had already diffused into and saturated the
amorphous layer in a sample that had been only allowed to undergo a mere 200 Å
of SPE. The saturation level of hydrogen is again dictated by the surface pinning
level, which is on the order of $1 \times 10^{19} \text{cm}^{-3}$ to $5 \times 10^{19} \text{cm}^{-3}$. Since the saturation
of the a-Si layer with hydrogen is almost instantaneous in comparison to the time
taken for the SPE process, the thin layer SPE measurements of the past show no
variation in rate, and thus the presence of hydrogen was not immediately evident.
Even SPE measurements done in a vacuum furnace are not immune to the effect, as Roth \textit{et al.}\cite{20} found that thin layer samples annealed at pressures of $10^{-5}$ Torr still suffered hydrogen saturation in the a-Si layer, to concentrations of the same magnitude as those annealed in air.

**Effect on Previous Measurements**

Given the above results, it is reasonable to state that nearly all of the previous SPE measurements based on thin layer Si samples have been implicitly measuring the effect of hydrogen on the solid phase epitaxial regrowth rate, in conjunction with the SPE rate itself. The only case of hydrogen-free thin layer data is that of McCallum\cite{51}, who measured SPE in buried a-Si layers. By maintaining a crystalline layer at the surface, the indiffusion of hydrogen was effectively prevented, and good agreement with the thick layer hydrogen-free data of Roth \textit{et al.}\cite{20} was obtained.

As Olson and Roth had previously reported on the Arrhenius behaviour of SPE in a-Si based on thin layer data\cite{13}, they used this to compare with their recent thick layer SPE data\cite{20}, and thus deduced how to interpret previous results that were now known to be hydrogen affected. They found that while the hydrogen did affect the SPE rate, it did not affect the activation energy of the process itself. This observation was consistent with the argument that the hydrogen removes dangling bond sites that would be used in the crystallization process, without actually altering the energy required for a crystallization event.

**Requirements for Hydrogen Liberation**

It is useful to numerically evaluate the mechanism for the generation of hydrogen at the Si interface proposed by Roth \textit{et al.}, where H is liberated from H$_2$O by the formation of SiO$_2$. They report the formation of a $\sim 50$ Å SiO$_2$ layer upon completion of the anneal\cite{19}. For curve 6 in Fig. 4.1, approximately 70\% of the anneal has completed, and thus assuming a linear rate of oxide formation, there should be a native oxide layer that is $\sim 35$ Å thick at that point during the anneal.

A SiO$_2$ layer 35 Å thick would contain approximately $2 \times 10^{16}$/cm$^2$ oxygen atoms, assuming a density of 2.3 g/cm$^3$. By taking the worst case scenario, and making
the claim that 100% of the oxygen contained in that SiO$_2$ layer was liberated from the H$_2$O in the ambient, and that none of the oxygen in the SiO$_2$ was sourced from the O$_2$ in the ambient, one would have the liberation of $3 \times 10^{16}$ H/cm$^2$ atoms from the formation of that oxide. From the SIMS data of curve 6 in Fig. 4.1, there is approximately $1.4 \times 10^{15}$/cm$^2$ of hydrogen incorporated into the a-Si at that point. This consistency check shows that the amount of incorporated hydrogen is indeed below the maximum possible amount of hydrogen that could be generated during the formation of this oxide. For thin a-Si layers, this becomes a non-issue since the formation of only a few Å of SiO$_2$ solely via H$_2$O decomposition would be sufficient to generate enough hydrogen to saturate a 0.5 µm a-Si layer with a constant H level of $1 \times 10^{19}$/cm$^3$.

The main point of the above analysis was to demonstrate that hydrogen incorporation via H$_2$O decomposition relies on the formation of a native oxide layer that contains at least one oxygen atom per cm$^2$ for every two hydrogen atoms per cm$^2$ that are found in the underlying amorphous layer. Thus the incorporation of hydrogen into a-Si layers during the annealing process is not really a direct result of the inherent properties of silicon itself, but rather the result of the properties relating to favourable formation of a native oxide.

### 4.2.7 Dopant Concentration SPE Effects in Germanium

In comparison to silicon, the amount of data in the literature on dopant-enhanced solid phase epitaxial regrowth for germanium is very meager. Needless to say, the Si data in the literature is relevant to the Ge system in that one expects similar trends in behaviour, and these results are discussed in conjunction with the Si studies of this work found in section 5.2.3.

The only reported measurements in the literature of dopant-enhanced solid phase epitaxial regrowth in (100) Ge is that of Suni et al.[7], who reported on arsenic and boron doping in 1982. Their study involved using the partial anneal/RBSC technique as described in section 2.6.6 to determine the average interface velocity between multiple vacuum annealing steps. The measurement was repeated for the two temperatures 300 °C and 325 °C with an $^{75}$As implanted sample, a $^{11}$B sample, and
4.2. BACKGROUND INFORMATION

A sample containing both $^{75}$As and $^{11}$B. The (100) Ge substrates were amorphized with $^{28}$Si to a depth of $\sim 7000$ Å prior to the implantation of dopants. It is worth noting that the implant parameters they chose were based on assuming a simple Gaussian distribution with respect to depth for the implanted dopant species, and that it was these calculated profiles that were correlated with the measured SPE rates. No determination or verification of the actual implanted doses was reported.

**Arsenic in Germanium**

For the arsenic sample, multiple $^{75}$As implants were used in an attempt to create a fairly broad concentration profile of approximately $10^{20}$ As/cm$^3$. The implant parameters that Suni et al.[7] chose are listed in Table 4.1. Suni et al. noted that the use of a Pearson 4 distribution would have been more accurate than their Gaussian assumption, but apparently they did not have the computer resources available for such a calculation at that point in time. In light of this, the expected $^{75}$As distribution of each implant listed in Table 4.1 has been recalculated here using a Pearson 4 distribution[108]. The recalculated profiles, including the summation of all the $^{75}$As profiles, are shown in Fig. 4.2. The resultant theoretical profile varies between $\sim 8.5 \times 10^{19}$ /cm$^3$ and $\sim 9.7 \times 10^{19}$ /cm$^3$ in the depth region from 750 Å to 3000 Å. At 325 °C, Suni et al. measured the interface location four times in the zero to 5000 Å range, whereas at the lower temperature of 300 °C, they were able to measure the interface location seven times in the same depth interval. As only the mean interface velocity can be determined between two successive interface location measurements, one can see that the partial anneal/RBSC technique is not very effective when non-constant interface velocities are encountered.

From the measurements performed at the two different temperatures, Suni et al. were able to demonstrate that doping with $\sim 10^{20}$ As/cm$^3$ resulted in a SPE enhancement of $\sim 1.5 \times$ for a-Ge on (100) Ge in that temperature range. However, with only data points for two temperatures, a relatively non-uniform concentration profile, and all the limitations associated with a furnace/RBSC SPE measurement (cf. section 2.6.6), it was impossible to infer just how this enhancement would relate to the associated activation energy and velocity prefactor.
Figure 4.2: Theoretical distributions for the various implants of $^{75}$As into Ge used by Suni et al.[7]. The resultant $^{75}$As distribution (circles) from summing the individual profiles is also shown. The individual dopant profiles were calculated using a Pearson 4 distribution[108] into c-Ge with a sample normal to beam tilt of 10°.
Table 4.1: The implantation energies and nominal doses used for creation of $^{75}\text{As}$ doped ($\sim 10^{20}/\text{cm}^3$) a-Ge layers on (100) Ge by Suni et al.[7]. Implants were performed at 77 K, with a $10^\circ$ tilt and in the order that they appear in the table.

<table>
<thead>
<tr>
<th>Implantation Energy (keV)</th>
<th>Nominal As Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>$3.6 \times 10^{14}/\text{cm}^2$</td>
</tr>
<tr>
<td>340</td>
<td>$6.6 \times 10^{14}/\text{cm}^2$</td>
</tr>
<tr>
<td>600</td>
<td>$1.3 \times 10^{15}/\text{cm}^2$</td>
</tr>
<tr>
<td>700</td>
<td>$1.24 \times 10^{15}/\text{cm}^2$</td>
</tr>
</tbody>
</table>

Two other important results pertaining to As in Ge were noted by Suni et al. Firstly they found that for Ge samples with $\geq 2 \times 10^{20}$ As/cm$^3$ ($\sim 0.5$ at. %), the SPE rate was no longer enhanced, but rather was retarded in comparison to the intrinsic value. They correlated this dopant concentration with the similar value reported by Trumbore[109] for the solubility of As in Ge. The second result arose from using X-ray diffraction to look for polycrystalline germanium in a regrown sample containing a peak concentration of $\sim 2.5 \times 10^{20}$ As/cm$^3$ to see if the formation of polycrystalline material in the amorphous layer could account for the retarded rate. Since they were unable to find any, they concluded that the formation of polycrystalline layers was a result of the retarded SPE rate, and not the cause of it.

**Boron in Germanium**

In a similar fashion to the arsenic study reviewed above, Suni et al.[7] repeated the same experiment by replacing the multiple As implant sequence in Table 4.1 with a dual $^{11}$B implant. They implanted $2.3 \times 10^{15}$ B/cm$^2$ at 100 keV followed by $2.95 \times 10^{15}$ B/cm$^2$ at 180 keV to create an $^{11}$B profile with a peak concentration of $\sim 10^{20}$/cm$^3$. The expected $^{11}$B profile as determined from a Pearson 4 distribution[108] is shown in Fig. 4.3. From the two measurements at 300°C and 325°C they determined that for a concentration of $\sim 10^{20}$ B/cm$^3$, the SPE rate on (100) Ge was enhanced by a factor of $\sim 2.5$. Again, the limited nature of the data did not allow any conclusions to be drawn as to how this enhancement would affect the activation energy or the velocity prefactor.
Figure 4.3: Theoretical distributions for the various implants of $^{11}$B into Ge used by Suni et al.[7]. The resultant $^{11}$B distribution (circles) from summing the two individual profiles is also shown. Individual dopant profiles were calculated using a Pearson 4 distribution[108] into c-Ge with a sample normal to beam tilt of 10°.

Figure 4.4: Theoretical distributions for the various implants of $^{11}$B and $^{75}$As into Ge used by Suni et al.[7]. The difference between the As and the B is shown as the amount of excess B (stars) and the amount of excess As (diamonds). Individual dopant profiles were calculated using a Pearson 4 distribution[108] into c-Ge with a sample normal to beam tilt of 10°.
Compensation: Both Arsenic and Boron in Germanium

Suni et al. [7] took $^{11}\text{B}$ (100) Ge samples implanted as shown in Fig. 4.3, and then added an additional $^{75}\text{As}$ implant overlapping the $^{11}\text{B}$ implant to investigate the interaction between n-type and p-type dopants. For reference, the total $^{75}\text{As}$, $^{11}\text{B}$, and the remaining 'uncompensated' dopant levels are shown in Fig. 4.4.

They found that the SPE rate followed the enhancement of the sample with only $^{11}\text{B}$ from $\sim 7000$ Å to $\sim 4500$ Å, but then the rate dropped down to a value essentially equal to that observed for an undoped sample when the interface entered a region containing comparable amounts of both dopants. Also, when they implanted $^{11}\text{B}$ and $^{75}\text{As}$ to concentrations that were less than $2 \times 10^{19} / \text{cm}^3$, they did not observe an enhancement or a compensating effect.

4.2.8 Summary

There is considerable uncertainty in the activation energy for SPE in (100) Ge based upon past results, and even more uncertainty in the value of the associated velocity prefactor. In addition, the temperature range that previous measurements were performed over is relatively narrow in most cases. The two recent measurements that were part of Si$_x$Ge$_{1-x}$ studies [39, 40] both use SPE data taken from the near-surface region, even though prior studies [5, 11] in the literature reported an observed reduction in the SPE rate in this region. The use of a narrow depth range also implies that the SPE rate extracted from the TRR data is based on only a single interference cycle or less.

There is also no published data on whether or not hydrogen contamination effects SPE in Ge as it does in Si. Should there be similar effects in Ge then the results currently in the literature have to be considered with this in mind. This is an important issue that has not been dealt with to date, even though the effect in Si was first reported [19] back in 1990.

The issue of how dopants effect the SPE rate in Ge has only been touched on by one journal article [7]. These measurements employed the partial anneal/RBSC technique instead of TRR, and were limited to two temperatures only separated by $25 ^\circ \text{C}$. The data was only sufficient to ascertain that dopant effects on the SPE
rate in Ge appeared to be qualitatively similar to those observed in Si.

The work detailed in this chapter addresses these concerns. It covers the largest temperature range possible without having to use cw-laser heating. SPE measurements to depths exceeding 3 µm are reported, with the velocity determination involving up to 22 full interference cycles for the 1.5 µm wavelength TRR signal. An extensive study of hydrogen effects on the SPE rate in Ge has been performed, including the effect of implanted hydrogen in addition to that which was present in the ambient. The effects of dopants on the SPE rate in Ge has been investigated with the use of various constant concentration multiple implant samples. These measurements have provided the first qualitative measurements of this kind ever reported for Ge, and an insight into the concentration and temperature dependence of dopant-enhanced SPE in Ge has been obtained.
4.3 Experimental Methods

The following section documents the experimental details that were specific to the germanium portion of this work. General experimental methods that were applied throughout the study are described in Chapter 3.

4.3.1 Sample Preparation

Substrate Material

All of the Ge wafers used in this study were of a \(<100>\) orientation. All substrates were determined to have a surface normal to within \(1^\circ\) of the \(<100>\) direction via combining RBSC measurements with simultaneous surface reflections of a 632.8 nm laser collinear with the ion beam. Wafers from different suppliers, and of different background doping levels and types were used in an effort to determine if there were any associated effects on the solid phase epitaxial regrowth rate. The following substrates were used:

- p-type Ge \((1-5\Omega\cdot\text{cm})\) from supplier “A”.
- n-type Ge \(<0.4\Omega\cdot\text{cm})\) from supplier “B”.
- undoped Ge \(>30\Omega\cdot\text{cm})\) from supplier “B”.
- undoped \(>20\Omega\·\text{cm}\) thick wafer (0.5mm) from supplier “C”

Formation of Amorphous Germanium

The self implantation of Ge into \((100)\) Ge wafers was used to create high purity amorphous layers of uniform thickness on the original crystal substrates listed in section 4.3.1. For the Ge implants, the primary mass analysis was maximized around \(^{74}\text{Ge}\) to give the most beam current, as it is the most abundant isotope of Ge. The secondary mass analysis further ensured an isotopically pure beam.

One general recipe for the formation of a-Ge was used for most of the samples studied in this chapter, including the samples that received further implants of dopants. This involved multiple-energy self-ion implants as shown in Table 4.2. All
Table 4.2: Implantation energies and nominal doses used for creation of $\sim 1.5 \mu m$ thick a-Ge layers on (100) Ge. Implants were performed at 77 K and in the order that they appear in the table.

<table>
<thead>
<tr>
<th>Implantation Energy (keV)</th>
<th>Nominal Ge Dose</th>
<th>a-Ge thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>$5.0 \times 10^{15}/cm^2$</td>
<td>$\sim 0.4$</td>
</tr>
<tr>
<td>1000</td>
<td>$5.0 \times 10^{15}/cm^2$</td>
<td>$\sim 0.9$</td>
</tr>
<tr>
<td>2000</td>
<td>$5.0 \times 10^{15}/cm^2$</td>
<td>$\sim 1.5$</td>
</tr>
</tbody>
</table>

Table 4.3: The implantation energies and nominal doses used for creation of thick ($\sim 3.25 \mu m$) a-Ge layers on (100) Ge. Implants were performed at 77 K and in the order that they appear in the table.

<table>
<thead>
<tr>
<th>Implantation Energy (MeV)</th>
<th>Nominal Ge Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>$1.0 \times 10^{15}/cm^2$</td>
</tr>
<tr>
<td>2.0</td>
<td>$1.5 \times 10^{15}/cm^2$</td>
</tr>
<tr>
<td>4.6</td>
<td>$1.5 \times 10^{15}/cm^2$</td>
</tr>
<tr>
<td>7.6</td>
<td>$1.5 \times 10^{15}/cm^2$</td>
</tr>
</tbody>
</table>

implants were performed at 77 K to ensure efficient amorphization as discussed in section 3.3.2 and to avoid formation of the damage structure previously described in section 4.2.2.

The thinner amorphous layers that were studied in this work were created by only using the 550 keV and 1.0 MeV implants out of the sequence shown in Table 4.2. To check on any amorphization dose dependence, the implant sequence in Table 4.2 was repeated with a lower dose of $1 \times 10^{15}/cm^2$ per implant for one set of samples. The formation of extremely thick ($\sim 3.25 \mu m$) a-Ge layers involved four implantation steps, as documented in Table 4.3.

The doses chosen in the above tables were required to be high enough to ensure complete amorphization from the sample surface to the c/a interface lying near the end of range of the highest energy implant. In addition it was important to select doses that were low enough to ensure that none of the samples had formed or were in the process of forming the undesirable damage structure described in
### 4.3. EXPERIMENTAL METHODS

<table>
<thead>
<tr>
<th>Series</th>
<th>Substrate and Implantation Sequence Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>undoped Ge (&gt;30kΩ-cm) from supplier “B”. Implanted as per Table 4.2.</td>
</tr>
<tr>
<td>2</td>
<td>p-type Ge (1-5kΩ-cm) from supplier “A”. Implanted as per Table 4.2.</td>
</tr>
<tr>
<td>3</td>
<td>undoped Ge (&gt;30kΩ-cm) from supplier “B”. Implanted as per Table 4.2 but at only one fifth the dose per implant step.</td>
</tr>
<tr>
<td>4</td>
<td>n-type Ge (&lt;0.4kΩ-cm) from supplier “B”. Implanted as per Table 4.2.</td>
</tr>
<tr>
<td>5</td>
<td>undoped (&gt;20kΩ-cm) thick wafer (0.5 mm) from supplier “C”. Implanted with $5\times10^{15}$ /cm$^2$ at 1.0MeV followed by $1\times10^{15}$ /cm$^2$ at 100keV.</td>
</tr>
</tbody>
</table>

Table 4.4: Some of the substrates and implantation sequences used in the creation of samples used to study solid phase epitaxial regrowth of (100) Ge with 1.15 µm TRR.

Section 4.2.2. An immediate visual inspection of the samples did not reveal any black discolouration indicative of this structure. Only a slight difference between the reflectivities of the implanted and unimplanted regions was evident. Furthermore, RBS measurements of any of the samples showed no loss in the Ge yield when compared to that taken from a virgin sample that had not been implanted. Had this damage structure started to form, the near surface (<1500 Å) Ge yield would be reduced as discussed in section 4.2.2.

The implantation schemes documented above in Tables 4.2 and 4.3 were combined with the bare substrate materials as described in section 4.3.1 to create a variety of a-Ge layers on (100) Ge substrates. The combinations are listed and indexed in Table 4.4 to allow concise references to be made in the results section later in this chapter.

It should be noted that while the above samples were used to determine the solid phase epitaxial regrowth behaviour of intrinsic a-Ge, they are in fact only approximations to true intrinsic germanium, as they contain background doping levels. For reference, dopant effects on silicon SPE are only observed for dopant concentrations in excess of $\sim10^{18}$ atoms/cm$^3$, for which a similar doping level in germanium would result in a resistivity of only $\sim10^{-2}$ Ω-cm, as compared to a resistivity of 47 Ω-cm for true intrinsic germanium[65]. In contrast, the undoped Ge samples used here have a resistivity on the order of 20 Ω-cm, corresponding to an impurity concentration of only about $\sim10^{14}$ atoms/cm$^3$, and hence the treatment of these samples as “intrinsic germanium” is justified for the purpose of this study.
Explosive Crystallization (XCR)

By including thicker layers in the SPE studies another difficulty became apparent. These samples had amorphous layers approximately 3.25 µm thick, and had a very high failure rate in obtaining solid phase epitaxial regrowth through to the surface. In most cases no variation in the TRR signal was evident. A simple inspection of a typical failed sample under an optical microscope revealed patterns of radial lines emanating from a particular point on the sample. Finer ring patterns also centered about the same point could also be viewed. In essence, the pattern appeared similar to that obtained by impacting a glass window with a small projectile. The source point for these patterns was typically a small chip that had formed during the process of cleaving the sample down to a workable size. Those samples that cleaved cleanly and had the the most fragment-free edges had the highest probability of successfully obtaining SPE.

Further investigation revealed that the failed samples had undergone explosive or self-sustained crystallization[110], a process in which the annealing temperature combined with the heat release from crystallization are sufficient to maintain a melt-mediated growth process, once initiated. There is only enough energy available to sustain this phenomenon above some critical temperature $T_c$, and it has been observed that $T_c$ generally decreases with increasing amorphous layer thickness[111]. This explains why the move to thicker amorphous layers exposed this particular problem. Since this melt-mediated growth has been observed to proceed at rates in excess of 1 m/s, it is no surprise that the TRR signal showed no result.

By working at temperatures around and below 440 °C, a sufficient SPE success rate was obtainable so that the solid phase epitaxial regrowth rate in thick a-Ge layers could be monitored. However, the investigation of thicker a-Ge layers would most likely prove difficult, since the move from 1.5 µm to 3.25 µm thickness was sufficient to make explosive crystallization a common result.

Hydrogen in Amorphous Germanium

SIMS measurements of hydrogen content were performed on as-implanted and partially annealed a-Ge samples from Series 1. These measurements were repeated
4.3. EXPERIMENTAL METHODS

multiple times to verify reproducibility and to enhance the low-count statistics. A
Cesium primary beam was used with a sputter rate of $\sim 200 \text{ Å/s}$. The SIMS was
performed by Charles Evans and Associates[112] as their system offered a H back­
ground signal level that was about an order of magnitude lower than that of the local
facility at the time of the experiment. This background level is shown in Fig. 4.5.

Also shown in Fig. 4.5 is the SIMS profile from the H reference sample that
was implanted at 100 keV to a total dose of $1.0 \times 10^{15} \text{ H/cm}^2$. This reference was
used to quantify the SIMS data into H concentration values for the a-Ge samples.
A considerable “surface contamina­tion” tail appears in the $0-2000 \text{ Å}$ region of the
signal, rapidly dropping below $\sim 10^{18} \text{ H/cm}^3$ for depths greater than $2000 \text{ Å}$.

In addition, hydrogen was implanted into a-Ge created as per Table 4.2 to
study the effect of hydro­gen on the solid phase epitaxial regrowth rate of germ­

manium. Three different implantation doses of 80 keV H were used, those be­
ing $3.0 \times 10^{14} /\text{cm}^2$, $6.0 \times 10^{14} /\text{cm}^2$, and $1.2 \times 10^{15} /\text{cm}^2$, giving peak concentrations
of approximately $1 \times 10^{19} /\text{cm}^3$, $2 \times 10^{19} /\text{cm}^3$, and $4 \times 10^{19} /\text{cm}^3$ respectively. The
expected hydrogen distributions as determined from computer simulations[108] are
shown in Fig. 4.6. The samples were implanted at room temperature at a rate
of $1 \mu\text{A/cm}^2$. One of the $1.2 \times 10^{15} /\text{cm}^2$ samples was subjected to a partial an­
neal at $420\text{ °C}$ for 318 seconds and was then also profiled for hydrogen content
using SIMS.

Formation of Arsenic Doped Samples

The samples that were implantation doped with arsenic were first amorphized with
Ge as per Table 4.2. A sequence of As implants was chosen that would give a rea­
sonably flat arsenic concentration profile over an extended depth range where SPE
could be monitored by TRR. The implantation energies had to also lie within the
operable range of the implanter being used, but in this case it was not a limiting fac­
tor. The theoretical implant profiles were determined using a commercially available
computer simulation code[108]. The implant parameters that were chosen are shown
in Table 4.5. These implant conditions give a constant As level of $\approx 1 \times 10^{20} /\text{cm}^3$ in
the region between $2500 \text{ Å}$ and $5500 \text{ Å}$, as shown in Fig. 4.7.
Figure 4.5: SIMS measurement of a hydrogen reference implant of $1.0 \times 10^{15}$ /cm$^2$ into silicon (circles). Note that there is a considerable “surface contamination” signal from the implanted sample in the 0–2000 Å region. The background level ($\sim 10^{17}$ H/cm$^3$) for the instrument is also shown (triangles).

Figure 4.6: As-implanted distribution for implants of 80 keV hydrogen ions to doses of $3.0 \times 10^{14}$ /cm$^2$, $6.0 \times 10^{14}$ /cm$^2$, or $1.2 \times 10^{15}$ /cm$^2$ as per Profile[108] simulation code. Resulting peak concentrations are approximately $1 \times 10^{19}$ /cm$^3$, $2 \times 10^{19}$ /cm$^3$, and $4 \times 10^{19}$ /cm$^3$ respectively.
4.3. EXPERIMENTAL METHODS

Figure 4.7: Theoretical arsenic implantation profiles used to create an overall constant As concentration of $\approx 1 \times 10^{20}$/cm$^3$ over the depth range from 2500 Å to 5500 Å. Individual implant profiles are shown in conjunction with the total As concentration, as calculated using computer simulations[108].
Implantation Energy (MeV) | Nominal As Dose  
--- | ---  
1.2 | \(4.94 \times 10^{15}/\text{cm}^2\)  
0.8 | \(9.49 \times 10^{14}/\text{cm}^2\)  
0.5 | \(1.27 \times 10^{15}/\text{cm}^2\)

Table 4.5: The implantation energies and nominal doses used for creation of As doped a-Ge layers on (100) Ge. Implants were performed at 77 K and in the order that they appear in the table. The predicted resultant As profile has a constant As level of \(\approx 1 \times 10^{20}/\text{cm}^3\) in the region between 2500 Å and 5500 Å.

It should be mentioned that the density parameter used in these simulations was 5.32 g/cm\(^3\), which is the accepted value for c-Ge. However, the actual implants were in fact into a-Ge, and it is probable that the density of a-Ge is fractionally less (\(\sim 1\%\)) than that of c-Ge, as discussed below in section 4.3.2. This difference in density would manifest itself as an expansion of the depth scale in Fig. 4.7 by the same fractional amount.

Two other constant arsenic concentration profiles in a-Ge were created, those being \(5 \times 10^{19}/\text{cm}^3\), and \(1 \times 10^{19}/\text{cm}^3\), which were formed by scaling the doses in Table 4.5 by factors of 0.5 and 0.1 respectively. The As profiles of these samples would be the same as similarly scaled versions of those shown in Fig. 4.7. Variations due to the different levels of surface sputtering are expected to be negligible for these implant doses.

Since the mass of \(^75\text{As}\) lies within the spread of masses for the various natural isotopes of Ge, it cannot be detected by means of an RBS measurement. However, the same is not true for arsenic implanted into silicon, and thus the accuracy of the implanted dose can be verified in that case. Hence the accuracy of the nominal dose determined by integration of the implanter beam current was verified using RBS measurements on arsenic implanted silicon samples that were prepared at the same time and under similar conditions as the arsenic implanted germanium. The implanted doses measured by RBS agreed to within 5% of the nominal dose as determined by charge integration during implantation.
Table 4.6: The implantation energies and nominal doses used for creation of Al doped a-Ge layers on (100) Ge. Implants were performed at 77 K and in the order that they appear in the table. The predicted resultant Al profile has a constant Al level of $\approx 1 \times 10^{20} / \text{cm}^3$ in the region between 5000 Å and 9000 Å.

**Formation of Aluminum Doped Germanium**

The aluminum doped samples were created in a similar fashion to the arsenic samples described above. One of the reasons aluminum was chosen over a more typical p-type dopant species such as boron was due to the fact that the range of an implanted boron ion is far greater than that of aluminum for a given implant energy. For $\sim 100$ keV implants into germanium, the range of boron ions is typically twice that of aluminum ions. In addition, there are no reports of aluminum-enhanced SPE for germanium in the literature. The other common p-type dopants, gallium and indium were not chosen for this study based on factors such as solubility limits, diffusion rates, and due to complications that can arise due to their low melting points. One example of such an effect is the polycrystalline transformation mediated by highly mobile molten precipitates that has been observed in Si doped with these impurities[113].

The aluminum implant energies were chosen to create a constant dopant profile, as was done in the arsenic case, and these values are shown in Table 4.6. In addition, the Al energies were chosen so that there would be partial overlap of the Al and As profiles for the dopant compensation measurement. This was best achieved by implanting the Al deeper than the As. Again, the theoretical implant profiles were determined using computer simulations[108]. The resultant profiles, and the expected sum profile, showing the total aluminum concentration are shown in Fig. 4.8. As can be seen, the predicted Al concentration is reasonably constant at $\approx 1 \times 10^{20} / \text{cm}^3$ over the depth range from 5000 Å to 9000 Å.

<table>
<thead>
<tr>
<th>Implantation Energy (keV)</th>
<th>Nominal Al Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>$6.00 \times 10^{15} / \text{cm}^2$</td>
</tr>
<tr>
<td>520</td>
<td>$1.65 \times 10^{15} / \text{cm}^2$</td>
</tr>
<tr>
<td>360</td>
<td>$2.00 \times 10^{15} / \text{cm}^2$</td>
</tr>
</tbody>
</table>
Figure 4.8: Theoretical aluminum implantation profiles used to create an overall constant Al concentration of $\approx 1 \times 10^{20}$/cm$^3$ over the depth range from 5000 Å to 9000 Å. Individual implant profiles are shown in conjunction with the resulting sum total Al concentration. The individual dopant profiles were calculated using computer simulations[108].
4.3. EXPERIMENTAL METHODS

Unlike the As case, silicon cannot be used as a host material to check the implanted dose with RBS. With aluminum having a mass just slightly less than that of silicon, the Al yield is small as compared to the yield from the Si host in this concentration regime and hence cannot be measured accurately. Thus Secondary Ion Mass Spectrometry (SIMS) was employed to look at the Al profile in the a-Ge layer. An 8 keV primary beam of O$_2$ was used, and positive secondary ions were monitored. The aluminum signal is shown in Fig. 4.9. The depth scale shown was established by measurement of the SIMS sputter crater with a profilometer, and then assuming a linear sputtering rate with respect to time. As can be seen, the shape of the aluminum profile and the depth scale are in good agreement with the predicted profile shown in Fig. 4.8. Absolute Al concentration could not be determined from the SIMS measurements so the doses obtained from the implant dosimetry were assumed to be correct (cf. As dosimetry).

Two other constant aluminum concentration profiles in a-Ge were created by scaling the doses in Table 4.6 by factors of 0.5 and 0.1 to create aluminum levels of $5 \times 10^{19}$/cm$^3$, and $1 \times 10^{19}$/cm$^3$, respectively. The shape of the Al profile in these lower dose samples would be the same as those shown in Fig. 4.8.

**Formation of a Compensation Doped Sample**

By implanting both As and Al into the same sample with the concentration profile partially overlapping over one depth region, the combined effect of p-type and n-type dopants on the solid phase epitaxial regrowth can be observed. The doses used for implanting arsenic and aluminum into this sample are the same as those listed in Table 4.5 and 4.6, except that the doses used were scaled by a factor of 0.5 to give an overall concentration of $\approx 5 \times 10^{19}$/cm$^3$ of each dopant, as shown in Fig. 4.10. It is worth noting that the creation of this sample involved a total of nine implantation steps, as it was amorphized according to Table 4.2 prior to the implantation of the dopant species. Yet there was still no direct evidence of formation of the porous structure as described in section 4.2.2.

The excess or uncompensated amount of each dopant is also shown on Fig. 4.10. The amount of compensated dopant is that for which there is an equal but opposite
Figure 4.9: SIMS profile of aluminum content in a-Ge after performing implants as listed in Table 4.6. The depth scale was determined from the depth of the sputter crater left from SIMS measurement, given that a constant sputter rate was used throughout the analysis. The profile was taken with an 8 keV O₂ primary beam.
### 4.3. EXPERIMENTAL METHODS

Figure 4.10: Total As and Al concentration after performing implants as listed in Tables 4.5 and 4.6. The total amount of excess n-type As dopant that is not compensated by p-type Al dopant is shown by the curve marked with diamond symbols. Similarly, the total amount of excess p-type Al dopant that is not compensated by n-type As dopant is shown by the curve marked with star symbols.
type of dopant present. From the surface to a depth of approximately 5600 Å, there is a surplus of the n-type As in comparison to the quantity of p-type Al, and thus an overall addition of n-type carriers to this region. The amount of the uncompensated As is indicated in Fig. 4.10 by the curve with the diamond symbols. Similarly, in the region from 5600 Å to about 15000 Å, there is an excess of the p-type Al in comparison to the quantity of n-type As, and hence an addition of p-type carriers to this region. The amount of the uncompensated Al is indicated in Fig. 4.10 by the curve with the star symbols.

4.3.2 TRR and Refractive Index Determination

The TRR measurements used in the a-Ge studies were performed over the temperature range from 300 °C to 540 °C. Most of the experiments were performed using a TRR wavelength of 1.152 µm, allowing observation to depths up to ~ 1 µm. A few thicker a-Ge layers were studied with a TRR wavelength of 1.523 µm. The following subsections present the criteria for the selection of the above parameters, along with the experimental method used for the determination of the index of refraction. General details of the TRR system can be found in section 3.2, as only specifics relating to its use for studying germanium are presented here.

Temperature Range of this Study

Samples were studied over the temperature range spanning from 300 °C to 540 °C. As will be shown in the following sections, this temperature range covers SPE growth rates ranging from ~ 0.01 Å/s to velocities in excess of 10^5 Å/s. The maximum temperature is limited by the fact that the total anneal time eventually becomes so small as to be comparable to the time required for the sample to reach steady-state temperature conditions. For a-Ge layers a few microns thick, this maximum temperature is ~ 540 °C. At the other end of the regime, the limiting factor is having the anneal complete in a reasonable amount of time. At 300 °C, the complete regrowth of a-Ge layers a few microns thick can take in excess of a week.
4.3. EXPERIMENTAL METHODS

Wavelength Considerations

Figure 4.11 shows a typical TRR curve obtained from the solid phase epitaxial regrowth of an amorphous germanium layer approximately 1.5µm thick. The wavelength of the TRR system is 1.152µm in this case, and the annealing temperature was 400 °C. The x-axis of the plot is the elapsed annealing time, and the y-axis is proportional to the amplitude of the 1.152µm signal that is reflected from the sample, normalized against the incident signal amplitude.

It is worth noting that just as the anneal completes and the c/a interface reaches the surface, the TRR signal makes a smooth transition from its oscillatory nature to that of the pure c-Ge signal, rather than the sharp instantaneous transition that a theoretical curve, such as that shown in Fig. 2.7 would predict. Factors such as interface roughness, surface contamination and surface roughness will contribute to the shape of the TRR curve in this region.

As can be seen from Fig. 4.11, for 1.152µm TRR in a-Ge, the useful depth range is about two thirds of the complete curve, which is from a 1.5µm a-Ge layer. For a-Ge, in the wavelength range of interest to TRR measurements (0.5µm – 1.5µm), the absorption coefficient increases with decreasing wavelength. This result is immediately apparent when viewing Fig. 4.12, which shows the TRR curve collected from the same sample as in Fig. 4.11, except the signal was collected at a wavelength of 632.8 nm. In this case, the attenuation of the penetrating beam is considerably larger, reducing the number of useful oscillations in the TRR curve to about one. Evidently, a 632.8 nm wavelength TRR system is not a useful tool for probing solid phase epitaxial regrowth in a-Ge.

The 1.152µm wavelength provides a reasonable intermediate value at which neither the maximum depth nor the depth resolution are compromised for studying a-Ge layers less than 1µm thick. Thus, it is used for most of the TRR studies presented in the following sections. For TRR studies where a large maximum depth in a-Ge was required, a 1.5µm TRR signal was used, allowing the TRR signal to probe depths in excess of 3µm.
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

Figure 4.11: Typical 1.15 µm TRR curve shown for the full anneal of an a-Ge layer approximately 1.5 µm thick at 400 °C.

Figure 4.12: Typical 632.8 nm TRR curve shown for the full anneal of an a-Ge layer approximately 1.5 µm thick at 400 °C.
Determination of the Index of Refraction of a-Ge

To date, TRR measurements of SPE in a-Ge have typically relied on the refractive index values for a-Ge reported by Connell et al.[89] and papers cited therein, where the indices were derived from measurements of the optical properties of sputter deposited or evaporated films. Measurements of optical constants based on sputter deposited or evaporated layers typically suffer from errors associated with factors such as density variations within the films, or relatively high levels of incorporated impurities (mainly oxygen). In fact, Connell et al. estimated that their a-Ge films contained oxygen concentrations ranging from <0.1 atomic percent to 0.5 atomic percent. On the other hand, amorphous layers formed by ion-implantation methods are of high purity, and a-Ge layers can be created with a very high degree of reproducibility. The value reported by Connell et al. has been used in recent studies such as those done by Lu et al.[11]. As discussed in section 2.6.3, it is this value which sets the depth scale for the theoretical curve of reflectivity versus depth. Unfortunately the refractive index value for crystalline germanium, which is readily available[114-117], only affects the amplitude of the TRR signal.

Here an independent determination of the index of refraction for the amorphous Ge layers that were produced by ion-implantation is presented. As mentioned in section 2.6.3, the index of refraction of the overlying amorphous layer must be known, so that the TRR data can be transformed into interface depth versus time.

A sufficiently thick amorphous layer can be stopped at any point in the annealing process. This is simply achieved by removing the sample from the heating stage. For all intents and purposes, the SPE process stops immediately upon removal, due to the exponential dependence on the temperature. These “stopped” samples can then be subjected to RBSC measurements to accurately determine the thickness of the remaining amount of amorphous material. Returning these same samples to the TRR measurement system verifies the stop point against the point at which the TRR curve is observed to resume. By overlaying the pre and post-RBS TRR curves, one obtains a full TRR curve, with a discontinuity that gives a clear indication of the point in the TRR curve at which the RBS measurement of the remaining amorphous layer was performed. While this second step of finishing the annealing process on
the TRR system is not necessarily required to determine the interruption point with respect to the TRR curve, it does however make its determination easier and more accurate.

Given an amorphous layer extending from the surface to a known depth, and the knowledge of what point in the TRR curve that this depth corresponds to, it can be seen from Eq. 2.52 that the real part of the index of refraction for the amorphous material can be determined. In particular, the real part of the index of refraction is simply given by

\[ n = \frac{\lambda}{2\Delta x} \]  

(4.1)

where \( \Delta x \) is the change in the amorphous layer thickness associated with one full TRR interference cycle, and \( \lambda \) is the wavelength of the TRR signal being used. It is worth noting that the TRR curve should be divided by a suitable exponential to remove the attenuation envelope prior to locating interference maxima and minima. Fig. 4.13 shows a typical case where this calibration technique has been used. The top portion of the figure shows the TRR curve collected during an uninterrupted anneal performed on a Ge sample having an amorphous layer approximately 1.5\( \mu \)m thick. The anneal was performed at a temperature of 420 °C.

The second portion of the figure shows the TRR curves collected during the anneals before (solid line) and after (dashed line) the RBS measurement. The TRR curve taken after the RBS measurement is offset by the duration of the first part of the anneal done before the RBS measurement, so that they may be presented in a format that allows meaningful comparison with the complete TRR curve shown in the top portion. The discontinuity that is evident at approximately 220 seconds consists of two things. The first is the drop of the signal to zero amplitude corresponding to the point in time that the sample was removed from the annealing stage. The second is the rise of the signal from zero to the point at which it left off from the first part of the annealing process. As can be seen from the figure, the loading and unloading of samples can be performed in a time frame that is insignificant in comparison to the time scale of the measurement that is being performed. To obtain an accurate determination of the index of refraction value for a-Ge, six samples were partially annealed for various times, and thus to various points on the TRR...
4.3. EXPERIMENTAL METHODS

Figure 4.13: The $1.15\mu m$ TRR curve for complete crystallization of a thick a-Ge layer at 420 °C (top) and for an interrupted anneal (bottom). The discontinuity in the bottom curve marks the point at which the anneal was stopped and the RBS measurement was performed.

Figure 4.14: RBS spectra taken from partially annealed a-Ge layers at 420 °C. The measured thickness is used in conjunction with the TRR data to determine the index of refraction for amorphous germanium at $1.15 \mu m$. 
curve similar to the one shown in the top half of Fig. 4.13. The RBSC data from these samples is shown in Fig. 4.14. By correlating the number of TRR interference cycles with the remaining a-Ge layer thickness, the amount of a-Ge per interference cycle can be determined. This result is displayed in Fig. 4.15. The location of the interruption point in the annealing sequence as seen on the TRR curve could be determined to within 0.05 cm of a full TRR interference cycle. For thicker a-Ge layers, the signal to noise ratio is smaller due to absorption of the laser light in the a-Ge layer. In these cases the accuracy of determining the interruption point in the annealing sequence was within 0.08 of a full TRR interference cycle. The resultant slope gives a value of 1078 Å per interference cycle, and thus an index of refraction for a-Ge at 1.152 µm and 420 °C of 5.34±0.15.

While this value is significantly higher than the value of 4.8 reported by Connell et al.[89] and used in other studies[11], it is felt that the difference can be attributed to the lower density and O content of the sputter deposited or evaporated a-Ge films used by Connell et al.[89]. The a-Ge layers of this work that were created with ion implantation techniques would have a higher density, and thus a higher index of refraction is to be expected.

It should be noted that the stopping powers of He in Ge used here to convert the RBS energy spectrum to a depth scale were those of crystalline germanium. This contains the implicit assumption that the density of a-Ge is the same as that of c-Ge, which is not unreasonable as the density of well-relaxed a-Ge has been verified to be close to that of c-Ge[118]. Once again, density measurements based on evaporated a-Ge layers are not applicable to those created by ion implantation of c-Ge. It is worth considering the data reported by Custer et al.[75] who performed measurements on the density change associated with the creation of a-Si from self ion-implantation into c-Si, and found that the density of the a-Si layer was typically 1.2% less than that of the c-Si value. If it is assumed that a similar density reduction would be observed for a-Ge created by self-implantation, then the thickness measurements reported in Fig. 4.14 will be underestimated by the same percentage. The propagation of this error would result in the calculated index of

CHAPTER 4. SPE OF AMORPHOUS GERMANIUM
Figure 4.15: Thickness data determined from RBS spectra taken from partially annealed a-Ge layers at 420 °C versus the number of remaining TRR interference oscillations. The index of refraction for a-Ge at 1.15 µm was determined from the slope of this curve.
refraction being over-estimated by the same percentage. The magnitude of this over-
estimation in the case of the above reported index of refraction value is within the
quoted error on the determined value. Also, the systematic use of an over-estimated
index of refraction value will not affect the activation energy determined from the
TRR data, as demonstrated in section 2.6.4. However, it will affect the absolute
value of the solid phase epitaxial regrowth rates that are determined.

Index of Refraction Variations with Temperature

A similar technique was used to determine if there was a significant variation in the
index of refraction as a function of temperature for a-Ge. This involved annealing
two samples from the same bulk material at two different temperatures to some
common point on the TRR curve, and then stopping the anneal. RBSC was then
used to measure the remaining a-Ge layer thickness for each of the two samples.
If there was a significant difference in the index of refraction associated with the
difference in temperature, then the a-Ge layer thickness associated with a complete
interference cycle would be different for each value of ‘n’ and this difference would
be given by

\[ \Delta x = \left\{ \frac{\lambda}{2} \cdot \frac{n_{T1} - n_{T2}}{n_{T1} \cdot n_{T2}} \right\} \]

(4.2)

where \( \lambda \) is the wavelength of the laser used by the TRR system, and \( n_{T1}, n_{T2} \) are
the respective indices of refraction for the two different temperatures.

For multiple interference cycles, the total difference between the two depth cal-
culations will simply be \( \Delta d = m \Delta x \), where \( m \) is the total number of interference
cycles. Since the difference in depth increases linearly with the number of cycles,
this comparison is best performed with relatively thick layers so that maximum
sensitivity to any small differences in the index of refraction at the two different
temperatures is achieved. However, this must be weighed against the accuracy with
which a common point on the respective TRR curves can be determined. This task
becomes increasingly difficult for points on the curve corresponding to increasingly
deeper interface locations, due to the decreasing signal-to-noise ratio.

Samples from the same bulk material were annealed until they reached the same
point on the TRR curve, and then RBSC measurements were performed on these
two samples. The samples were stopped with the \( c/a \) interface \( \sim 0.5 \mu m \) from the surface, and the temperatures used were \( 340 \, ^\circ C \) and \( 440 \, ^\circ C \). This stop point results in approximately 4.5 interference cycles to be observed upon completing the anneal after the RBSC measurements. To simplify the problem of stopping the two anneals at the same point on the TRR curve, the higher temperature anneal was performed first, and the lower temperature anneal second. The slower SPE rate of the lower temperature anneal enables the operator to duplicate the two stop points with a high degree of accuracy. The RBSC measurements showed no variation in the remaining \( a\)-Ge layer thickness for the two temperatures studied.

The study of \( a\)-Ge in this chapter covers the temperature range from \( 300 \, ^\circ C \) to \( 540 \, ^\circ C \). The measurement of the index of refraction was performed approximately midway in this range at \( 420 \, ^\circ C \). To within the experimental errors, no detectable change in the index of refraction could be observed between measurements performed at \( 340 \, ^\circ C \) and \( 440 \, ^\circ C \). Hence for the studies presented here, the index of refraction was treated as constant over the range of \( 300 \, ^\circ C \) to \( 540 \, ^\circ C \). For reference, it should be noted that Li[115] estimates \( \frac{dn}{dT} \) at \( \sim 6 \times 10^{-4} /K \) for \( c\)-Ge at a wavelength of \( 1.152 \mu m \), based upon extrapolations to fits of data sets for \( \lambda \geq 2 \mu m \). If one were to assume this same value was also valid for \( a\)-Ge, then this would amount to a \( \Delta n = \pm 0.07 \) for the temperature range of \( \pm 120 \, ^\circ C \), which is within the error limits of the \( n \) value quoted earlier.

**Variation of Index of Refraction with Dopant Concentration**

In all cases, the peak concentrations of dopants used in this study were less than 0.25 atomic percent, which would not be expected to have a significant effect on the index of refraction of the amorphous material. Lohner et al.[119] measured the ellipsometric parameters \( \Psi \) and \( \Delta \) (from which values of \( n \) and \( k \) can be calculated) for silicon implanted with 40–80 keV Si, Al, As and P, to doses between \( 10^{14} /\text{cm}^2 \) and \( 10^{17} /\text{cm}^2 \). Even at the highest dose studied, where the peak concentrations were in excess of 10 atomic percent, they found no clear evidence of an impurity effect on the ellipsometric parameters \( \Psi \) and \( \Delta \). They did observe variations in the ellipsometric parameters for low dose implants, and used RBS measurements to
Table 4.7: The number of remaining full TRR oscillations versus the remaining thickness of a-Ge as measured by RBS. These values were used to determine the a-Ge layer thickness per oscillation, and thus directly measure the index of refraction of a-Ge at 1.523 µm wavelength.

Table: 
<table>
<thead>
<tr>
<th>Thickness via RBS</th>
<th>Number of TRR oscillations</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800±75</td>
<td>0.51±0.05</td>
</tr>
<tr>
<td>2200±100</td>
<td>1.49±0.05</td>
</tr>
<tr>
<td>3600±100</td>
<td>2.45±0.05</td>
</tr>
<tr>
<td>7500±100</td>
<td>4.97±0.05</td>
</tr>
</tbody>
</table>

verify that these variations were due to the transition from crystalline to amorphous material. This indicates that the lower limit on the sensitivity of their apparatus was sufficient to detect changes in \( n \) of the order associated with the transition from c-Ge to a-Ge, and that any dopant induced effects fall below this level for a few atomic percent in a silicon host matrix. Hence, for this study, the index of refraction has been taken as invariant with respect to the doping levels used.

**Index of Refraction of a-Ge at 1.523 µm**

To monitor SPE in the few thick layer (>3 µm) a-Ge samples that were studied, the utilization of a longer wavelength TRR system was required, as was discussed in section 4.3.2. Given the rapid rate of change in the absorption coefficient of a-Ge around the 1 µm point, the move from a 1.15 µm laser to a 1.5 µm laser was more than sufficient to probe well beyond a depth of 3 µm in a-Ge.

Once again, the index of refraction for a-Ge had to be determined for this particular wavelength. Using the same partial anneal technique as described above, the data presented in Table 4.7 was obtained. Note that the point (0, 0) is taken for granted, as there are no remaining oscillations once the remaining a-Ge thickness is reduced to zero. The data in Table 4.7 is displayed graphically in Fig. 4.16.

The slope of the curve in Fig. 4.16 gives a result of 1501 Å per full interference cycle for 1.523 µm TRR of a-Ge. Combining this result with Eq. 2.52 gives the index of refraction of a-Ge for 1.5 µm and 420 °C as 5.07±0.17, which is the value
Figure 4.16: The number of remaining full TRR oscillations versus the remaining thickness of a-Ge as measured by RBS. These values were used to determine the a-Ge layer thickness per oscillation, and thus directly measure the index of refraction of a-Ge at 1.523 \( \mu m \) wavelength.
used in the analysis of the following TRR data. Connell et al. [89] report a low variation in the index of refraction of a-Ge with temperature for incident radiation of around 1 eV. Thus the value of $n$ reported above was considered constant with respect to temperature for the limited temperature range in which the 1.523 µm TRR data was collected.
4.4 SPE of Intrinsic a-Ge Layers

To accurately study the effect of dopants on the solid phase epitaxial regrowth behaviour of amorphous germanium, an accurate determination of the intrinsic growth behaviour in the absence of any other possible effects is needed first. Ideally these measurements should be taken on the same experimental apparatus so there is at most one set of systematic errors introduced, rather than comparing data sets taken from different systems, and on different samples under different conditions.

The primary limitation of the past measurements is that of a relatively small temperature range, coupled with a temperature measurement that is not accurate enough in light of the observed exponential temperature dependence. By comparing the activation energy reported for each past study (as listed in section 4.2 and summarised in Table 4.9) it is evident that it has not yet been determined to an equivalent accuracy as that of the corresponding silicon value. It is safe to say that the value lies somewhere between 2.0 and 2.3 eV. However, such a margin is not sufficiently narrow to allow conclusions about doping effects, if their presence only alters the activation energy at the 5% level or less. The following section addresses these problems by reporting on the solid phase epitaxial regrowth behaviour for various samples containing intrinsic amorphous germanium layers which have been measured as part of the current work.

4.4.1 Measurement of SPE Rate on (100) Ge

Samples from Series 1 as described in Table 4.4 were used as the basis for determining the solid phase epitaxial regrowth behaviour of intrinsic high purity a-Ge. TRR data was collected in 20 °C intervals from 300 °C to 540 °C for a total of 13 measurements. The c/a interface velocity for a given temperature was then extracted from the TRR curve by the mapping process described in section 3.2.11. This data is presented in an Arrhenius form in Fig. 4.17. The activation energy for this curve is $E_a = 2.13 \pm 0.05$ eV with a velocity prefactor of $V_o = 1.9 \times 10^7$ m/s.

To ensure that the data presented in Fig. 4.17 is an accurate representation of the solid phase epitaxial regrowth process in intrinsic a-Ge material, a large number of other a-Ge samples were also examined in an identical fashion. These different
Figure 4.17: The Arrhenius behaviour of solid phase epitaxial regrowth of undoped (>30 \(\Omega\cdot\text{cm}\)) a-Ge (Series 1). The activation energy from this curve is \(E_a = 2.13\) eV with a velocity prefactor of \(V_o = 1.9 \times 10^7\) m/s. Error bars shown represent \(\pm 15\%\) for velocity values and \(\pm 1.5\) °C for temperature values.
4.4. **SPE OF INTRINSIC A-GE LAYERS**

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>$E_a$ (eV)</th>
<th>$V_o$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td>2.13</td>
<td>$1.9 \times 10^7$</td>
</tr>
<tr>
<td>Series 2</td>
<td>2.16</td>
<td>$3.2 \times 10^7$</td>
</tr>
<tr>
<td>Series 3</td>
<td>2.15</td>
<td>$2.6 \times 10^7$</td>
</tr>
<tr>
<td>Series 4</td>
<td>2.16</td>
<td>$3.0 \times 10^7$</td>
</tr>
<tr>
<td>Series 5</td>
<td>2.14</td>
<td>$2.2 \times 10^7$</td>
</tr>
</tbody>
</table>

Table 4.8: The activation energies and velocity prefactors obtained from the various series of samples of a-Ge studied in this work.

substrates either varied in their origin and background doping or in the implantation conditions used to create the amorphous layer as documented in Table 4.4. The actual annealing process was left unchanged. The $c/a$ interface velocity was only calculated from the TRR data at 40 °C intervals for most of these additional runs. In addition, some of the low temperature measurements were left out of these subsequent sample sets due to the long annealing times required at low temperatures. The results from these additional runs are shown in Fig. 4.18.

By displaying the $c/a$ interface velocity data for each of these substrates all on one Arrhenius plot, it is difficult to see any difference between them. In fact they appear to lie directly on top of each other, as can be seen in Fig. 4.18. For clarity, only the fit line for the undoped data associated with Series 1 is shown on the graph. However, it is instructive to normalize the respective velocities of each data set against the expected interface velocity for a strict Arrhenius dependence with an activation energy of $2.13$ eV and a velocity prefactor of $V_o = 1.9 \times 10^7$ m/s. These normalized data sets are shown in Fig. 4.19. The respective activation energies and velocity prefactors for each series of samples are summarised in Table 4.8.

As with the Arrhenius curve, differences in activation energy show up as a change in slope, and differences in the velocity prefactor produce a vertical shift. Small differences that are not evident on the Arrhenius plot become much more apparent on a normalized velocity plot, as demonstrated in section 2.6.5. Note that the scale on the y axis is relatively small, indicating that the data sets are indeed very similar. This indicates that there is no significant variation in the solid phase epitaxial regrowth
Figure 4.18: Arrhenius behaviour of solid phase epitaxial regrowth of various a-Ge layers studied in this work. Only the fit to the Series 1 data is shown for clarity. Substrates are: Series 1, undoped (circles), Series 2, p-type (diamonds), Series 3, low-dose amorphization (crosses), Series 4, n-type (stars), Series 5, 0.5 mm substrate (triangles).
4.4. **SPE OF INTRINSIC A-GE LAYERS**

Figure 4.19: Normalized plot for solid phase epitaxial regrowth of various a-Ge layers. The solid line at y=1 corresponds to $E_a = 2.13$ eV and $V_o = 1.9 \times 10^7$ m/s, as determined from Fig. 4.17. The c/a interface velocities for all of the a-Ge data sets have been normalized to this strict Arrhenius dependence. The two dashed lines mark the boundaries that are obtained by considering a systematic temperature error of $+1$ °C and $-1$ °C respectively. Substrates are: Series 1, undoped (circles), Series 2, p-type (diamonds), Series 3, low-dose amorphization (crosses), Series 4, n-type (stars), Series 5, 0.5 mm substrate (triangles).
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

<table>
<thead>
<tr>
<th>a-Ge Study</th>
<th>( E_a ) (eV)</th>
<th>( V_o ) (m/s)</th>
<th>Method</th>
</tr>
</thead>
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<tr>
<td>Csepregi et al. [5]</td>
<td>2.0</td>
<td>Not Reported</td>
<td>Furnace/RBS</td>
</tr>
<tr>
<td>Lu et al. [11]</td>
<td>2.17±0.2</td>
<td>1.2\times10^7</td>
<td>DAC/TRR</td>
</tr>
<tr>
<td>Donovan et al. [6]</td>
<td>2.17</td>
<td>4.1\times10^7</td>
<td>Calorimetry</td>
</tr>
<tr>
<td>Olson et al. [14]</td>
<td>2.26</td>
<td>Not Reported</td>
<td>TRR</td>
</tr>
<tr>
<td>Kringhøj et al. [39]</td>
<td>2.02±0.015</td>
<td>(6.1±1.6)\times10^6</td>
<td>TRR</td>
</tr>
<tr>
<td>Haynes et al. [40]</td>
<td>2.19±0.02</td>
<td>7.4\times10^7</td>
<td>TRR</td>
</tr>
<tr>
<td>This work</td>
<td>2.15±0.04</td>
<td>(2.6±0.5)\times10^7</td>
<td>TRR</td>
</tr>
</tbody>
</table>

Table 4.9: The activation energies and velocity prefactors from past a-Ge studies reported in the literature.

...behaviour due to using substrates of different intrinsic background doping levels. Of course this result is only valid for samples with intrinsic resistivities that are at least as high as the ones studied here. For a sufficiently low resistivity substrate, and thus equivalently a sufficiently high background doping level, dopant effects on the solid phase epitaxial regrowth rate would be expected. Also, no variations due to initial amorphous layer thickness or base substrate material thickness were observed.

Furthermore, the a-Ge created using the low-dose implantation series does not exhibit a significant variation from that of the other samples studied. This reinforces the view that none of the a-Ge samples used in this study had developed the porous damage structure described above. If this was not the case, there would have been a significant difference between the low dose result and the others shown, since it is known that this damage structure seriously impedes the solid phase epitaxial regrowth process.

Fig. 4.20 shows the results of other studies of solid phase epitaxial regrowth in a-Ge, together with the data shown previously in Fig. 4.17, in a standard Arrhenius format. Table 4.9 summarizes the results from each of the studies shown in Fig. 4.20. The significance of the differences in the values reported in Table 4.9 are more easily visualized by the use of a normalized plot as mentioned earlier. The results from each study were normalized against the results from this study, shown earlier in Fig. 4.17. This normalized plot is shown in Fig. 4.21.
Figure 4.20: Arrhenius plot of various data sets taken from other studies involving solid phase epitaxial regrowth of amorphous germanium.

Figure 4.21: Plot of various data sets taken from solid phase epitaxial regrowth studies of amorphous germanium. Data sets have been normalized against the activation energy and velocity prefactor obtained in this study (solid line).
4.4.2 Consideration of Past Results

It is worthwhile to now consider briefly each of the individual Ge SPE measurements discussed in section 4.2 in light of the results of this study while also keeping in mind the need for an accurate measurement of the solid phase epitaxial regrowth behaviour of intrinsic germanium before moving on to studies of dopant concentration effects.

The measurement from Csepregi et al. [5] primarily suffers from all the shortcomings listed in section 2.6.6 that are associated with being a furnace/RBSC measurement. The temperature range spanned by this measurement is less than 40 °C, and the accurate determination of the sample temperature and the temperature-time profile in a vacuum furnace is even more difficult. In addition, the implantation sequence used to create the a-Ge used in their study resulted in a very high dose of implanted ions per unit depth, thus possibly placing the samples into the regime where the damage structure described in section 4.2.2 begins to form. The fact that they observed the Ge implanted samples to have a more retarded SPE rate than the Si implanted samples tends to support this hypothesis.

The calorimetry measurement by Donovan et al. [6] also only covers a temperature range of about 40 °C, and this technique is unable to be used for temperatures below ~ 400 °C. Despite this, their results are in good agreement with those of this work.

The results of Lu et al. [11] obtained from the diamond anvil cell (DAC) involve a similar method of measurement as that used in the current study because a TRR system was utilised. However, the temperature range is again limited to only 60 °C, with four data points taken at 20 °C intervals, since the main goal of the experiment was to measure pressure effects on the SPE rate. The temperature calibration was estimated to be ±5 °C based upon temperature indicating lacquers. It is worth noting that in the process of calibrating the systems used in the present work, temperature indicating lacquers from the same manufacturer were also tested. However, after many attempts, it was eventually concluded that the reproducibility and detection of the transition associated with these lacquers was not sufficient for the level of accuracy desired for the present study. Hence, custom temperature indicating samples were created as described in section 3.2.9. Furthermore, as was
demonstrated in section 2.6.5 a temperature difference of only ±2 °C can translate into SPE rates that vary in excess of ±10%.

The recent result in the review article from Olson et al.[14] is difficult to comment on since the full details of the experiment are not reported. However, the detailed documentation of their apparatus in general[13,14] would tend to indicate that their experiment was performed in a method similar to that used in the current study, whereas the other results discussed up to this point differ significantly in the manner of execution. A comparison of the hydrogen-free a-Si SPE data taken on their apparatus[19] and that collected as a part of this work (section 5.4) indicate that the temperature calibrations of the two systems are in agreement to within ±1 °C in the temperature range from 450 °C to 650 °C. The temperature range covered by their study is 100 °C, which is larger than any of the previous measurements, but still somewhat limited in light of the requirements of this study.

The temperature range covered in the measurement by Kringhøj et al.[39] is larger than all the the previous ones, covering a span of 150 °C. They used the original Si SPE rates reported by Olson et al.[13] for determining an absolute temperature calibration. However those Si SPE rates are now known to be hydrogen affected[20] and will be substantially less than the intrinsic Si value. Since the extent of the hydrogen penetration tends to scale with the thickness of the original amorphous layer, a temperature calibration of this form that is based upon comparisons of SPE rates in thin layer Si samples would not be reliable. The same methodology applied to thick a-Si samples for calibration against the published hydrogen-free thick layer data[19] would provide a more reliable temperature calibration. In addition, the SPE rates were measured in the near surface region (900 Å - 2800 Å) which would not yield a value representative of that of the bulk due to hydrogen contamination, as will be demonstrated later in this chapter (section 4.5).

Haynes et al.[40] performed their a-Ge SPE measurements over a span of 100 °C but they suffer from the same problem as the above, in that the SPE rates are derived from a relatively narrow depth window which is positioned near the surface (800 Å to 1600 Å). The fact that the value they used for the index of refraction for a-Ge is about 5% lower than that determined in this study would also account for some
of the difference between the two velocity prefactors. The lower value of $n$ reported by Haynes et al. may be a result of the fact that they averaged values determined from $\text{Si}_x\text{Ge}_{1-x}$ samples of various high Ge content, and stated that the observed compositional dependence on the order of 5% was neglected.

It is felt that the activation energy and prefactor as determined in this work represent the most accurate values currently available for SPE of a-Ge on (100) Ge. The calculated SPE rates were based on multiple TRR interference cycles associated with $>5000$ Å of linear growth while still allowing exclusion of the near surface ($<2000$ Å) data for which velocity reductions were observed. Particular attention was devoted to obtaining an accurate temperature calibration since the calculated activation energy relies heavily on this. In addition, an independent evaluation of the index of refraction for a-Ge was performed so that absolute SPE rates could be determined for calculating a velocity prefactor. The only outstanding issue with respect to this data is whether or not it is an accurate reflection of the bulk (i.e. depths $>2$ µm) SPE behaviour in light of the hydrogen contamination that is observed in silicon. This concern is dealt with in the following section.
4.5 Hydrogen Effects

Based on the fact that the presence of hydrogen can significantly reduce the SPE rate in Si as discussed in section 4.2.6, this section sets out to determine whether or not the same effect is present in a-Ge systems.

In light of the Si results, the first test on the germanium system was to determine whether there was any detectable SPE rate difference observed between that measured for thin layers and that measured for thick layers. As the a-Ge layers studied in section 4.4 were up to ~ 1.5 \( \mu \text{m} \) thick, the next logical step was to try thicker layers, formed by higher energy self-implantation. This also involved moving to a longer wavelength TRR signal, as the 1.15 \( \mu \text{m} \) laser has a maximum useful depth of approximately 1 \( \mu \text{m} \) in a-Ge, as discussed in section 4.3.2.

4.5.1 TRR of Thick a-Ge Layers at 1.523 \( \mu \text{m} \)

Fig. 4.22a shows the TRR data collected from one of the 3.25 \( \mu \text{m} \) thick a-Ge samples, annealed at 440 °C. Given the previous result (section 4.3.2) of 1501 A per full interference cycle, combined with the fact that there are approximately 22 full interference cycles observed, puts the a-Ge layer thickness at approximately 3.25 \( \mu \text{m} \).

While not essential to this study, it is worthwhile noting that the complex part of the index of refraction (also known as the extinction coefficient) for a-Ge at 1.523 \( \mu \text{m} \) was also determined. This was done as part of the process of matching the exponential envelope of the theoretical curve with that of the curves similar to that shown in Fig. 4.22(a). The value determined from this technique was

\[
k = 0.095 \pm 0.008.
\]

Thus the full complex index of refraction for a-Ge at 1.523 \( \mu \text{m} \) at 440 °C is

\[
N = (5.07 \pm 0.17) - j(0.095 \pm 0.008).
\]

Fig. 4.22(b) shows the \( c/a \) interface depth as determined from the mapping of the curve in Fig. 4.22(a) to the theoretical curve generated by using the above value of \( N \). As can be seen, the interface moves toward the surface in a reasonably linear fashion, without any dramatic velocity changes. The instantaneous interface velocity as a function of depth can be obtained by taking a point by point derivative of the curve shown in Fig. 4.22(b), or the mean velocity can be obtained by taking the slope of the linear portion of the curve. The result of the former is shown in
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

Figure 4.22: TRR curve from annealing of a 3.25 µm thick a-Ge layer at 440°C (a) and corresponding a-Ge/c-Ge interface depth (b) as derived from (a).

Figure 4.23: The interface velocity as a function of depth as determined from the TRR data in Fig. 4.22. Sample was 3.25 µm of a-Ge annealed at 440 °C.
Fig. 4.23, and the result of the latter gives a mean velocity of 209 Å. From inspection of Fig. 4.22(b) and Fig. 4.23 it is clear that the velocity remains essentially constant over the majority of the depth range. No large scale velocity reductions are observed at or around the 2 µm mark, in contrast to the results reported by Roth et al. for silicon[20]. However, a slight velocity reduction is visible in the final stages of the anneal, similar to that reported by Lu et al.[11] who speculated that it may be due to surface impurities known to retard SPE growth that have been driven into the sample during the multiple amorphization implants. Olson and Roth[14] also mention having observed a near surface reduction in the a-Ge SPE rate in some of their unpublished data, and they attribute this to hydrogen diffusing into the amorphous material.

Similar data to that shown in Fig. 4.22 was collected at temperatures of 400 °C and 360 °C for the same thick a-Ge sample material. While the temperature range is not as comprehensive as the study of the thinner a-Ge layers covered in section 4.4, it is worth reporting the Arrhenius dependence for comparison. As shown in Fig. 4.24, the activation energy determined from this data set is 2.16 eV, with a velocity prefactor of $3.3 \times 10^7$ m/s. This value is in good agreement with the value previously determined from the 1.15 µm TRR study of thinner layers.

There are a number of possible ways to interpret the lack of a large velocity change in the a-Ge system, as compared to the a-Si system. Some of the possibilities are as follows:

1. There is no intake of H from the environment into the a-Ge layer to large depths as observed in a-Si.

2. There is a hydrogen intake, but the amount is not significant enough to cause SPE velocity variations in a-Ge.

3. Hydrogen may not have a retardation effect on the solid phase epitaxial regrowth rate in a-Ge systems.

4. There is a H intake from the ambient, and a subsequent velocity reduction effect, but the maximum H penetration depth, and the associated velocity decrease takes place at a depth greater than 3.25 µm.
Figure 4.24: The Arrhenius dependence for SPE of 3.25 µm thick a-Ge layers formed by ion implantation as per Table 4.3.

\[ E_a = 2.16 \text{ eV} \]
\[ V_o = 3.3 \times 10^7 \text{ m/s} \]
5. The diffusion rate of hydrogen in a-Ge is too slow with respect to the rate of SPE to allow hydrogen penetration to any significant depth.

Since the thick layer SPE data was not sufficient to determine which of the above reasons correctly explains the lack of a significant H retardation of the SPE rate compared to that observed in Si, further measurements were undertaken. These included SIMS analysis of partially annealed samples, similar to the measurements performed by Roth et al.\cite{Roth19}, and also TRR and SIMS measurements on H implanted a-Ge layers. These results are presented below.

4.5.2 SIMS Measurements of Hydrogen in a-Ge Layers

For the silicon system, Roth et al.\cite{Roth20} were able to detect the indiffused hydrogen by SIMS measurements of partially annealed samples, as described in section 4.2.6. Hence, SIMS measurements were performed on a-Ge samples at three different stages of partial annealing. The first sample was analyzed in the as-implanted state to determine the background level of H and to verify that there was no hydrogen intake from the implantation process. The second sample was annealed at 420 °C for 121 seconds, and the third was annealed for 227 seconds. The H profiles from the SIMS measurements on these three samples are shown in Fig. 4.25. The expected $c/a$ interface depths as determined from TRR data for these two partial anneals are $7900\pm200$ Å and $2400\pm150$ Å respectively. The shorter of the two partial anneals was chosen so that if there was a surface-based source of H, its associated profile could be viewed prior to interaction with the $c/a$ interface. The longer duration partial anneal was chosen to allow observation of any interaction between the $c/a$ interface and any hydrogen which infiltrated the a-Ge layer from the surface of the sample.

The H profile in the as-implanted a-Ge prior to annealing indicates that the H concentration is at the measurement background level ($\sim 10^{17}$/cm$^3$) for most of the layer, but rises sharply from about 2000 Å through to the surface. The shape and size of this surface tail are identical to that shown in the 0–2000 Å region on the H implanted reference in Si (Fig. 4.5) that was used to calibrate the H in a-Ge measurements.
Figure 4.25: SIMS profiles of the hydrogen content in an as-implanted a-Ge sample, and two partially annealed a-Ge samples. The duration of the two individual partial anneals were 121 seconds and 227 seconds respectively. The expected c/a interface depths for each of these partial anneals based on the TRR data were 7900 Å and 2400 Å respectively.
4.5. HYDROGEN EFFECTS

After annealing for 121 s, the H profile penetrated into the a-Ge layer slightly further, to just over 3000 Å. At this point, the c/a interface has advanced 6200 Å, still leaving 7900 Å of a-Ge, so that the c/a interface is well beyond the range of the hydrogen. This is contrasted against the Si case, where Roth et al.[20] report H penetration to depths of 1 µm after only 2000 Å of regrowth. After 1.4 µm of regrowth in the Si case, the H has penetrated to a depth of 2.7 µm.

After the 227 s anneal, the c/a interface is at a depth of 2400 Å and has come into contact with the indiffused H. The hydrogen content is observed to drop to background levels upon crossing from the a-Ge side of the interface to the c-Ge side. A peak in the H concentration profile is formed on the a-Ge side of the interface as the hydrogen is progressively pushed ahead of the advancing c/a interface. Roth et al.[20] observed similar zone-refinement of the H in Si by the c/a interface, as shown in Fig. 4.1. The level of H as seen by the interface at this point in the anneal is \( \sim 6 \times 10^{18}/\text{cm}^3 \). This value is of the same order as reported by Roth, who observed values between \( 2 \times 10^{18}/\text{cm}^3 \) and \( 1.5 \times 10^{19}/\text{cm}^3 \), depending upon how far the interface was allowed to progress, and hence how much hydrogen it had collected.

These results show that hydrogen does diffuse into a-Ge layers from the ambient during thermal processing, but that the depth range over which this effects SPE measurements is about one order of magnitude less than that which is observed in silicon. For a-Ge layers 1.4 µm thick, the SPE rate reduction that is associated with this indiffused H is observed to be limited to the first \( \sim 2000 \) Å. For thicker layers, the affected depth is expected to increase, as the H profile has a longer time to diffuse into the a-Ge layer before coming in contact with the c/a interface. This appears to hold true, as the velocity data for a 3.25 µm a-Ge layer as shown in Fig. 4.23 begins to exhibit a SPE rate reduction when the c/a interface reaches within \( \sim 4000 \) Å of the surface.

4.5.3 TRR of a-Ge Layers Implanted with Hydrogen

To determine whether H concentrations similar to those observed to retard SPE in a-Si layers have a similar effect in a-Ge, some hydrogen implants were performed
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

directly into the amorphous germanium. The implantation conditions were chosen to create peak hydrogen concentration levels comparable to those measured in silicon and reported by Roth et al.[20]. Three implantation doses were studied, giving as-implanted peak hydrogen concentrations of $1 \times 10^{19}$ /cm$^3$, $2 \times 10^{19}$ /cm$^3$ and $4 \times 10^{19}$ /cm$^3$ respectively. Fig. 4.26 shows the SPE velocity profiles determined from the raw TRR data for each of these three H doses.

As can be seen, the interface velocity quickly drops to less than half that of the unimplanted sample when it encounters the hydrogen profile. This holds true for all three hydrogen doses. It should be noted that after that point, the observed interface velocity cannot be correlated with the as-implanted H profile since it is expected that the interface will cause a redistribution of the H as was observed for the indiffused H (Fig. 4.25) and based on the observed behaviour of H in Si systems. However, some observations can be made based on the total hydrogen content in the sample if one assumes that there is no large scale loss of H out through the surface of the sample during the initial stages of the annealing process. For example, the degree of retardation of the SPE rate between the $3 \times 10^{14}$ /cm$^2$ sample and the unimplanted case is large with respect to the difference between the $3 \times 10^{14}$ /cm$^2$ case and the other two higher implant doses. This tends to indicate that there is a threshold or saturation level of hydrogen, and that increases of the H content beyond that level do not have as dramatic a reduction on the SPE rate. This threshold behaviour is consistent with that observed for implanted hydrogen in silicon as reported by Oberlin et al.[50] and Roth et al.[19, 20] and discussed earlier in section 4.2.6.

In Fig. 4.26 the interface velocity is observed to be fairly constant in the region from 2000 Å to 5000 Å for all three hydrogen implanted cases. By taking the mean velocity in this region at various temperatures, an activation energy associated with SPE in the $1.2 \times 10^{15}$ H/cm$^2$ implanted samples was determined. This is shown in Fig. 4.27 along with the data collected from the hydrogen-free thick a-Ge layer samples for comparison. The activation energy and velocity prefactor for the $1.2 \times 10^{15}$ H/cm$^2$ samples are 2.17 eV and $8.9 \times 10^6$ m/s respectively.

It is evident that the addition of hydrogen does not alter the activation energy of the SPE process in a-Ge. However, the velocity prefactor is reduced by a factor
Figure 4.26: The effect of 80 keV implanted hydrogen on the solid phase epitaxial regrowth rate in a-Ge, for hydrogen doses of $3 \times 10^{14}$ /cm$^2$, $6 \times 10^{14}$ /cm$^2$, and $1.2 \times 10^{15}$ /cm$^2$. The theoretical as-implanted profile obtained from the profile code[108] for the $1.2 \times 10^{15}$ /cm$^2$ case is shown for comparison. The as-implanted profiles for the other two doses would be identical except for a vertical scaling factor of 0.25 and 0.5 respectively.
Figure 4.27: The Arrhenius dependence for SPE of 3.25 µm thick a-Ge layers. The effect of $1.2 \times 10^{15} / \text{cm}^2$ 80 keV implanted hydrogen on the Arrhenius behaviour of solid phase epitaxial regrowth rate in a-Ge (circles). Interface velocities were taken as the mean velocity in the region from 2000 Å to 5000 Å. The data collected from the hydrogen-free thick layer samples is shown for comparison (triangles).
4.5. HYDROGEN EFFECTS

of ~ 3.7 from that of the hydrogen-free case. The fact that the activation energy of the SPE process remains unchanged is consistent with that observed in the a-Si system as reported by Roth et al.[20]. For models that explain SPE in terms of dangling bonds, the effect of hydrogen is usually explained in terms of the hydrogen passivating dangling bonds and thus reducing the number of crystallization sites available to the SPE process. Thus, the energy associated with a crystallization event remains the same, but the overall absolute crystallization rate is reduced.

4.5.4 SIMS of a-Ge Layers Implanted with Hydrogen

As mentioned earlier, it is not clear what level of hydrogen is present at the interface during the annealing process, since it is expected that the interface will zone-refine the H to the remaining a-Ge layer as SPE progresses. To determine the H concentration at the interface associated with the activation energy reported above, another portion of the a-Ge sample containing 1.2x10^{15} H/cm^2 was subjected to a partial anneal followed by a SIMS measurement, the results of which are shown in Fig. 4.28. This sample was annealed for 318 s at 420 °C and the expected location of the c/a interface is 4800±200 Å in this case. This puts the c/a interface within the region used for the velocity determinations in the activation energy measurement reported above. The theoretical as-implanted distribution for the 1.2x10^{15} /cm^2, 80 keV H is also shown for comparison. Based on this measurement, the hydrogen concentration at the c/a interface associated with the velocity measurements taken in the 2000 Å to 5000 Å region (and hence the activation energy and velocity prefactor reported above) is taken to be 6x10^{19} /cm^3.

As was seen with the H that indiffused from the annealing ambient, the level of H drops abruptly to background levels upon passing from the a-Ge to the c-Ge side of the interface, and the remaining hydrogen in the a-Ge layer exhibits a zone-refined concentration profile with an enhanced peak concentration. Integration of the hydrogen profile obtained from the SIMS measurement over the region from 1500 Å to 6000 Å indicates a total retained dose of 8x10^{14} /cm^2 in the hydrogen peak.

Olson and Roth[14] found that the SPE rate in Si decreased linearly with increasing interfacial hydrogen concentration up to approximately 3x10^{19}/cm^3, and that
Figure 4.28: SIMS profile (circles) of the hydrogen content in an a-Ge sample that has been implanted with 80 keV, \(1.2 \times 10^{15}\) /cm\(^2\) H, and then partially annealed for 318 s. The expected c/a interface location as determined from the TRR data was 4800 Å. The theoretical as-implanted H profile is shown for comparison (triangles). Integration of the SIMS profile gives a retained H dose of \(8 \times 10^{14}\) /cm\(^2\).
for concentrations beyond that there was little change in the SPE rate. They correlated this threshold value with the density of dangling bonds in ion-amorphized a-Si and cite this as evidence for the involvement of dangling bonds in the SPE process. While the results presented here are not sufficient to ascertain the exact concentration dependence for Ge, they do in fact provide bounding values on the hydrogen concentration threshold value at which point the SPE rate becomes essentially invariant for further increases in hydrogen content. From Fig. 4.26 it is evident that this threshold has been reached for the $1.2 \times 10^{15} \text{ H/cm}^2$ implant, which from Fig. 4.28 corresponds to an interfacial hydrogen concentration of $6 \times 10^{19} / \text{cm}^3$. The lower bound on this value is set by the interfacial concentration of $6 \times 10^{18} / \text{cm}^3$ for indiffused H as observed in Fig. 4.25. In this case the SPE rate is still a strong function of the hydrogen concentration as displayed in Fig. 4.26. Thus the hydrogen saturation concentration level in a-Ge lies somewhere between $6 \times 10^{18} / \text{cm}^3$ and $6 \times 10^{19} / \text{cm}^3$. This value is comparable to the value of $4 \times 10^{19} / \text{cm}^3$ reported by Roth et al. [20] for hydrogen in silicon. However, in contrast to the Si system, the SPE rate at or near the H saturation level in Ge systems observed here is a factor of $\sim 3.7$ times slower than the intrinsic value, as compared to the factor of $\sim 2$ reported by Roth et al. for Si.
4.6 Dopant Effects in Amorphous Germanium

Csepregi et al.[17] were the first to report that typical group III and V dopant impurities would actually enhance the solid phase epitaxial regrowth rate of a-Si. Following on from Csepregi’s work, Suni et al.[16] then found that having similar concentrations of both group III and V dopants present had a compensating effect on the SPE rate in a-Si, returning it to a value comparable to the intrinsic rate. Since then there have been a substantial number of similar experiments on doped a-Si, as outlined in section 2.3.

With respect to germanium, Suni et al.[7] performed some initial measurements for boron and arsenic in germanium at two different temperatures, and reported qualitatively similar effects to those observed in silicon. However, this is the only information of its type that is available for dopant-enhanced solid phase epitaxial regrowth rates in germanium, and as discussed in section 4.2.7, it is not quantitative enough to allow any substantial conclusions to be drawn.

Results from the current work showing the effect of the group V dopant arsenic on solid phase epitaxial regrowth of a-Ge are presented first, followed by results demonstrating the effect of the group III dopant aluminum. Finally, the results from samples containing an overlapping profile of both of the above dopants are presented.

4.6.1 Doping with Arsenic

As described in section 4.3.1, multiple arsenic implants were used to create three different a-Ge sample sets, each containing a constant As concentration. The three concentrations produced were $1 \times 10^{19} / \text{cm}^3$, $5 \times 10^{19} / \text{cm}^3$ and $1 \times 10^{20} / \text{cm}^3$ respectively, with the region of constant concentration covering the depth range from 2500 Å to 5500 Å. The SPE regrowth of these samples was monitored via TRR in the same fashion as for the undoped samples discussed in section 4.4. The TRR data for a $1 \times 10^{20}$ As/cm$^3$ sample annealed at 500 °C is shown in Fig. 4.29 (lower curve), and the associated TRR data obtained from an undoped sample at the same temperature is shown for comparison (upper curve).

It is evident that the As implanted a-Ge sample has finished annealing long before the undoped a-Ge sample, but it is not easy to see over what region the accelerated
4.6. DOPANT EFFECTS IN AMORPHOUS GERMANIUM

Figure 4.29: TRR curve from annealing of an a-Ge layer at 500°C (upper curve) and corresponding TRR curve for the anneal of a similar layer with a region containing $1 \times 10^{20}$ As/cm$^3$ As over the depth region from 2500 Å to 5500 Å (lower curve).

Figure 4.30: The corresponding c/a interface location as a function of annealing time, as extracted from the TRR curves shown in Fig. 4.29. The upper curve associated with an undoped sample exhibits an essentially constant SPE rate, whereas the lower curve associated with the arsenic doped sample shows an enhanced SPE rate in the region containing As ($\sim 2500$ Å to $\sim 5500$ Å).
SPE rate has taken effect. By converting these two TRR curves into interface location data, the region of enhanced SPE becomes more apparent. The interface data corresponding to the two curves shown in Fig. 4.29 is shown in Fig. 4.30 with the same time axes. The lower curve of Fig. 4.30 exhibits an increased slope in the region that contains arsenic (as indicated in the profile shown previously in Fig. 4.7) and the enhanced slope in this region is essentially constant. The enhanced SPE rate associated with the arsenic doping was determined from the slope of the curve over the depth range where the As concentration was constant (~2500 Å to ~5500 Å).

This measurement was then repeated at regular temperature intervals in a similar fashion as was performed for the undoped samples of section 4.4. The whole process was then repeated for the other two arsenic concentrations. The results of all these SPE rate measurements are displayed in an Arrhenius format in Fig. 4.31. Vertical error bars are on the order of the symbol size, and hence have been omitted for clarity. The activation energy and velocity prefactor determined from fitting the SPE data in Fig. 4.31 are summarised in Table 4.10. The lowest dose of only $1 \times 10^{19}$ As/cm$^3$ does not appear to have any large effect on the activation energy or the velocity prefactor as compared to the undoped values. This is also evident in Fig. 4.31, as the fit to the $1 \times 10^{19}$ As/cm$^3$ data is nearly coincident with that of the undoped data. In contrast, the $5 \times 10^{19}$ As/cm$^3$ case shows a considerable deviation from the $1 \times 10^{19}$ As/cm$^3$ case. The deviation between the $5 \times 10^{19}$ As/cm$^3$ and the $1 \times 10^{20}$ As/cm$^3$ case is not as significant, tending to qualitatively indicate a non-linear or saturation effect for the SPE enhancement as the arsenic concentration is progressively increased.

The Arrhenius curves in Fig. 4.31 also appear to converge upon the undoped values as the temperature is increased, and it is interesting to examine this behaviour in more detail. The temperature dependence of each of the curves is more readily observed when the respective arsenic-enhanced SPE rates are normalized against the SPE rates obtained earlier for undoped a-Ge. The resulting normalized data for each of the three As concentrations studied are shown in Fig. 4.32. The error associated with only the fitting of the slope of the linear portion of curves such as the lower curve of Fig. 4.30 is on the order of 1% or less, however it does not take
Figure 4.31: The Arrhenius behaviour of arsenic implanted a-Ge for three different constant arsenic concentrations, $1 \times 10^{19}$ /cm$^3$ (diamonds), $5 \times 10^{19}$ /cm$^3$ (triangles), and $1 \times 10^{20}$ /cm$^3$ (circles). The arsenic-free data from this work is shown for comparison (solid line, no symbols). Interface velocities shown here were measured in the region containing a constant concentration of As ($\sim 2500$ Å to $\sim 5500$ Å).

Figure 4.32: SPE rates of As implanted a-Ge are shown normalized against the SPE velocity at that temperature for undoped a-Ge as presented earlier. Three different constant concentrations of As are shown: $1 \times 10^{19}$ /cm$^3$ (diamonds), $5 \times 10^{19}$ /cm$^3$ (triangles) and $1 \times 10^{20}$ /cm$^3$ (circles). Solid lines are best fits to the data assuming a $V/V_i = 1 + N_{impl}/N_i$ dependence as per Eq. 4.3.
Table 4.10: The activation energies and velocity prefactors obtained from the various series of arsenic implanted a-Ge samples. Quoted error values for the doped samples are only the fitting errors representative of the statistical noise in the data. The value obtained from the samples studied earlier that had no arsenic implants is shown for comparison.

<table>
<thead>
<tr>
<th>Arsenic Concentration (/cm$^3$)</th>
<th>$E_a$ (eV)</th>
<th>$V_o$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>2.15±0.04</td>
<td>(2.6±0.5)×10$^7$</td>
</tr>
<tr>
<td>$1\times10^{19}$</td>
<td>2.149±0.011</td>
<td>(2.8±0.5)×10$^7$</td>
</tr>
<tr>
<td>$5\times10^{19}$</td>
<td>2.074±0.008</td>
<td>(1.2±0.2)×10$^7$</td>
</tr>
<tr>
<td>$1\times10^{20}$</td>
<td>2.041±0.008</td>
<td>(1.05±0.15)×10$^7$</td>
</tr>
</tbody>
</table>

Such normalized velocity plots also lend themselves well to comparison against models which express their predictions in a similar format, such as the Fractional Ionization (FI) Model (section 2.4.9) by the Walser group[12,24] and the Generalized Fermi-Level Shifting (GFLS) Model (section 2.4.11) from Lu et al.[11]. For both of these models, the normalized SPE rate can be expressed as

$$\frac{V_i}{V_i} = 1 + \frac{N_{impl}}{N_i} \quad \text{with} \quad N_i = N_o \exp(-\Delta E/kT)$$ (4.3)

and hence the exponential behaviour becomes more prominent at lower temperatures. As discussed previously (section 2.4), the interpretation of $N_o$ and $\Delta E$ is different for each of the FI and GFLS models, and it is this difference that may make one model more favourable than the other when compared with experimental data. The Walser group[12,24,25,49] typically plotted $V/V_i$ against $N_{impl}/N_i$ when comparing experimental data for Si to the predictions of Eq. 4.3. While this method of displaying the data is useful to verify that an extrapolation of the data goes through the expected point of (0,1) it obscures the temperature dependence of the SPE enhancement for a given doping level. The temperature dependence is easily seen in a normalized velocity plot as shown in Fig. 4.32.

The best fits of Eq. 4.3 to the data are shown as solid lines in Fig. 4.32,
Table 4.11: Fitting parameters to the experimental arsenic-enhanced SPE rates assuming a functional form as per Eq. 4.3. Error values are based on the estimated error from the fitting process. In the lowest dose case, $N_{impl}$ is sufficiently small as to allow a wide range of parameters to match the data.

<table>
<thead>
<tr>
<th>$N_{impl}$ ($10^{20}$/cm$^3$)</th>
<th>$\Delta E$ (eV)</th>
<th>$N_0$ ($10^{20}$/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.133±0.015</td>
<td>5.9±1.6</td>
</tr>
<tr>
<td>0.5</td>
<td>0.14±0.03</td>
<td>7.6±4.7</td>
</tr>
<tr>
<td>0.1</td>
<td>0.007±0.09</td>
<td>0.7±1.2</td>
</tr>
</tbody>
</table>

the associated $\Delta E$ and $N_0$ values listed in Table 4.11. For the lowest dose of only $1\times10^{19}$ As/cm$^3$, within errors there is essentially no SPE rate enhancement to fit, or in terms of Eq. 4.3, the $N_{impl}$ quantity is too small to have a significant effect. Hence a wide range of $\Delta E$ and $N_0$ parameters will fit that data set. In contrast, the values of $\Delta E$ and $N_0$ determined for the other two higher As concentrations are reasonably consistent with each other.

Suni et al.[7] observed SPE rate enhancements on the order of $1.5\times$ for their measurements of $\sim 1\times10^{20}$ As/cm$^3$ in a-Ge at the two temperatures of 300 °C and 325 °C (section 4.2.7). The $1\times10^{20}$ As/cm$^3$ case from this study, as shown in Fig. 4.32 exhibits at least a three times enhancement over the undoped SPE rate in that temperature range. One contributing factor to the difference in observed enhancements may be due to the fact that the region containing As for which the mean SPE rate was determined by Suni et al. had less than the expected $1\times10^{20}$ As/cm$^3$, as shown in Fig. 4.2.

The Olson group reported a concentration-dependent offset between the SPE velocity profile in Si and the expected arsenic profile for single implant samples (section 2.3.3). However, the Walser group (section 2.3.5) did not observe such a shift for their study of SPE in arsenic implanted Si. The samples from this study used multiple implant, constant concentration dopant profiles to avoid the difficulty of assigning a common depth scale to both quantities. However, for completeness it is noted that no significant shift was observed between the two for As in Ge. Shown in Fig 4.33 is the arsenic profile, determined from a SIMS measurement, compared
Figure 4.33: Comparison of the implanted arsenic profile as determined from a SIMS measurement with the enhancement in the SPE rate due to the implanted arsenic. The depth scale for the SIMS profile comes from a measurement of the sputter crater depth, whereas the depth scale assigned to the SPE profile relies on the index of refraction determined for the amorphous germanium.
to the arsenic-enhanced SPE rate as a function of depth at 340 °C. In addition, the peak concentrations of As used in this work lie near the lowest concentration of As used by the Olson group, for which they reported no significant shifting, and hence the lack of an offset in the present work is not surprising.

### 4.6.2 Doping with Aluminum

The effect on the SPE rate in a-Ge for three constant concentrations of aluminum was then investigated in a similar manner as that performed for the arsenic doped a-Ge samples. From section 4.3.1, the samples each respectively contained a constant Al concentration of $1 \times 10^{19}$ /cm$^3$, $5 \times 10^{19}$ /cm$^3$, or $1 \times 10^{20}$ /cm$^3$ over a depth range from 5000 Å to 9000 Å.

The TRR data for a $1 \times 10^{20}$ Al/cm$^3$ sample annealed at 500 °C is shown in the lower curve of Fig. 4.34, and the associated TRR data obtained from an undoped sample at the same temperature is shown for comparison (upper curve). The total duration of the anneal is substantially shorter for the Al implanted sample as compared to the undoped sample, which is similar to the observed behaviour for the arsenic implanted case. A section of the TRR curve for the Al implanted case has a section in the middle where the oscillation period is shorter than the upper curve, indicating enhanced SPE regrowth.

The corresponding $c/a$ interface location for the two TRR curves of Fig. 4.34 as a function of time are shown in Fig. 4.35. The upper curve corresponding to the undoped sample has a relatively constant slope over most of the depth range, indicating a constant SPE rate. The lower curve exhibits a larger slope in the Al implanted region between 5000 Å and 9000 Å which indicates an enhanced SPE rate. Furthermore, the enhanced SPE rate as given by the slope of the curve in this region is reasonably constant, in conjunction with the constant concentration of Al that is present.

Similar measurements for all the other temperature intervals gave the SPE enhancement as a function of temperature for a doping level of $1 \times 10^{20}$ Al/cm$^3$. The process was then repeated for the two other aluminum concentrations used, and the resulting SPE rates are all displayed on the Arrhenius plot in Fig. 4.36. Vertical
Figure 4.34: TRR curve from annealing of an a-Ge layer at 400°C (upper curve) and corresponding TRR curve for the anneal of a similar layer with a region containing $1 \times 10^{20} \text{Al/cm}^3$ (lower curve).

Figure 4.35: The corresponding c/a interface location as a function of time as extracted from the TRR curves shown in Fig. 4.34. The upper curve associated with an undoped sample exhibits an essentially constant SPE rate, whereas the lower curve associated with the aluminum doped sample shows an enhanced SPE rate in the 5000 Å to 9000 Å region containing Al.
error bars are on the order of the symbol size, and hence have been left out for clarity. The undoped SPE rates, as measured previously in section 4.4 are also shown for comparison. The resulting activation energies and velocity prefactors associated with fitting an Arrhenius dependence to the enhanced SPE rates in Fig. 4.36 are listed in Table 4.12.

When the results for the two higher doses of aluminum are contrasted against the arsenic data of the previous section (Table 4.10), it is evident that the relative changes in the activation energy and velocity prefactor for Al are not nearly as large as those observed for As. The difference between the SPE rate enhancement of aluminum and arsenic is also evident when the aluminum SPE data are plotted in normalized form, as in Fig. 4.32. The error bars shown are representative of the reproducibility of the data and the RMS noise in the determined velocity curve. Error bars for the other two concentrations are of similar magnitude and are omitted for clarity. The normalized arsenic data (Fig. 4.32) exhibited a reasonably clear temperature dependence for a given doping level, whereas the temperature dependence of the normalized Al SPE data as shown in Fig. 4.37 is not as obvious. From the solid lines in Fig. 4.37, it appears that the SPE rate enhancement for a fixed doping concentration also increases with decreasing temperature, but there is little value in reporting the parameters determined from fitting a function of the form of Eq. 4.3.

<table>
<thead>
<tr>
<th>Aluminum Concentration (/cm³)</th>
<th>Eₐ (eV)</th>
<th>V₀ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>2.15±0.04</td>
<td>(2.6±0.5)×10⁷</td>
</tr>
<tr>
<td>1×10¹⁹</td>
<td>2.133±0.017</td>
<td>(2.2±0.7)×10⁷</td>
</tr>
<tr>
<td>5×10¹⁹</td>
<td>2.119±0.011</td>
<td>(2.1±0.4)×10⁷</td>
</tr>
<tr>
<td>1×10²⁰</td>
<td>2.115±0.005</td>
<td>(2.6±0.3)×10⁷</td>
</tr>
</tbody>
</table>

Table 4.12: The activation energies and velocity prefactors obtained from the various series of aluminum implanted a-Ge samples. Quoted error values for the doped samples are only the fitting errors representative of the statistical noise in the data. The value obtained from the samples studied earlier that had no aluminum implants is shown for comparison.
Figure 4.36: The Arrhenius behaviour of aluminum implanted a-Ge for three different constant aluminum concentrations, $1 \times 10^{19}$ / cm$^3$ (diamonds), $5 \times 10^{19}$ / cm$^3$ (triangles), and $1 \times 10^{20}$ / cm$^3$ (circles). The aluminum-free data from this work is shown for comparison (solid line, no symbols). Interface velocities shown here were measured in the region containing a constant concentration of Al ($\sim 5000$ Å to $\sim 9000$ Å).

Figure 4.37: SPE rates of Al implanted a-Ge are shown as normalized against the SPE velocity at that temperature for undoped a-Ge as presented earlier. Three different constant concentrations of Al are shown: $1 \times 10^{19}$ / cm$^3$ (diamonds), $5 \times 10^{19}$ / cm$^3$ (triangles) and $1 \times 10^{20}$ / cm$^3$ (circles). Solid lines are best fits to the data assuming a $V/V_i = 1 + N_{\text{impl}}/N_i$ dependence as per Eq. 4.3.
4.6.3 Doping with Arsenic and Aluminum

The expected dopant profile for the samples implanted with both arsenic and aluminum was shown in Fig. 4.10. These samples are expected to have equal concentrations of As and Al at a depth of $\sim 5600 \, \text{Å}$, and to have less than $5 \times 10^{18} / \text{cm}^3$ of uncompensated dopant in the depth region from $\sim 4400 \, \text{Å}$ to $\sim 6400 \, \text{Å}$. The SPE rates for these samples were investigated following the same procedure that was employed for the samples with only arsenic or aluminum.

The TRR data for annealing a compensation doped sample at $460 \, ^\circ \text{C}$ is shown in the lower curve of Fig. 4.38, with the upper curve indicating the corresponding TRR data for the annealing of an undoped sample. In contrast to the previous TRR data of samples containing only one dopant species (Figs. 4.29 and 4.34) there does not appear to be any significant change in the period of the resolvable interference oscillations. Yet the overall annealing time is somewhat shorter than that for the undoped a-Ge layer of the same thickness.

The difference in annealing time can be understood in terms of the net doping profile of Fig. 4.10 and the SPE rate determined from the $c/a$ interface location shown in Fig. 4.39. These are shown together in Fig. 4.40. At and beyond the depth resolution of the $1.15 \, \mu \text{m}$ TRR signal, the net doping level is dominated by the aluminum implants, with a peak concentration of approximately $4 \times 10^{19} \text{Al/cm}^3$. For the depth range from $\sim 8200 \, \text{Å}$ to $\sim 12000 \, \text{Å}$, the net uncompensated concentration is greater than $2.8 \times 10^{19} \text{Al/cm}^3$. Thus the SPE rate will be enhanced in this region as compared to an undoped sample, which in turn leads to the shorter annealing time that is observed. As can be seen in Fig. 4.40, the SPE rate in the compensated sample tracks the net Al concentration for depths beyond $\sim 7000 \, \text{Å}$. For the rest of the sample, the net doping level is less than $2.8 \times 10^{19} / \text{cm}^3$ and the SPE rate roughly follows the net doping level in this region as well.

For the purpose of correlating SPE rates to dopant compensation in a-Ge the interface velocity was taken as the mean velocity within the region between $\sim 4400 \, \text{Å}$ to $\sim 6400 \, \text{Å}$. From Fig. 4.40 this corresponds to the range over which the net doping level will be less than $5 \times 10^{18} / \text{cm}^3$ and it is evident that the SPE rate is essentially constant within this depth window. The activation energy and velocity prefactor
Figure 4.38: TRR curve from annealing of an a-Ge layer at 460 °C (upper curve) and corresponding TRR curve for the anneal of a similar layer with partially overlapping implants of $5 \times 10^{19} / \text{cm}^3$ of both As and Al (lower curve).

Figure 4.39: The corresponding c/a interface location as a function of time as extracted from the TRR curves shown in Fig. 4.38. The upper curve associated with an undoped sample exhibits an essentially constant SPE rate. The net doping level for the Al and As implanted sample (lower curve) is less than $2.8 \times 10^{19} / \text{cm}^3$ from the surface to $\sim 8200 \text{ Å}$ based upon Fig. 4.10. Hence the SPE rate associated with the slope of the lower curve is also relatively constant to this depth.
Figure 4.40: The SPE rate in compensation doped Ge, as determined from the interface location as a function of time (Fig. 4.39). The two dopant profiles for As and Al combine to give a net dopant profile (solid line). The SPE rate in undoped Ge at the same temperature (460 °C) is shown for comparison.

Figure 4.41: The SPE rates in compensation doped Ge as a function of temperature after being normalized to the undoped SPE rates. The normalized SPE rates associated with samples containing the same concentration of either As or Al, but not both simultaneously, are shown for comparison.
obtained from fitting an Arrhenius equation to the resulting compensation doped SPE data are 2.170±0.007 eV and (3.8±0.5)×10^7 m/s respectively, with the quoted error values being statistical only.

Once again, the significance of the difference between the compensated samples and the undoped samples is best observed on a normalized velocity plot such as Fig. 4.41. The results of sections 4.6.1 and 4.6.2 indicated that the identical As and Al dopant profiles would be responsible for an enhanced SPE rate when treated separately, as also shown in Fig. 4.41. Yet, when combined in the same sample, the SPE rate is returned to a value comparable to that observed for the undoped material. The individual rate enhancements for 5×10^{19}/cm^3 turned out to be smaller than expected, but they are still sufficient to allow observation of the compensation effect. This compensation behaviour is similar to that reported by Suni et al.[7] for overlapping single implants of boron and arsenic in a-Ge at peak concentrations on the order of 1×10^{20}/cm^3. The slight offset of the normalized velocity in Fig. 4.41 for the compensation doped samples from 1.0 for intrinsic material to ∼ 1.1 is consistent with the normalized SPE rates observed in samples doped with 1×10^{19}/cm^3 As or Al (Fig. 4.32 and 4.37 respectively). The error in the concentrations for the two dopants in the compensation sample may be of similar magnitude, or the incomplete compensation may arise from some other effect.
4.7 Discussion

It is now fruitful to review the Ge SPE results of the previous sections in light of the models discussed in section 2.4. However, prior to applying any of the Fermi level shifting models to the germanium data just reported, one must first consider what state the germanium is in during the SPE process, i.e. can it be validly treated as an extrinsic nondegenerate semiconductor for the temperature range and dopant levels used for the SPE measurements. This issue is treated in detail since it is generally assumed that a nondegenerate treatment is adequate.

4.7.1 Undoped Germanium and the Kinetic Model

The extended kinetic model derived by Lu et al.[11] as described in section 2.4.4 does not explicitly predict any doping behaviour without considering some additional mechanism(s). However it does allow some comparisons with the undoped Ge data presented in section 4.4. Within the context of this model, the velocity prefactor in Eq. 2.4 is given by

$$v_o = 2\sin(\theta)v_sn_r \exp \left( \frac{\Delta S_f + \Delta S_m}{k} \right)$$

where $\theta$ is the misorientation from $\{111\}$ ($55^\circ$ for the (100) surface), $v_s$ is the speed of sound, $n_r$ is the net number of jumps a dangling bond makes before it is annihilated, $\Delta S_f$ is the entropy of formation of a dangling bond pair, and $\Delta S_m$ is the entropy of motion of the dangling bond at the interface.

By using the same bounds on the entropy terms as used by Lu et al. it is possible to refine their estimate for the number of crystallization events per formation of a dangling bond pair, $N_r = 2rn_r$, where $r$ is the ratio of crystallization events to configurational coordinate steps. The factor of two arises since $n_r$ is per dangling bond, whereas $N_r$ is per dangling bond pair. Substituting in the average value of $v_o$ from Table 4.8, and using the same $r = 3/9$ value[60] and $v_s$ as was used by Lu et al. results in $65 \leq N_r \leq 2600$. In this case, the additional uncertainty associated with the velocity prefactor value is only $\sim 20\%$ instead of the previous amount of $\sim 50\%$ as estimated by Lu. If one further assumes that the dangling bond “appears” at a kink site and then tracks along a ledge while transferring $N_r/2$ Ge atoms into the
crystal phase, then this would indicate that a single dangling bond may migrate up to $\sim 0.5 \mu m$.

### 4.7.2 Hydrogen and SPE in Intrinsic a-Ge

From the results of this work it is clear that SPE of a-Ge does not suffer from H contamination to the same extent as that found in SPE of a-Si. In section 4.5, some possibilities were listed for the reason why this is so. The idea of an effect occurring beyond the maximum depth of the 3.25 $\mu m$ thick a-Ge samples studied here is ruled out by the SIMS measurements of partially annealed samples that show limited (i.e. $\sim 5000 \AA$ or less) H penetration. The possibility of H simply not effecting the SPE rate of a-Ge is clearly incorrect given the large reduction in SPE rate observed for H implanted a-Ge samples studied here. In fact, the only remaining reason is that there simply wasn’t enough H present to saturate the a-Ge layer to the extent that is observed in partially annealed a-Si layers. The quantity of H that was observed in the partially annealed intrinsic Ge samples supports this.

The proposed source for the hydrogen presence in the a-Si layers was the formation of a native oxide and the subsequent liberation of H into the a-Si layer (section 4.2.6). A numerical case was considered, and the point made that the liberation of this H was in fact due to the properties of the native oxide, and not of the base material itself. While elemental silicon and germanium have very similar properties in many respects, their respective oxides differ substantially. Most people associate the native oxide of silicon with that found in common substances like sand and glass. However the native oxide of germanium is relatively unstable, and actually dissolves in water. This property is commonly exploited in chemical processing of germanium[120,121]. This is in considerable contrast to the native oxide of silicon, which is reasonably inert, and hence requires strong chemicals such as hydrofluoric acid for removal. Another useful indication of the instability of GeO$_2$ is the research done by Liu et al.[122] who have shown that the GeO$_2$ in their Ge$_x$Si$_{1-x}$ dioxide samples reduces to elemental Ge, but the Si remains in the form of SiO$_2$ even in the presence of forming gas.

In light of this, it is felt that the lack of a significant hydrogen effect in the SPE
4.7. DISCUSSION

of as-implanted a-Ge layers, compared to a-Si layers, is a direct result of the failure of the Ge to form a significant oxide layer during the annealing process. Without the formation of a substantial oxide layer, there is not enough H available to penetrate into the a-Ge layer at a large enough concentration to cause a SPE rate reduction.

4.7.3 Doped Ge as Extrinsic and Nondegenerate

Consideration as Extrinsic

To treat germanium as extrinsic, the number of carriers ($N_c$ for donor impurities) associated with the doping level ($N_d$) must be much larger than the intrinsic carrier concentration ($N_i$). The worst case in this study (i.e. minimum doping and maximum intrinsic carriers) would be $N_d = 1 \times 10^{19}$ As/cm$^2$ combined with an annealing temperature of 540 °C. It is common practice to assume full ionization of the dopant impurities (section 2.4.5), but as will be shown later (section 4.7.5), this is no longer valid in the dopant and temperature regime of typical SPE measurements. For these parameters, the ionization of donors is actually about 71%, and hence $N_c = 0.71 N_d$. From Fig. 2.4, the intrinsic carrier concentration at 540 °C is $\simeq 1.4 \times 10^{18}$/cm$^3$ and so the treatment as extrinsic material is valid, since $N_c$ is still about five times greater than $N_i$.

Nondegeneracy and Density of States

The question of whether or not the germanium is degenerately doped can be quickly answered by a comparison of the majority carrier level with the effective density of states. If the ratio of the carrier concentration to the effective density of states for that carrier approaches one ($\xi_c = N_c/N_e \sim 1$ or $\xi_h = N_h/N_v \sim 1$), then the nondegenerate approximation is no longer valid[26]. Expressed in another way, if the carrier concentration in the band is much less than the density of states at the band edge, then there are more than enough states at the band edge to 'hold' all the carriers, and hence a treatment as classical particles is valid. However, if the carrier concentration approaches the density of states at the band edge, then quantum effects become significant and the carriers will start occupying states further away from the band edge and on into the band.
For the purposes of a quick determination of carrier concentration to compare with the density of states, it is sufficient to estimate the fractional ionization at

\[ N_e = \frac{(E_f - E_c)}{kT} \]

for \( N_e \) and

\[ N_v = \frac{(E_v - E_t)}{kT} \]

for \( N_v \).

With addition of dopants will push the Fermi level towards the conduction or valence. I means that the intrinsic case is already close to the limiting case. Subsequent material even at the highest temperature studied, however, the band gap is about 6\( kT \) wide. If the \( kT \ln(m_h/m_e) \) term in the expression for the Fermi-energy is neglected, then the Fermi level is mid-gap, and thus \( \eta_c = \eta_t \simeq -3 \). Hence the approximation is valid for undoped material even at the highest temperature studied, however, the small band gap means that the intrinsic case is already close to the limiting case. Subsequent addition of dopants will push the Fermi level towards the conduction or valence

\[ \xi = N_e/N_c = \frac{2/\sqrt{\pi}}{F_{1/2}(\eta)} \]

and thus when \( N_e \geq 0.5 N_c \) then \( \eta \geq -1 \) already.

For the intrinsic case at 540 °C, \( E_g = 0.42 \text{ eV} \) (from Fig. 2.2), and a thermal energy of \( kT = 0.07 \text{ eV} \), so the band gap is about 6\( kT \) wide. If the \( kT \ln(m_h/m_e) \) term in the expression for the Fermi-energy is neglected, then the Fermi level is mid-gap, and thus \( \eta_c = \eta_t \simeq -3 \). Hence the approximation is valid for undoped material even at the highest temperature studied, however, the small band gap means that the intrinsic case is already close to the limiting case. Subsequent addition of dopants will push the Fermi level towards the conduction or valence

\[ \eta = (E_f - E_c)/kT \] for \( N_e \) and \( \eta = (E_v - E_t)/kT \) for \( N_v \).

Nondegeneracy and the Relative Fermi Level Location

The actual criteria for nondegeneracy come from the assumption that the Fermi level \( (E_f) \) is several \( kT \) away from both band edges. This is required so that the Fermi-Dirac integral \( F_{1/2}(\eta) \) that appears in the exact expression\(^1\) for \( N_e \) (and \( N_v \)) can be replaced with its limiting form \( (\sqrt{\pi}/2) \exp(\eta) \) which is a good approximation for \( \eta \leq -2 \), but diverges rapidly from \( F_{1/2}(\eta) \) for \( \eta \geq -1 \). The previous simple comparison between \( N_e \) and \( N_c \) to determine if the semiconductor is degenerate works because

\[ \xi = N_e/N_c = \frac{2/\sqrt{\pi}}{F_{1/2}(\eta)} \tag{4.5} \]

with \( \eta = (E_f - E_c)/kT \) for \( N_e \) and \( \eta = (E_v - E_t)/kT \) for \( N_v \).
band edge, and thus \( \eta \leq -2 \) will not be maintained for dopant concentrations above a certain limit. In addition, high doping levels can cause a further narrowing of the band gap as mentioned in section 2.4.5.

To determine the maximum donor doping level for which the nondegenerate approximation is valid, one can consider Eq. 4.5 with the approximation in place, i.e. \( N_c/N_e = \exp(\eta) \), and then solve for \( N_e \), using \( \eta = -2 \) as the limiting condition, and obtaining \( N_e \) from Fig. 2.3 at the desired temperature. For 300 °C, the lowest temperature studied, \( N_e \) has its lowest value of \( 2.8 \times 10^{18} \) /cm\(^3\), which gives an \( N_e \) of \( 3.8 \times 10^{18} \) /cm\(^3\). In the case of arsenic in germanium, a concentration of \( N_d \sim 5.5 \times 10^{18} \) /cm\(^3\) will have a fractional ionization calculated to be about 72% at this temperature (section 4.7.5), thus giving \( N_e \sim 4 \times 10^{18} \) /cm\(^3\). A similar treatment for acceptor impurities (\( N_v \approx 1.4 \times 10^{19} \) /cm\(^3\), \( \eta = -2 \)) gives an upper limit of \( N_v \approx 1.9 \times 10^{18} \) /cm\(^3\). For aluminum in germanium, a concentration of \( N_h \sim 3.5 \times 10^{18} \) /cm\(^3\) will result in a fractional ionization of about 57% at 300 °C, which corresponds to the \( N_h \sim 2 \times 10^{18} \) /cm\(^3\) limit.

Thus for arsenic concentrations above \( \sim 5 \times 10^{18} \) /cm\(^3\), or for aluminum concentrations above \( \sim 3 \times 10^{18} \) /cm\(^3\), the Fermi level can be expected to lie within \( 2kT \) of the respective band edge in germanium at 300 °C, and hence a degenerate semiconductor treatment will be required.

### 4.7.4 Fermi Levels in Doped Germanium

Since the nondegenerate expression for the Fermi level is not applicable for these doping levels and temperatures, a proper treatment must start directly from the statement of charge neutrality and evolve from there. In its most basic form, charge neutrality in a doped semiconductor can be written as

\[
N_e + N_a^- = N_d^+ + N_h
\]

(4.6)

where \( N_d^+ \) and \( N_a^- \) are the number of ionized donor and acceptor impurities.

In the following discussion, an n-type semiconductor is considered first, with the generalization to p-type (\( N_d^+ = 0 \), \( N_a^- \neq 0 \)) being relatively straightforward. To maintain a degenerate treatment, \( N_e \) will be given as per Eq. 4.5, without making
the Boltzmann approximation. However $N_h$ can be written in the Boltzmann approximation form (i.e. no explicit $F_{1/2}(\eta)$ term) because the Fermi level will move even further away from the valence band with the addition of donors. Using Eq. 4.5, the expression for the fraction of ionized donors (Eq. 2.18) and the approximation for $N_h$, the neutrality condition becomes

$$\frac{2N_c}{\sqrt{\pi}} F_{1/2} \left( \frac{E_f - E_c}{kT} \right) = \frac{N_a}{1 + 2 \exp \left( \frac{E_f - E_a}{kT} \right)} + N_v \exp \left( \frac{E_v - E_f}{kT} \right)$$

where $E_a$ is the introduced donor level, 12.7 meV for As in Ge[63]. For a p-type semiconductor, the roles are reversed, in that $N_h$ will retain a Fermi integral, while $N_e$ will be written in the Boltzmann approximation form. The resulting expression when this is done is

$$N_e \exp \left( \frac{E_f - E_c}{kT} \right) + \frac{N_a}{1 + 4 \exp \left( \frac{E_a - E_f}{kT} \right)} = \frac{2N_v}{\sqrt{\pi}} F_{1/2} \left( \frac{E_v - E_f}{kT} \right)$$

where $E_a$ is the introduced acceptor level, 10.2 meV for Al in Ge[63].

Unfortunately the appearance of the $F_{1/2}(\eta)$ term means that there is little else that can be done analytically to further simplify Eq. 4.7 and 4.8 to a point where an explicit expression for $E_f$ can be written. At this point it makes sense to then move to a numerical treatment of Eq. 4.7 or 4.8 so that the Fermi level can be determined for the various dopant concentrations and temperature ranges.

The easiest way to deal with Eq. 4.7 or 4.8 numerically is to write it in the form of $y = \mathcal{F}(E_f) = 0$ and then solve for $E_f$, given all the other parameters. Furthermore, to avoid having to do multiple numerical integrations for each given temperature and doping level, the Fermi integral can be replaced with the Aymerich-Humet approximation[123], which is given by

$$F_{1/2}(\eta) \simeq \left\{ \frac{3\sqrt{2}}{b + \eta + (|\eta - b|^c + a)^{1/c}} \right\}^{3/2} + \frac{2}{\sqrt{\pi}} \exp(-\eta)$$

with $a = 9.6$, $b = 2.13$ and $c = 12/5$. It is clear from inspection of Eqn 4.9 that the exponential term will dominate for $\eta \ll 1$, thus giving the same behaviour as the Boltzmann approximation in that regime. A comparison of the values obtained from Eqn 4.9 with those obtained from a numerical integration of the Fermi integral
reveals that the difference between the two is less than 0.54% for $\eta < 10$, and so use of the approximation is valid well beyond the degenerate regime covered by this work.

The Aymerich-Humet approximation was substituted into each of the two neutrality equations (Eq. 4.7 and 4.8), along with the thermal band gap narrowing as given by Eq. 2.9, and the resulting expressions were then solved via computer for the doping levels and SPE temperatures used in this work. The resultant Fermi level values that were determined are displayed in Fig. 4.42 and 4.43. As discussed in section 2.4.5, the Fermi level must be about $2kT$ or more away from both band edges for a nondegenerate treatment to be valid. In Fig. 4.42, a $2kT$ boundary below the conduction band is shown for reference. Clearly, the Fermi levels do not lie outside the $\eta < -2$ window defined by this boundary. In the case of the highest arsenic concentration used, the Fermi level is essentially on the conduction band, indicating that $\eta \sim 0$. For aluminum, a similar $2kT$ boundary is shown above the valence band on Fig. 4.43, and again the Fermi levels shown do not lie outside this region. The highest aluminum concentration used actually results in the Fermi level lying below the valence band over the whole temperature range.

### 4.7.5 Fractional Ionization in Doped Germanium

In section 2.4.5 the general behaviour of the fractional ionization as a function of the Fermi level was described. It was shown that the population of the dopant state would be expected to fill in significantly (i.e. lower fractional ionization) as the Fermi level approached the energy level of the dopant. What is not immediately obvious is how the fractional ionization will behave with respect to the dopant concentration and temperature, since the Fermi level, as written in the fractional ionization equation (Eq. 2.18), is implicitly understood to be $E_f = E_f(N_d, T)$. With the Fermi level now explicitly determined by the numerical degenerate treatment, the fractional ionization can also be determined numerically and then graphed so that the behaviour can be studied. Shown in Fig. 4.44 is the fractional ionization for arsenic in germanium for the doping levels used in this work as a function of temperature. Similarly, the fractional ionization curves for the corresponding aluminum
Figure 4.42: Fermi levels as a function of temperature for various concentrations of arsenic doped germanium. The conduction band edge $E_c$, which is equal to the band gap energy when the valence band edge is taken as the zero reference, and the boundary associated with a $2kT$ window below the conduction band are also shown.

Figure 4.43: Fermi levels as a function of temperature for various concentrations of aluminum doped germanium. The valence band edge $E_v$, which is taken as the zero reference, and the boundary associated with a $2kT$ window above the valence band are also shown.
Table 4.13: The net ionized dopant concentration for the gross arsenic and aluminum concentrations used in the SPE measurements of this work. The ranges of values listed correspond to the temperature range covered by this study.

Table 4.13: The net ionized dopant concentration for the gross arsenic and aluminum concentrations used in the SPE measurements of this work. The ranges of values listed correspond to the temperature range covered by this study.

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<thead>
<tr>
<th>Dopant Concentration (/cm(^3))</th>
<th>Arsenic: (N_{\text{As}}^+ (/\text{cm}^3))</th>
<th>Aluminum: (N_{\text{Al}}^- (/\text{cm}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 \times 10^{19})</td>
<td>((0.62-0.71) \times 10^{19})</td>
<td>((0.39-0.48) \times 10^{19})</td>
</tr>
<tr>
<td>(5 \times 10^{19})</td>
<td>((1.69-2.16) \times 10^{19})</td>
<td>((0.94-1.24) \times 10^{19})</td>
</tr>
<tr>
<td>(1 \times 10^{20})</td>
<td>((2.40-3.22) \times 10^{19})</td>
<td>((1.31-1.77) \times 10^{19})</td>
</tr>
</tbody>
</table>

From these figures, it is clear that the assumption of 100% ionization of the dopant species at these concentrations and temperatures is not valid. For the highest concentration of aluminum used, the level of ionization lies between 13% and 18%. Even in the best of the cases studied as part of this work, the ionized fraction is still only 71%. The fractional ionization values for the other concentrations of As and Al used in this work are summarised in Table 4.13 as ranges corresponding to the temperature span over which the SPE measurements were performed.

In the previous discussion on fractional ionization in section 2.4.5, three general regions were introduced corresponding to the location of the Fermi level with respect to the introduced dopant level. The first was for a Fermi level somewhere deep in the band gap with respect to the dopant level, such that nearly 100% ionization of the dopants took place, which corresponds to the full ionization approximation. The second was for a Fermi level that was close to or at the introduced dopant level, for which the ionized fraction would be reduced to 50% or less depending on the degeneracy of the introduced dopant level. The third case was for a Fermi level that was between the introduced dopant level and the respective band edge or possibly even past the band edge, in which case the ionized fraction of dopants would be expected to rapidly decrease to zero. Based upon the values in Table 4.13, it is evident that the samples of this study lie in the second regime, with the highest concentration cases bordering on the third regime.
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

Figure 4.44: Fractional ionization of arsenic atoms in germanium as a function of temperature and for various As concentrations. The values were calculated from Eq. 2.18 and the Fermi levels shown in Fig. 4.42.

Figure 4.45: Fractional ionization of aluminum atoms in germanium as a function of temperature and for various Al concentrations. The values were calculated from Eq. 2.18 and the Fermi levels shown in Fig. 4.43.
4.7.6 Dopant Enhanced SPE and Nondegenerate Models

The explicit calculation of the Fermi levels brings up an important point in light of the doped Ge SPE data from this study as shown in Fig. 4.31 (arsenic) and Fig. 4.36 (aluminum). It is evident that significant SPE rate enhancements in a-Ge are only observed for $N_d \gtrsim 1 \times 10^{19} \text{ /cm}^3$. But from the previous discussion, it has been demonstrated that the Fermi level will not be at least $2kT$ away from each band edge for the dopant concentrations at which enhanced SPE is observed. Hence any model that considers dopant enhanced SPE as a result of Fermi level shifting or other band gap behaviour should include a degenerate semiconductor treatment if that model is to be compared with the experimentally observed SPE enhancements in a-Ge.

Doped Germanium and the GFLS Model

There are now two problems with trying to apply the GFLS model of Lu et al.[11] in its present form to the doped germanium SPE data. In section 2.4.11, it was shown that the model has an implicit assumption that full impurity ionization takes place. However, as shown in section 4.7.5, this is clearly not the case. It is possible to substitute the ionized fraction in place of the total dopant concentration, and then use the values that have just been determined, but then the velocity enhancement as a function of doping would no longer be written in closed form, due to the doping dependence of the fractional ionization.

The second problem arises because Lu et al. used the law of mass action (Eq. 2.15) for a nondegenerate semiconductor to get the quadratic expression for $N_e$ as shown in Eq. 2.42. However, the law of mass action for a degenerate semiconductor is more complex. For example, the difference between the approximation $\eta = \ln(\xi)$ and the true value given for $\eta$ as per Eq. 4.5 can be written as a converging power series in $\xi$. When this is done, it can be shown[26] that the law of mass action can be written as

$$N_e N_h = N_i^2 \exp \left[ -\frac{1}{\sqrt{8}} \xi + \left( \frac{3}{16} - \frac{\sqrt{3}}{9} \right) \xi^2 + \ldots \right] \quad \text{with } \xi = \frac{N_e}{N_c} \quad (4.10)$$

Note the appearance of $N_e$ on the right hand side inside the exponential term. It
is plausible to only keep the first term in the expansion, which will then extend the validity of the approximation into the degenerate region (up to \( \eta \approx 4 \) or equivalently \( \xi \approx 5 \)) and then attempt to work out an analytical expression for \( \frac{v}{v_i} \) but the resulting expression would most likely be too complex to be useful.

Returning to the derivation of the velocity ratio predicted by the GFLS model as detailed in section 2.4.11, the restriction to nondegenerate material comes about early in the derivation due to the application of the law of mass action in the form of Eq. 2.15. To get back to a point where the velocity ratio is still general enough to include degenerate material, one has to go right back to the original expression (Eq. 2.32) given with the treatment of the kink site model (section 2.4.8). Of course the problem with Eq. 2.32 is that it gives the velocity ratio in terms of the Fermi levels of the doped and undoped material, rather than in terms of the experimentally determined doping concentration.

Instead of using an analytical expression for the Fermi Level as a function of dopant concentration and temperature, the calculated Fermi level values shown in Fig. 4.42 can be used to see if the velocity ratios predicted by Eq. 2.32 can be fitted to the experimental SPE data shown in Fig. 4.32. To reiterate, the velocity ratio as per the kink site model, and the GFLS adaptation is expected to be of the form

\[
\frac{v}{v_i} = \frac{1 + g \exp \left( \frac{E_f - E_k}{kT} \right)}{1 + g \exp \left( \frac{E_f - E_k}{kT} \right)}
\]

(4.11)

which is not constrained to nondegenerate material. The only implicit assumption in Eq. 4.11 is that both the (as yet unspecified) charged and neutral defect that control the SPE rate on the whole are equally as efficient in causing SPE events.

In terms of the calculated quantities, the only parameters in Eq. 4.11 that need to be determined are the energy level and the associated degeneracy of the controlling defect. The intrinsic Fermi level is given by equating the square of the left hand side of Eq. 2.13 with the left hand side of Eq. 2.15, which gives

\[
E_{fi} = \frac{E_g}{2} + 3kT \ln \left( \frac{m_h}{m_e} \right)
\]

(4.12)

and the Fermi level in the doped material is given by the degenerate calculations of section 4.7.4. If Eq. 4.11 is a correct description of the dopant-enhancements
observed in SPE measurements, then a fit to experimental data should be possible for reasonable values of \( g \) and \( E_k \).

The normalized velocity data for the arsenic doped samples are shown in Fig. 4.32 seems to be a better candidate for this type of fit than the aluminum data (Fig. 4.37) since it exhibits a larger change in the velocity ratio with respect to temperature. By using the Fermi levels in Fig 4.42 and allowing both \( g \) and \( E_k \) to vary in Eq. 4.11, fits to the normalized As SPE rates that are of equal quality to the previous fits for the fractional ionization model (Fig. 4.32) can be obtained, as shown in Fig. 4.46. As with the previous fits, a large range of fitting parameters can be used on the \( 1 \times 10^{19} / \text{cm}^3 \) data, due to the fact that the velocity ratio is essentially invariant, and hence it is excluded. However, the values obtained from such a fit to the other two concentrations are \( g \sim 58 \) with \( E_k = 0.731 \) eV, and \( g \sim 84 \) with \( E_k = 0.732 \) eV for the \( 5 \times 10^{19} / \text{cm}^3 \) and \( 1 \times 10^{20} / \text{cm}^3 \) As SPE data respectively. This results in a defect level that is about 0.2 eV above the conduction band edge, and a degeneracy value that does not seem physically realistic.

On the other hand, if the degeneracy of the unspecified defect is fixed at a more plausible value of say four, and then only \( E_k \) is allowed to vary in the fitting process, one obtains \( E_k = 0.51 \) eV, and \( E_k = 0.50 \) eV for the \( 5 \times 10^{19} / \text{cm}^3 \) and \( 1 \times 10^{20} / \text{cm}^3 \) cases respectively. From a comparison with Fig. 4.42, this puts the defect level just slightly above or below the conduction band, depending on the particular temperature. But with the extra degree of freedom removed from the fitting process, these fits (Fig. 4.47) are not as good as the previous ones. In particular, the temperature dependence appears too strong, with the curves converging too quickly at higher temperatures to \( v/v_i = 1 \).

An Extension to the GFLS Model

A minor modification to the basic premises of the GFLS model can be introduced which makes the predicted enhancements equivalent to those shown in Fig. 4.46, while still maintaining a reasonable degeneracy value of four. The fractional ionization model claims that SPE is controlled by the amorphous phase, while the GFLS model postulates that the properties of the crystal control the SPE rate. In light of
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

Figure 4.46: Fits to the arsenic-enhanced SPE data of this work as per the degenerate generalized Fermi level shifting (GFLS) model. Both the energy level and the degeneracy of the proposed defect responsible for controlling SPE have been left free as fitting parameters.

Figure 4.47: Fits to the arsenic-enhanced SPE data of this work as per the degenerate generalized Fermi level shifting (GFLS) model. The energy level of the proposed defect controlling SPE has been left free as the only fitting parameter, while the degeneracy of the defect has been fixed at a value of four.
this Lu et al.[11] note that since “...the relevant defects reside at the c/a interface, it might now be appropriate to call for a third type of doping model based on the density of states in the interface”. The proposed extension to the GFLS model is to postulate that the charged defect concentration at the interface is controlled by the band structure at the interface, and not by the band structure of the crystalline bulk.

The difficulty comes in assigning a quantitative description to the band structure at the the interface. A qualitative description of the band structure would be expected to be similar to that of a p-n junction[26] as shown in Fig. 4.48, with the continuity of the Fermi level across the interface implying that band-bending takes place at the interface. In the case of the p-n junction, the Fermi level is close to opposite band edges on opposite sides of the interface, whereas for a c/a interface, the Fermi level is close to a band edge in the doped crystalline material and near mid-gap in the amorphous material, as shown in Fig. 4.49. This sort of description for the c/a interface has been proposed previously by Williams and Elliman[70], although it has not yet been incorporated quantitatively into any model.

The quantity of interest for dopant-enhanced SPE rates in the GFLS model as per Eq. 4.11 is the relation of the Fermi level to the proposed defect. Furthermore it is assumed that the introduced defect level remains at a constant location with respect to the band edges as one crosses the interface. Hence, it is convenient to consider the band structure of Fig. 4.49 from the perspective of the band edges, in which case they will be flat lines and the Fermi level will appear to move away from the conduction band and towards mid-gap as one crosses the interface. If the band bending is equally shared across both phases as depicted in Fig. 4.49, then the Fermi level at the interface will be halfway between the bulk crystalline value ($E_{Fc}$) and the intrinsic ($E_{Fi}$) or mid-gap value. However, if the band bending is not equally shared in both phases, then the Fermi level at the interface can be written as

$$E_F = W (E_{Fc} - E_{Fi}) + E_{Fi}$$  (4.13)

where $W$ is a weighting factor representing how much effect moving the bands in the crystalline material has on the Fermi level at the interface. A value of $W = 1$ corresponds to 100% effectiveness, i.e. the Fermi level at the interface is equal to the bulk crystalline value, which gives the same result as the original GFLS model.
Figure 4.48: The band gap structure of a p-n junction or common diode. The constancy of the Fermi level across the interface implies that band bending must take place.

Figure 4.49: Band gap structure for a c/a interface in n-type material, patterned after that of a p-n junction. The Fermi level is assumed to be mid-gap in the amorphous material. (After Williams and Elliman[70].)
as shown in Fig. 4.47. For the case of equal sharing of the bending as discussed previously, a value of $W = 0.5$ applies. Finally, a value of $W = 0$ is equivalent to saying the Fermi level at the interface is essentially pinned at mid-gap by the amorphous material, and moving the bands about in the crystalline material by varying the doping level has almost no effect on it.

When this extension to the model is applied to the arsenic doped germanium data, so that the postulated Fermi levels at the interface are used in Eq. 4.11, it is found that a value of $W \sim 0.22$ results in fits similar to those in Fig. 4.46 while maintaining a reasonable degeneracy value. In terms of the model extension, this is equivalent to suggesting that $\sim 78\%$ of the band bending takes place within the crystalline phase. In this calculation, a band gap magnitude equal to that of crystalline Ge has been assumed for the a-Ge side since there is no information available on the band structure of a-Ge. Since the band structure of a-Ge is unknown, there is little value in reporting the values of $g$ and $E_k$ here, but this calculation does suggest that the GFLS model with degenerate doping taken into account can provide a plausible fit to the data if band bending is taken into consideration.

So in summary, the GFLS model in the form of Eq. 4.11, with plausible values for $g$ and $E_k$, appears to correctly predict the general behaviour of the temperature dependence of the normalized SPE rate for a given dopant concentration, even in the degenerate regime. However, the actual magnitude of the predicted temperature dependence appears to be too strong when compared to the experimental data for arsenic. Extending the model to consider the band structure at the interface instead of the band structure of the bulk crystalline material alleviates this problem, but given that there are only two data sets with a considerable level of scatter in each, and since the band structure of a-Ge is unknown, it would be unwise to draw conclusions based upon this alone.

### 4.7.7 SPE in Compensation Doped Germanium

From Fig 4.41, it is evident that nearly complete compensation takes place in the samples implanted with both As and Al, such that the SPE rate is very close to that observed for the intrinsic material. Most models usually attribute compensation to
an interaction between electrically active dopants of opposite type. In light of this, it is instructive to apply similar numerical calculations to this material so that the fractional ionization of each individual dopant is known. The calculation is similar to that which was done in section 4.7.4 and 4.7.5.

The Fermi level will have to be determined first, as it is required for evaluating the fractional ionization of each dopant species as given by Eq. 2.18. The neutrality equation (Eq. 4.6) will no longer have any zero terms, and hence the expression to solve for the Fermi level in a semiconductor with both p-type and n-type impurities present will become

\[
N_e \exp \left( \frac{E_f - E_c}{kT} \right) + \frac{N_a}{1 + 2 \exp \left( \frac{E_c - E_f}{kT} \right)} = \frac{N_d}{1 + 2 \exp \left( \frac{E_f - E_d}{kT} \right)} + N_n \exp \left( \frac{E_v - E_f}{kT} \right)
\]

(4.14)

where the Boltzmann approximation is now being used on both sides, since it is expected that the presence of both n-type and p-type dopants in similar concentrations will push the Fermi level back to the middle of the band gap. The resulting Fermi level as a function of temperature as determined from solving Eq. 4.14 is shown in Fig. 4.50.

Also shown in Fig. 4.50 are the boundaries of the regions within \(2kT\) of either band edge. Since the Fermi level shown lies outside both of these regions, the condition \(\eta \leq -2\) is maintained, and thus the use of the Boltzmann approximation on both sides of Eq. 4.14 is justified. Furthermore, the Fermi level sits at about the middle of the band gap, as expected. With the Fermi level of the material now known, the ionized fraction of each of the dopants can be determined by direct substitution into Eq. 2.18. The resulting values for both the arsenic and the aluminum are displayed in Fig. 4.51.

At the lower SPE temperatures, both the As and Al have nearly identical fractional ionizations, being just below 99%. As the temperature is increased, the fractional ionization begins to drop, with the value for the Al decreasing more rapidly than that for As. At the highest SPE temperature used, the fractional ionization for As has dropped to 89% whereas the Al has dropped to 86%. For the \(5 \times 10^{19} / \text{cm}^3\) concentration of each dopant used, this difference corresponds to a 'surplus' of ionized arsenic on the order of \(2 \times 10^{18} / \text{cm}^3\) at 540 °C. However, this is about an order of
Figure 4.50: The Fermi level in compensation doped germanium containing a concentration of $5 \times 10^{19}$/cm$^3$ of both arsenic and aluminum. The conduction and valence bands are shown for reference, along with the size of a $2kT$ window into the band gap from each band edge.

Figure 4.51: Fractional ionization of both aluminum and arsenic atoms in germanium as a function of temperature, for a gross concentration of $5 \times 10^{19}$/cm$^3$ of each dopant species. The values were calculated from Eq. 2.18 and the Fermi levels shown in Fig. 4.50.
magnitude lower than the minimum As concentration required to cause a significant enhancement in the SPE rate as per section 4.6.1, and indeed no significant temperature dependence is evident in the experimental compensation data of Fig. 4.41. Yet, for compensation experiments with higher overall concentrations, it is expected that the difference in fractional ionizations may become a significant factor.
4.8 Conclusions

The solid phase epitaxial crystallization rate of Ge layers formed by self-ion implantation of various (100) Ge substrates obtained from different suppliers was measured at temperatures ranging from 300 °C to 540 °C. No significant variation was observed between samples of different substrates. The implantation dose and energy was also varied, and again the SPE rate showed no observable change. From these measurements, an activation energy of 2.15±0.04 eV and a velocity prefactor of (2.6±0.5)×10^7 was determined for the solid phase epitaxial regrowth process on (100) Ge. This result provided the base value that all the measurements of impurity doped a-Ge layers were compared with.

The effects of hydrogen on the SPE process in Ge were then investigated. There was no evidence of large scale indiffusion of hydrogen from the annealing ambient into a-Ge to the extent that is seen for silicon. The c/a interface velocity was observed to be essentially constant from depths of ~3.25 µm to within ~2500 Å of the surface. Some retardation effects were observed in the remaining surface layer. SIMS measurements of samples annealed to within ~2500 Å of the surface showed peak concentrations of up to 6×10^18 H/cm^3 directly in front of the c/a interface. Hydrogen was then implanted into a-Ge layers at concentrations ranging from 1×10^19 H/cm^3 to 4×10^19 H/cm^3, in accordance with the hydrogen concentration observed in partially annealed a-Si layers. SIMS measurements of partially annealed H-implanted a-Ge samples showed that the H was collected or zone-refined at the c/a interface, indicating a lower solubility for H in c-Ge as opposed to a-Ge, similar to that which is observed for H in Si. SPE measurements on these samples showed a c/a interface velocity reduction similar to that observed during regrowth of a-Si layers. The activation energy was determined for the region in which the c/a interface motion was retarded, and was found to be the same as the intrinsic value quoted above. This finding is consistent with the argument that hydrogen occupies "dangling bonds" that could otherwise be involved in a crystallization event, and hence reduces the overall crystallization velocity without altering the energetics of the SPE process. The proposed source of hydrogen in the silicon case is from the dissociation of water vapour during the formation of SiO₂. It is concluded that the
lack of hydrogen in germanium is a result of the instability of GeO$_2$.

The effect of implanted arsenic on the solid phase epitaxial regrowth process was then investigated. The presence of As in concentrations greater than $1 \times 10^{19}$ /cm$^3$ caused an increase in the SPE rate. A constant concentration of $1 \times 10^{20}$ As/cm$^3$ reduced the activation energy by 0.11 eV and the velocity prefactor was also reduced by about 40%. For a fixed As concentration, the SPE enhancement was observed to increase with decreasing temperature in what appeared to be an exponential fashion. While the data could be fitted by the SPE rate enhancement as predicted by the fractional ionization model, it is not conclusive enough to prove the model correct.

Similar measurements were performed on aluminum implanted amorphous germanium samples to investigate the effect of Al on the SPE rate. Concentrations greater than $1 \times 10^{19}$ Al/cm$^3$ were also observed to cause an enhancement in the SPE rate. The presence of a constant concentration of $1 \times 10^{20}$ Al/cm$^3$ was observed to reduce the activation energy by only 0.04 eV which is within experimental error, and the velocity prefactor remained unchanged. The enhancement becomes greater at lower SPE temperatures, but the form of the temperature dependence was not as clear. The enhancement for a given temperature and concentration was always less for Al than it was for As.

SPE measurements were also performed on a-Ge samples containing overlapping profiles of $5 \times 10^{19}$ As/cm$^3$ and $5 \times 10^{19}$ Al/cm$^3$. The SPE rate through the region containing comparable concentrations of both dopants was observed to return to a value very close to that observed in undoped a-Ge, indicating nearly complete compensation between the n-type and p-type dopants. The remaining slight enhancement was similar to that observed for a sample containing $\sim 1 \times 10^{10}$ /cm$^3$ of either dopant.

Theoretical semiconductor statistical calculations were undertaken to determine the quantum state of the carriers in the crystalline germanium during the SPE process. It was demonstrated that the material would be degenerate for the dopant concentrations and temperatures at which enhanced SPE rates were observed. The immediate ramification of this result was that any theory that was designed to predict dopant enhanced SPE in germanium could not take the simplifying assumptions
associated with nondegenerate semiconductor statistics. Furthermore, a degenerate numerical treatment indicated that the fraction of dopant atoms that contributed a carrier to the material and were left in an ionized state ranged from 13% to 71%, depending on temperature, dopant concentration and dopant species. This is another factor that has to be considered in modeling, since it is commonly assumed that 100% of the dopants will be ionized.

The basic expression for dopant-enhanced SPE rates as given by the kink site model and the GFLS model was then compared to the experimental arsenic data without making any nondegenerate simplifications. The general shape of the SPE enhancement predicted by this expression was similar to that observed experimentally. However, to fit the data exactly required a defect degeneracy value that seems unrealistic. A modification to the GFLS model was proposed which involved the SPE enhancement relying on the band structure at the interface and not on the band structure of the bulk crystalline material. With this in place, the model fits the experimental data while still maintaining a reasonable degeneracy value. Given the lack of information about the band structure of a-Ge in addition to the difficulty associated with obtaining reasonably scatter-free velocity enhancement factors as a function of temperature and doping level, the comparison to the arsenic data alone is not sufficient to allow substantial conclusions about the correctness of the model to be drawn.
CHAPTER 4. SPE OF AMORPHOUS GERMANIUM

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Chapter 5

Solid Phase Epitaxial Regrowth of Amorphous Silicon and Silicon-Germanium Alloys
5.1 Introduction

Silicon was first discovered by the Swedish chemist, Jöns Jacob Berzelius in 1824, about 60 years prior to the discovery of germanium. As is the case with germanium, silicon is not found naturally in a pure form, but rather in minerals like silica and various silicates. However, in contrast to germanium for which the relative abundance is measured in parts per million, silicon accounts for nearly 30% of the matter found in the Earth’s crust[105]. Chances are that Berzelius had no idea that silicon would become one of the most studied elements some 150 years later. With silicon replacing germanium in the late 1960’s as the semiconductor material of choice, research on silicon became very prominent in the related materials science journals, and has not let up since. Given that various groups have been investigating silicon for the last 30 years, the naïve might expect that all the answers are in the literature by now. Unfortunately this is far from the reality of the situation, as each question answered seems to raise at least two more new ones.

The situation for solid phase epitaxial regrowth in silicon follows this trend. Even though SPE measurements in Si have been taking place for over 20 years now, it has only recently been revealed that hydrogen contamination has managed to implicitly play a role in all the previous measurements. How this hydrogen effects the SPE rate in undoped silicon has only been treated by the group that first reported it, and the impact on dopant-enhanced SPE measurements has yet to be considered. The use of constant concentration doping profiles in thick a-Si layers, combined with longer wavelength TRR measurements has yet to be exploited to address this issue. In the case of Si$_x$Ge$_{1-x}$, there simply are no dopant-enhanced SPE measurements yet.

The results in the literature that are relevant to the current work are first presented in section 5.2. Section 5.3 then details the sample preparation and other experimental aspects specific to this chapter. The results associated with solid phase epitaxial regrowth of intrinsic a-Si and hydrogen contamination are detailed in section 5.4. Following that, the effects of arsenic, aluminum and the simultaneous presence of both on the SPE rate in a-Si are reported in section 5.5, along with similar measurements on Si$_x$Ge$_{1-x}$ alloys. The chapter closes with a discussion of the above results in section 5.7 and the final conclusions are detailed in section 5.8.
5.2 Review

In section 2.3, the results of several important SPE measurements in Si were summarised in order to lay a background for the SPE models that currently exist. In this section, the same results are considered, but with more of a focus on the methodology of the measurements, and implications thereof. A similar consideration of the Si$_x$Ge$_{1-x}$ alloy results discussed in section 2.5 is also detailed in this section.

5.2.1 SPE of Undoped Silicon

It has now been over 20 years since Csepregi et al.[9] first reported quantitative measurements on the solid phase epitaxial regrowth rate for a-Si on a crystalline substrate. They were one of the first groups to exploit implantation techniques to create a-Si layers essentially free from impurities. By using the partial anneal/RBSC technique (section 2.6.6), they measured the SPE rate on (100) Si at four temperatures between 475 °C and 550 °C, and reported an activation energy of $2.3 \pm 0.1$ eV. Lietoila et al.[18] performed similar measurements over the same temperature range in 1982, and reported an activation energy of 2.85 eV for SPE of 4000 Å thick a-Si layers. They used a new sample for each partial anneal which limited the effects associated with the time required for the sample to reach equilibrium temperature.

In 1983, Olson et al.[46] reported an activation energy and velocity prefactor of $2.68 \pm 0.05$ eV and $3.1 \times 10^6$ m/s for (100) Si, as outlined in section 2.3.3. These results were based upon TRR measurements of ion implanted a-Si layers 2500 Å thick, and for temperatures ranging from $\sim 550$ °C to $\sim 950$ °C. Their measurements at higher temperatures[47] were based upon a-Si layers only 1600 Å thick. The Arrhenius parameters associated with the measurements on the 2500 Å thick layers remained as the accepted values for intrinsic SPE of a-Si layers on (100) Si until the hydrogen contamination effect was discovered.

5.2.2 Hydrogen Effects

As discussed in section 2.3.6, Roth et al.[19,20] recently showed that all previous SPE measurements performed on thin (< 2 µm) a-Si layers were most likely influenced
by the presence of hydrogen in the amorphous layer created as a by-product of the formation of a surface oxide layer. The nature and extent of the effect was considered in detail in section 4.2.6 prior to looking for a similar effect in germanium, and hence it will not be repeated here. In summary, they found that concentrations exceeding $1 \times 10^{19}$ H/cm$^3$ were present in thin layer samples even when annealed in a vacuum furnace[20], and that this hydrogen was responsible for SPE rate reductions of up to 40%. The effect was reported as being limited to the absolute SPE rates, in that the activation energy for SPE of thin H contaminated layers was the same as for SPE in thick H free layers to within experimental error. Based upon this, they argued that all prior thin layer Si SPE measurements, including those involving dopants, had hydrogen present at concentrations above $1 \times 10^{19}$ /cm$^3$. Since there was no thick layer SPE data prior to their own measurements, this essentially applied to all the prior Si SPE measurements.

5.2.3 Dopant Effects

There have been a considerable number of measurements of the SPE rate in silicon associated with the presence of dopants. These can generally be categorized according to the measurement technique. The earlier measurements relied on the partial anneal/RBSC technique, whereas most of the recent measurements have employed the TRR technique. Both measurement techniques were described earlier and compared in section 2.6.

Early Measurements

The measurements of Csopregi et al.[17] were the first to document the effect of dopants on the SPE rate. Their data was based upon partial anneal/RBSC measurements (section 2.6.6) of 4300 Å thick (100) a-Si layers implanted with phosphorous, arsenic and boron. In the case of the arsenic doped sample, the SPE rate was only measured at one temperature, and the peak concentration of As was within 1500 Å of the surface.

Suni et al.[7,16] also used partial anneal/RBSC measurements to determine the SPE enhancement caused by arsenic, boron and phosphorous in (100) Si. The arsenic
profile used was highly non-uniform, varying from $\sim 0.5 - 2.0 \times 10^{20}/\text{cm}^3$ from 500 Å to 4500 Å. The measurements were conducted at only two temperatures separated by 25 °C. Their compensation measurements, while being the first of their kind, were also similarly limited.

In 1982, Lietoila et al.[18] made improved measurements on doping effects by employing multiple-energy implants to obtain reasonably constant concentration profiles for phosphorous and boron. However, the use of partial anneal/RBSC measurements still limited the temperature range that they could access. For their phosphorous doped sample, only three temperatures were used to determine the reported activation energy of 2.5 eV, based on the SPE data for the depth range spanning 300 Å to 2500 Å.

**Time Resolved Reflectivity Measurements**

The measurements of the Olson group on arsenic implanted silicon (section 2.3.3) involved high concentrations (up to $1.4 \times 10^{21}$ As/cm$^3$), with the peak concentration lying at a relatively shallow depth of only 1300 Å. The concentration gradient in such samples is particularly large. Olson and Roth[13] suggested that the observed retardation and asymmetry between the SPE rate profile and the concentration profile may be due to As-vacancy complexes and arsenic clustering in the amorphous phase. These measurements, combined with the earlier high concentration measurements of Williams and Elliman[45] tend to indicate that SPE rate enhancement measurements will become complicated by other effects for peak concentrations greater than $\sim 4 \times 10^{20}$ As/cm$^3$.

In 1986, Licoppe and Nissim[124] used 632.8 nm TRR to measure the SPE enhancement due to the presence of arsenic implanted into (100) Si. Their samples consisted of single implant arsenic profiles at 100 keV or 158 keV, which should result in a peak concentration at a depth around or just below 1000 Å[108]. The implants were performed at room temperature, although this had already been reported in the literature to cause non-ideal SPE due to extended defects[125]. The arsenic concentration associated with a particular SPE measurement was taken as
the mean concentration between the two minima of the TRR signal, which translates to averaging over the depth range from 650 Å to 1300 Å. Based on this averaging, they reported SPE data for concentrations ranging from \(2 \times 10^{19}\) As/cm\(^3\) to \(1.5 \times 10^{20}\) As/cm\(^3\).

The Walser Group

The Walser group have also investigated SPE in implantation doped a-Si layers, including boron\[49\], arsenic\[25\], phosphorous\[24\], aluminum\[22\] and also B + P compensation\[23\], as mentioned in section 2.3.5. These measurements are the most recent dopant enhancement measurements in silicon. In fact, TRR was also employed in all of these measurements, although the authors elected to refer to it as "high precision in situ isothermal cw laser interferometry" instead. All the measurements were performed in a moderate vacuum (\(10^{-3}\) Torr to \(10^{-6}\) Torr) which makes temperature calibration more difficult. SPE rates were associated with a particular dopant concentration, for single implant samples, by mapping the interface velocity to the interfacial concentration over the depth range from the peak concentration to the surface of the sample.

In the case of arsenic\[25\], their three samples consisted of single 180 keV implants of different doses, which resulted in a peak concentration at only 1100 Å. They reported that no asymmetry between the arsenic profile and the SPE rate enhancement was observed. However, the problem associated with using near surface measurements is immediately evident from inspection of their data. For example, the SPE rate at 510 °C, associated with \(6 \times 10^{19}\) As/cm\(^3\) at 1100 Å is reported to be 30 Å/min, but for the same concentration at a depth of 400 Å, it is reported to be only about 16 Å/min.

The situation is similar for their aluminum measurements. Three single energy implants of 90 keV to 100 keV were used to create the three samples used in their measurements. This implantation energy results in a peak concentration at about 1500 Å. The reported retardation associated with low aluminum concentrations was based on an observed increase in the SPE rate as the \(c/a\) interface moved through the last 1500 Å of material. It is plausible that at such low concentrations,
the aluminum plays no significant role in the SPE rate, and the increase observed was just the tail end of the hydrogen contaminated SPE rate as shown in Fig. 4.1. In fact, Roth et al.[20] note that H was expected to be present in a concentration of the same order of magnitude as the intentionally introduced dopants for all of the measurements performed by the Walser group.

5.2.4 Silicon-Germanium Alloys

As discussed in section 2.5, the SPE rate has recently been measured in unstrained Si\textsubscript{x}Ge\textsubscript{1-x} alloys of varying composition. The SPE rates appear to follow an Arrhenius behaviour as they do for pure Si and Ge. However, all of these measurements have been performed over a relatively narrow depth range lying within 4000 Å of the surface and hence the possibility of near surface SPE retardation playing a role exists. In the case of the most recent data reported by Haynes[40], this limited depth range has resulted in the SPE rate being determined from only half of a 1.5 μm TRR interference cycle.

SPE measurements involving Si\textsubscript{x}Ge\textsubscript{1-x} alloys that have significant amounts of electrically active dopants present have only been reported by Pai et al.[36] for boron. However, in that case it is assumed that the boron enhances the SPE rate by the removal of strain and by the ‘usual’ electronic effect associated with dopant-enhanced SPE in Si. Thus, it is not possible to unambiguously separate the two in order to comment quantitatively on what sort of dopant-enhanced SPE rates are to be expected for Si\textsubscript{x}Ge\textsubscript{1-x} alloys.

5.2.5 Summary

In the case of SPE in undoped a-Si, little has been done since Roth et al.[19, 20] reported the hydrogen contamination effect. No other independent measurements on thick a-Si layers have been performed to corroborate or contradict their experimental observations. The situation for SPE measurements in doped a-Si samples is similar, in that the most recent set of doping measurements performed by the Walser group must be assumed to also suffer from hydrogen contamination. However, the issue of how the simultaneous presence of hydrogen and a doping impurity may affect
the SPE rate has not yet been considered in the literature, and currently there is no experimental data that would provide insight as to what sort of combined effect would be expected.

Another issue with most of the dopant-enhanced SPE measurements, including the most recent ones, is that they have been performed on samples containing non-uniform concentration profiles, usually resulting from only a single implant of an impurity. These implants have typically been performed at energies of less than 200 keV, which results in the majority of the dopant lying within 2000 Å of the surface and with relatively large concentration gradients. The correlation of an enhanced SPE rate to a specific dopant concentration then requires a highly accurate matching of the depth scales of the SPE rate profile and the dopant profile. There is also evidence of an asymmetry effect, indicating that the SPE rate may depend on the concentration gradient as well as the local concentration. These issues make the use of constant concentration samples an attractive solution for avoiding such additional complications. Yet, the use of samples with a constant concentration of a dopant over a significant depth interval in TRR SPE measurements remains to be fully exploited.

While the temperature span of SPE measurements in undoped a-Si is considerably large, the temperature span of the earlier dopant measurements involving constant concentration profiles was very limited due to the use of the partial anneal/RBSC technique. The possible error in extracting the temperature dependence (e.g., activation energy) from only a few measurements spanning approximately 50 °C is quite large.

The case of a-Si doped with aluminum also warrants considerable attention. The effect of Al on the SPE rate has only been considered once in the literature, and an anomalous effect involving a rate reduction for low concentrations has been reported. This result appears to be in stark contrast to those for other dopant impurities, which all exhibit a monotonic increase in the SPE rate for an increase in concentration.

The use of constant concentration profiles in compensation experiments using the partial anneal/RBSC technique has also been shown to be an improvement over
combined single implant profiles. Yet, TRR SPE measurements using reasonably thick a-Si layers containing overlapping constant concentration profiles of n-type and p-type dopants have yet to be performed.

In addition, all the compensation measurements of the past have exclusively used boron as the p-type dopant. It has been simply assumed that all other p-type dopants such as aluminum will play similar roles in compensation measurements, even though this has never been demonstrated experimentally.

Dopant-enhanced SPE measurements in Si$_x$Ge$_{1-x}$ alloys are currently an unexplored area. The recent ability to create thick Si$_x$Ge$_{1-x}$ layers has allowed several measurements of the SPE rate in undoped material to be performed, but the effect of doping has yet to be reported. Measurements of this type may provide additional insight into the mechanisms of SPE enhancement, and SPE itself.

The work of this chapter addresses these issues. Firstly, the SPE rate in thick a-Si layers is considered, with a particular focus on the nature of the hydrogen contamination issue. Then SPE measurements from constant concentration samples containing arsenic and aluminum are reported, which provide some insight into how hydrogen contamination effects dopant enhancement. The use of aluminum as a p-type doping impurity provides a comparison to the anomalous retardation effect reported in the literature. Aluminum has also been used in compensation measurements, which provides the first set of compensation SPE data that has not used boron as a p-type dopant. Finally, measurements on the SPE enhancement in two different Si$_x$Ge$_{1-x}$ alloys due to constant concentration arsenic profiles are reported.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

5.3 Experimental

This section documents the experimental aspects specific to the solid phase epitaxial regrowth measurements in silicon and silicon-germanium alloys. The more general details pertaining to the TRR system, RBS measurements and implantation conditions can be found in Chapter 3.

5.3.1 Formation of Undoped Samples

Silicon wafers of a (100) orientation and a resistivity of 20–30 Ω·cm were used as the substrate material. Samples that were to be implantation doped with arsenic or aluminum were first amorphized to a depth of \( \sim 3 \) µm. Amorphization was achieved by using a four step multiple-energy self-implant sequence as listed in Table 5.1, with the implantation conditions described in section 3.3.2. This sequence is based upon values published by Roth et al.[19] for the creation of thick a-Si layers.

Two other samples with amorphous silicon layers were created for investigation into hydrogen SPE retardation effects. One was created as per the implantation sequence of Table 5.1 but without the 3 MeV implant, and the second consisted of a single implant of \( 5 \times 10^{15} \) Si/cm\(^2\) at 100 keV. The resulting a-Si layer thickness for these implant conditions was \( \sim 0.25 \) µm and \( \sim 2.2 \) µm respectively.

The substrate material for the silicon-germanium alloy samples consisted of MBE grown layers on (100) Si substrates. Further details on the MBE facility at Aarhus University, as well as typical growth conditions are documented in the literature[38]. A buffer layer 2 µm thick with a linearly increasing germanium content up to the desired Ge concentration was grown on the Si substrate prior to the deposition of the final alloy layer. The final layer was grown to a thickness of 1–1.5 µm on top of this buffer layer. The resultant alloy composition of these substrates has been measured by RBS and reported elsewhere[39] as part of an independent study. From these measurements, the two different substrates were determined to have a composition of \( \text{Si}_{0.79}\text{Ge}_{0.21} \) and \( \text{Si}_{0.47}\text{Ge}_{0.53} \) respectively. Substrates of both alloy compositions were then amorphized with implants of \( 2 \times 10^{15} \) Si/cm\(^2\) at 500 keV and at 1 MeV. These implants resulted in an amorphous layer \( \sim 1.4 \) µm thick in \( \text{Si}_{0.79}\text{Ge}_{0.21} \) and \( \sim 1.2 \) µm thick in \( \text{Si}_{0.47}\text{Ge}_{0.53} \).
Table 5.1: The implantation energies and nominal doses used for creation of a-Si layers on (100) Si approximately 3 µm thick. Implants were performed at 77 K and in the order that they appear in the table.

5.3.2 Formation of Implantation Doped Samples

The 3 µm thick a-Si layers were then subjected to implants of arsenic and aluminum to create dopant profiles favourable for SPE measurements. Multiple-energy implants were employed to create constant doping profiles in the host a-Si material. Computer simulations[108] were used to determine the individual implantation parameters required to achieve an overall constant concentration over the desired depth range. The simulations assumed implantation into Si with a density equal to that of c-Si, although the actual implants were into a-Si, which has been reported to be 1.2% less dense[75].

Arsenic in a-Si

The arsenic implantation energies and doses that were used to create a constant arsenic concentration profile within the a-Si layer are shown in Fig. 5.1 along with the resulting theoretical profiles. The values shown result in an overall concentration of $1 \times 10^{20}$ As/cm$^3$ from 3500 Å to 8000 Å. The doses listed were also scaled by factors of 0.5, 0.2 and 0.1 to create samples containing constant concentrations of $5 \times 10^{19}$ As/cm$^3$, $2 \times 10^{19}$ As/cm$^3$ and $1 \times 10^{19}$ As/cm$^3$ respectively. The arsenic profile has been assumed to remain invariant throughout the crystallization process, since SIMS measurements[13] of samples containing peak concentrations up to 14× greater than the maximum concentration used here have shown no variation between the pre-anneal and post-anneal profiles.

The final arsenic profiles for each of the two highest concentrations were verified
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

Figure 5.1: Theoretical arsenic implantation profiles used to create an overall constant As concentration of $\sim 1 \times 10^{20}/\text{cm}^3$ over the depth range from 3500 Å to 8000 Å. Individual implant profiles are shown in conjunction with the resulting total As concentration, as calculated using computer simulations[108].

Figure 5.2: RBS measurement (3 MeV He) of the arsenic concentration after performing implants as per Fig. 5.1 at half the indicated dose. The error in the plateau concentration associated with this measurement is ±10%.
5.3. **EXPERIMENTAL**

with 3 MeV RBS measurements. Figure 5.2 shows the dopant profile resulting from such a measurement on the $5 \times 10^{19}$ As/cm$^3$ sample. Multiple RBS measurements of 80–100 µC each were required to obtain a statistically significant number of counts in the arsenic signal. The measured plateau concentrations were in agreement with the expected nominal dose to within the error of the RBS measurements (±10%). Due to the difficulty in obtaining significant statistics for the two lower concentrations, they were not measured with RBS. Instead it was assumed that the results of the two higher concentration samples would be representative of the lower dose samples since they were implanted at the same time under identical conditions.

**Aluminum in a-Si**

Multiple-energy implants were also employed to create a constant concentration profile of aluminum within an a-Si layer. The energies and implantation doses used to achieve this are listed on Fig. 5.3, along with the individual profiles and the resultant sum Al profile. The individual profiles were calculated in the same fashion as for the arsenic case. The final dopant profile has a reasonably constant concentration of $\sim 5 \times 10^{19}$ Al/cm$^3$ spanning the region from $\sim 8000$ Å to 12500 Å.

**Arsenic and Aluminum in a-Si**

A compensation sample was also created which contained both arsenic and aluminum, with an overlap of each sum dopant profile. The substrate material was amorphized according to Table 5.1 prior to the implantation of any dopants. The sample contained arsenic as per the implants listed on Fig. 5.1 (half dose) and aluminum as per the implants listed on Fig. 5.3. The arsenic and aluminum profiles are shown on Fig. 5.4, along with the absolute value of the difference between the concentrations of the two dopants. There is a surplus of arsenic up to depths of $\sim 8000$ Å and a surplus of aluminum from $\sim 8000$ Å to $\sim 2$ µm. The net dopant concentration is less than $1 \times 10^{19}$/cm$^3$ from $\sim 6500$ Å to $\sim 9000$ Å.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

Figure 5.3: Theoretical aluminum implantation profiles used to create an overall constant Al concentration of $\sim 5 \times 10^{19}$ /cm$^3$ over the depth range from 8000 Å to 12500 Å. Individual implant profiles are shown in conjunction with the resulting total Al concentration. The individual dopant profiles were calculated using computer simulations[106].

Figure 5.4: Total As and Al concentration after performing implants as listed on Figs. 5.1 (half dose) and 5.3. The individual As profile (circles) and Al profile (triangles) are shown along with the absolute difference between the two curves. There are regions containing surplus As (diamonds) and surplus Al (stars).
Arsenic in $\text{Si}_x\text{Ge}_{1-x}$ Alloys

Some silicon-germanium alloys were also implantation doped with arsenic. These samples were amorphized with $1.2 \times 10^{15} /\text{cm}^2$ of 500 keV Si at 77 K prior to any arsenic implants. Different implantation parameters were required for each alloy due to the density difference between the two. The alloy density used in the simulations was taken to be the interpolated value lying between the density of c-Si and c-Ge associated with that alloy composition. This results in densities of 3.91 g/cm$^3$ and 2.96 g/cm$^3$ for $\text{Si}_{0.47}\text{Ge}_{0.53}$ and $\text{Si}_{0.79}\text{Ge}_{0.21}$ respectively. The arsenic implantation energies and doses along with the resulting simulated profiles for both the $\text{Si}_{0.79}\text{Ge}_{0.21}$ and the $\text{Si}_{0.47}\text{Ge}_{0.53}$ alloy samples are shown in Figs. 5.5 and 5.6 respectively. There is a constant concentration of $\sim 1 \times 10^{20}$ As/cm$^3$ ranging from 3000 Å to 6500 Å for the $\text{Si}_{0.79}\text{Ge}_{0.21}$ sample, and from 2500 Å to 6000 Å for the $\text{Si}_{0.47}\text{Ge}_{0.53}$ sample.

5.3.3 TRR Measurements and Index of Refraction Values

In section 3.2.3, the significance of the wavelength used in TRR measurements was discussed. A longer wavelength laser gives less signal absorption per unit depth and thus a larger overall depth can be probed, although at the expense of a reduced depth resolution. The first TRR measurements by Olson et al.\cite{41} were performed at a wavelength of 632.8 nm, which gives a maximum useful depth range in a-Si somewhere between 3000 Å and 3500Å. Most of the other TRR studies performed after this have also used this wavelength. Roth et al.\cite{19} then used a 1152 nm laser to measure SPE rates for a-Si layers in excess of 4 µm thick. As will be seen later in this chapter, the signal attenuation at this wavelength becomes a non-issue, since the signal absorption associated with traversing a 1 µm thick a-Si layer is insignificant. Since the measurements of this work are concerned with SPE at depths well in excess of 3000 Å, a wavelength of 1152 nm has also been used for the measurements reported here.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

Figure 5.5: Theoretical arsenic implantation profiles used to create an overall constant concentration of \( \sim 1 \times 10^{20} \) As/cm\(^3\) in Si\(_{0.70}\)Ge\(_{0.21}\) over the depth range from 3000 Å to 6500 Å. Individual implant profiles are shown in conjunction with the resulting total As concentration, as calculated using computer simulations[108].

Figure 5.6: Theoretical arsenic implantation profiles used to create an overall constant concentration of \( \sim 1 \times 10^{20} \) As/cm\(^3\) in Si\(_{0.47}\)Ge\(_{0.53}\) over the depth range from 2500 Å to 6000 Å. Individual implant profiles are shown in conjunction with the resulting total As concentration, as calculated using computer simulations[108].
5.3. EXPERIMENTAL

Silicon

The reduction of raw TRR data into c/a interface versus time data relies on the knowledge of the index of refraction for the amorphous material as described in section 2.6.3. For germanium, there was no suitable refractive index data, and hence it was determined independently by combining RBS and TRR measurements as a part of this work as discussed in section 4.3.2. Fortunately, such a measurement is not necessary for silicon. Olson et al. [13, 41] originally reported an index of refraction of \( n = 4.85 - 0.612i \) for a-Si at 632.8 nm. Roth et al. [19] then used this value to determine the index of refraction for a-Si at 1.15 \( \mu m \) by simultaneously collecting 632.8 nm and 1.15 \( \mu m \) TRR data. The 632.8 nm data was used in conjunction with this index of refraction value to assign a depth scale to the 1.15 \( \mu m \) data in the 0 – 3500 Å region. The index of refraction at 1.15 \( \mu m \) was determined from the interface movement per 1.15 \( \mu m \) interference cycle. Based upon this, they reported a real index of refraction of 4.05 with an absorption coefficient of \( 1.2 \times 10^3 \) cm\(^{-1}\) for a-Si at 1.15 \( \mu m \). The index of refraction value was verified with RBS measurements of partially annealed samples, similar to that performed in section 4.3.2 for germanium, and the results were reported to be in agreement to within 1%.

The 632.8 nm data from this work has been used in a similar fashion. Even though the TRR data from the shorter wavelength is limited to depths of 3500 Å or less, it still provides an independent measurement of the SPE rate over this depth interval which can be compared to the longer wavelength SPE data. The SPE rates determined within this depth region for both wavelengths typically only differed by between one and two percent when the Olson and Roth index of refraction values were used, indicating that the values are self-consistent.

Silicon-Germanium Alloys

For the silicon-germanium alloys, the absorption in traversing the amorphous layer at 632.8 nm is too large to make this wavelength of any use. Hence the Si\(_x\)Ge\(_{1-x}\) SPE data is derived exclusively from the 1152 nm signal. As was the case for germanium, there have been a number of measurements of the index of refraction for crystalline
Si_{x}Ge_{1-x} of varying compositions[126–129], but there is no suitable data for amorphous Si_{x}Ge_{1-x} that can be extrapolated to this wavelength. The index of refraction at this wavelength was taken as the linear extrapolation between the silicon value of Roth et al.[19] and the germanium value determined in section 4.3.2, scaled according to the alloy composition. This gives values of $n = 4.32$ for Si_{0.79}Ge_{0.21} and $n = 4.73$ for Si_{0.47}Ge_{0.53}. It is worth recalling that the dependence on $n$ (section 2.6.3) limits the effect of a constant error in $n$ to a constant scaling factor of the absolute SPE rates determined from the TRR measurement. Data on the temperature dependence of $n$ for a-Si_{x}Ge_{1-x} is also unavailable, but if it is assumed to be similar to the $3 \times 10^{-4}$ K$^{-1}$ value reported for c-Si_{x}Ge_{1-x}[130], then the introduced error can be expected to be on the order of ±1% as per the discussion in section 2.6.4.
5.4 Intrinsic Growth Behaviour of Si

The measurement of the SPE rate in (100) Si has been reported a number of times for thin (< 5000 Å) layers, but at most a couple of times[19,51] for layers that are 2 µm thick or more. This distinction becomes important in light of the hydrogen contamination problem first reported by Roth et al.[19,20] which is capable of reducing the SPE rates by up to 30% in thin layers.

This section presents the data associated with measuring the SPE rate for ~ 2 µm thick a-Si layers on (100) Si. Such a measurement is required to form a baseline for normalization of dopant-enhanced SPE rates as measured on the same apparatus, and also allows a comparison to the hydrogen contamination effects reported by Roth et al.[19,20].

5.4.1 Measurement of the SPE Rate on (100) Si

Samples consisting of a ~ 2 µm a-Si layer on (100) Si as described in section 5.3.1 were annealed at 20 °C intervals from 480 °C to 660 °C. The raw TRR data for an anneal at 580 °C is shown in the upper curve of Fig. 5.7. A slight increase in the period of the interference oscillations is evident after the anneal has been in progress for more than 2500 s. This change in period is also reflected in the change in slope of the c/a interface location as a function of time shown as the lower curve of Fig. 5.7.

The SPE rate, as given by the slope of the lower curve in Fig. 5.7 is shown as a function of depth in Fig 5.8. From this curve it is evident that the SPE rate is not constant as a function of depth for the full duration of the anneal. For depths beyond approximately 1.5 µm the SPE rate is observed to be constant. Between ~ 1.25 µm and ~ 0.75 µm the SPE rate takes on an almost linear decrease, which saturates at about 0.5 µm before making a slight recovery in the final stages of the anneal.

The overall behaviour of the SPE rate as a function of depth is identical to that reported by Roth et al.[20] and shown in the upper half of Fig. 4.1. As mentioned earlier in section 5.2.2, this reduction in the SPE rate has been shown to be due to hydrogen intrusion originating from the surface of the sample during the annealing process, and subsequently being pushed ahead of the c/a interface during annealing. The minimum SPE rate of the hydrogen affected area in Fig. 5.8 is about 30% less
Figure 5.7: TRR curve from annealing of a 2 μm a-Si layer at 580°C (upper curve) and corresponding c/a interface location as a function of time (lower curve) as determined from the TRR curve.

Figure 5.8: SPE rate in a ~ 2 μm thick a-Si layer at 580 °C as a function of depth. Hydrogen intrusion from the surface is responsible for the rate reduction that is observed to begin at approximately 1.5 μm. Curve shown is from a direct differentiation of the lower curve of Fig. 5.7, followed by a transformation to a depth scale by applying the same curve.
than that associated with the hydrogen-free rate beyond 1.5 µm, which is also in agreement with the reduction observed by Roth et al.[20]. Furthermore, the location of the minimum at 0.5 µm is also a shared result.

The only difference between the two measurements is the depth at which the SPE rate reduction is observed to start. For this work, the reduction in the SPE rate was observed to start at 1.5 µm, whereas the measurement by Roth et al. shown in Fig. 4.1 indicates the effect was underway once the remaining a-Si thickness was less than 2.25 µm. The nature of this difference can be understood in terms of of the initial amorphous layer thickness. There are two competing processes taking place during the anneal. The first is SPE which starts from the initial c/a boundary and moves toward the surface, and the second is the diffusion of hydrogen, which starts at the physical sample surface and moves into the amorphous layer. Thus, the point at which a reduction in the SPE rate is first observed will correspond to the depth at which these two processes meet. As the c/a interface collides with the tail of the hydrogen diffusion profile and a significant amount of H is collected in front of the c/a interface, the SPE rate will start to drop. Roth et al.[21] performed some measurements on diffusion of H in a-Si in this concentration regime, and found that the activation energy for the diffusion process was the same as that for the SPE process to within experimental error. Thus, the depth at which the SPE rate reduction first begins will scale with the thickness of the original amorphous layer, and to a first order approximation for thick layers, the depth at which this occurs will be somewhere near the midpoint of the original amorphous layer thickness.

The activation energy for SPE of undoped a-Si on (100) Si can be determined by using the constant SPE rate observed beyond 1.5 µm. The SPE rate as a function of temperature for this hydrogen-free region is shown as a function of depth in an Arrhenius form in Fig. 5.9 (circles). The velocity error bars lie within the size of the plotting symbols and hence are not shown. The fit to the data gives an activation energy of 2.71 ± 0.01 eV and a velocity prefactor of (4.7 ± 0.6) × 10^6 m/s, where the quoted error values given are from the fitting process only. These values are in good agreement with the $E_a = 2.70$ eV and $V_o = 4.64 \times 10^6$ m/s reported by Olson and Roth[14] for their hydrogen-free thick layers.
Figure 5.9: Arrhenius behaviour for solid phase epitaxial regrowth of undoped a-Si. Two curves are shown, corresponding to the hydrogen-free region (>1.5 µm) and the hydrogen contaminated region (2500 Å to 6500 Å) respectively.

Figure 5.10: SPE data for hydrogen contaminated a-Si normalized to the hydrogen-free data associated with interface depths beyond >2 µm. Thick layer data (circles) taken from the hydrogen contaminated region (2500 Å to 6500 Å) is shown along with thin layer data (triangles). The solid line is a guide to the eye only.
5.4.2 SPE Rate Reduction Due to Hydrogen Contamination

The broadness of the minimum in the SPE rate around the 5000 Å region in Fig. 5.8 allows an activation energy and velocity prefactor to be assigned to the hydrogen contaminated region as was done for the hydrogen-free region. Also shown in Fig. 5.9 is the Arrhenius behaviour of the SPE rate as a function of temperature for the hydrogen affected area (triangles). The SPE rates used represent the average SPE rate in the region between 2500 Å and 6500 Å. Based upon the SIMS results of Roth et al. [20], the associated hydrogen concentration in this depth range is expected to be on the order of $1.5 \times 10^{19} / \text{cm}^3$. The activation energy and velocity prefactor obtained from fitting this data are $2.82 \pm 0.01 \text{ eV}$ and $(1.6 \pm 0.2) \times 10^6 \text{ m/s}$. Since both the hydrogen-free data and the hydrogen affected data come from the same sample at each temperature, any experimental errors in temperature or in the SPE rate determination are identical for both. This provides a higher degree of confidence in comparing the two results in an effort to look for small changes. The increase of $\sim 0.1 \text{ eV}$ in the activation energy over that of the hydrogen-free region is evident in Fig. 5.9 as a difference in slope between the two curves. Furthermore, the two data sets appear to converge as the SPE temperature is increased, tending to indicate that the magnitude of the hydrogen retardation effect decreases with increasing temperature.

A normalized plot such as Fig. 5.10 provides a better indication of the temperature dependence of the hydrogen SPE rate reduction effect. The data of Fig. 5.9 is shown in a normalized fashion (circles) along with the SPE data associated with TRR measurements from thin (2500 Å) layers. Some additional scatter in the thin layer data is expected since it has to be normalized against the thick layer data, and thus slight temperature differences between the two separate runs will play a role in the normalized data. The mean rate reduction is observed to vary between $\sim 20\%$ and $\sim 40\%$ as the temperature is decreased from 660 °C to 480 °C.

This result is in slight contrast with the conclusion made by Roth et al. [14, 20], in which they state that the effect of the hydrogen contamination appears to be limited to the velocity prefactor, and that the activation energy is the same as that for thick layer hydrogen-free SPE.
5.5 Dopant Effects on the Growth Rate of Si

As outlined in section 5.2.5, the use of a longer wavelength TRR system to measure the solid phase epitaxial regrowth rate associated with thick a-Si layers containing a constant dopant concentration profile has yet to be exploited. Also, the effect of doping with aluminum and its role in compensation measurements is unclear.

In this section, measurements of the SPE rate for thick layers of a-Si doped with various concentrations of arsenic and aluminum on (100) Si are presented. Compensation measurements involving the simultaneous presence of both dopants are also reported.

5.5.1 Doping with Arsenic

The arsenic samples described in section 5.3.2 were annealed at temperatures ranging from 480 °C to 660 °C on the heater stage of the TRR system. A typical 1.15 µm TRR curve for the anneal of a sample containing $1 \times 10^{20}$ As/cm$^3$ at 620 °C is shown in the upper half of Fig. 5.11. The period of the TRR curve near the final stages of the anneal is clearly a lot shorter than the period for the first 1000 s of the anneal, indicating an enhanced SPE rate. Based upon Fig. 5.1, a constant concentration of $1 \times 10^{20}$ As/cm$^3$ is expected over the depth range from 3500 Å to 8000 Å in these samples. The c/a interface location as a function of time is shown in the lower half of Fig. 5.11, with the slope of this curve indicating the SPE rate. An essentially constant SPE rate is observed until the c/a interface is within ~10000 Å of the surface. At this point, a larger slope is observed due to the presence of the arsenic.

The effect of the presence of arsenic is more easily viewed when the data of the lower half of Fig. 5.11 is differentiated to give the actual SPE rate instead of the c/a interface location. The same data can then be used again to transform the time axis into an interface depth, resulting in data that gives the SPE rate as a function of depth. The data of the lower half of Fig. 5.11 after such a differentiation and transformation is shown in Fig. 5.12. The SPE rate associated with the plateau of this curve is ~140% higher than the undoped rate beyond 2 µm.

Similar data for the other concentrations of implanted arsenic are shown in
5.5. DOPANT EFFECTS ON THE GROWTH RATE OF SI

Figure 5.11: TRR curve from annealing at 620 °C of an a-Si layer containing a region with $1 \times 10^{20}$ As/cm$^3$ (upper curve) and the corresponding c/a interface location as a function of time (lower curve) as determined from the TRR curve.

Figure 5.12: The SPE rate as a function of depth for an a-Si layer containing a constant concentration of $1 \times 10^{20}$ As/cm$^3$ in the region between 3500 Å and 8000 Å. The curve shown results from a direct differentiation of the lower curve of Fig. 5.11, followed by a transformation to a depth scale by using the same data.
Fig. 5.13, along with the undoped data of section 5.4.1 that exhibits hydrogen contamination. The sample containing $1 \times 10^{19}$ As/cm$^3$ results in an SPE rate essentially equivalent to that of the hydrogen-free region beyond 2 µm. The higher concentrations of arsenic give SPE rate enhancements above the hydrogen-free SPE rate.

From Fig. 5.13, it is evident that there is a significant amount of SPE data for each of the arsenic implanted samples associated with the region beyond the maximum range of the highest energy arsenic implant. In particular, the arsenic enhancement is essentially finished by 1.2 µm, and the hydrogen retarded background is observed from about 1.2 µm up to at most 2 µm. In light of this, the SPE data from beyond 2 µm for each of the arsenic implanted samples can be used to further refine our knowledge of the growth behaviour for undoped, hydrogen-free (100) a-Si, as previously reported in section 5.4.1. The SPE rates associated with depths beyond 2 µm for each of the arsenic implanted samples are listed in Table 5.2, along with the data from the undoped sample that was taken from the region between 1.5 µm and 2 µm.

Table 5.2: The SPE rates (in Å/s) for the undoped portion of the arsenic implanted samples. The values were calculated from the SPE data associated with depths beyond 2 µm for which the material is essentially arsenic and hydrogen-free. The SPE rates from the 1.5 µm to 2 µm region of the undoped samples of section 5.4.1 are also shown for comparison.

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<thead>
<tr>
<th>Temp. °C</th>
<th>10</th>
<th>5</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.0329</td>
</tr>
<tr>
<td>500</td>
<td>0.0995</td>
<td>0.0982</td>
<td>0.1018</td>
<td>—</td>
<td>0.0952</td>
</tr>
<tr>
<td>520</td>
<td>0.2817</td>
<td>0.2766</td>
<td>0.2815</td>
<td>—</td>
<td>0.2644</td>
</tr>
<tr>
<td>540</td>
<td>0.7197</td>
<td>0.7009</td>
<td>0.7255</td>
<td>—</td>
<td>0.6923</td>
</tr>
<tr>
<td>560</td>
<td>1.799</td>
<td>1.799</td>
<td>1.793</td>
<td>—</td>
<td>1.787</td>
</tr>
<tr>
<td>600</td>
<td>10.32</td>
<td>10.23</td>
<td>10.12</td>
<td>10.25</td>
<td>9.622</td>
</tr>
<tr>
<td>620</td>
<td>22.07</td>
<td>22.01</td>
<td>23.04</td>
<td>23.07</td>
<td>22.53</td>
</tr>
<tr>
<td>640</td>
<td>50.20</td>
<td>48.67</td>
<td>50.65</td>
<td>51.17</td>
<td>48.50</td>
</tr>
<tr>
<td>660</td>
<td>108.6</td>
<td>108.5</td>
<td>110.5</td>
<td>109.9</td>
<td>106.4</td>
</tr>
</tbody>
</table>
5.5. **DOPANT EFFECTS ON THE GROWTH RATE OF Si**

Figure 5.13: SPE rates of a-Si samples implanted with various concentrations of arsenic for an annealing temperature of 620 °C. The SPE rate for undoped a-Si is also shown for comparison. Hydrogen retardation of the SPE rate is observed to start at a depth of approximately 2 µm.

Figure 5.14: The Arrhenius behaviour of arsenic implanted a-Si for four different constant arsenic concentrations. Interface velocities shown here were measured in the region containing a constant concentration of As (≈ 3500 Å to ≈ 8000 Å).
Table 5.3: The activation energies and velocity prefactors obtained from fitting the SPE data (Table 5.2) of the arsenic and hydrogen-free region (2–3 μm) of the arsenic implanted samples. Error values quoted are from the fitting process only. The linear regression and chi squared values from each fit are also shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_a ) (eV)</th>
<th>( V_o ) ( \times 10^6 \text{ m/s} )</th>
<th>( 1 - r )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{20} \text{ As/cm}^3 )</td>
<td>2.701 ± 0.010</td>
<td>4.5 ± 0.7</td>
<td>1.7 \times 10^{-3}</td>
<td>5.1 \times 10^{-3}</td>
</tr>
<tr>
<td>( 5 \times 10^{19} \text{ As/cm}^3 )</td>
<td>2.703 ± 0.012</td>
<td>4.6 ± 0.8</td>
<td>1.8 \times 10^{-3}</td>
<td>6.1 \times 10^{-3}</td>
</tr>
<tr>
<td>( 2 \times 10^{19} \text{ As/cm}^3 )</td>
<td>2.703 ± 0.011</td>
<td>4.7 ± 0.7</td>
<td>1.8 \times 10^{-3}</td>
<td>5.3 \times 10^{-3}</td>
</tr>
</tbody>
</table>

The undoped data in Table 5.2 for ~ 2 μm thick layers is slightly, but consistently, lower than the data associated with the arsenic samples, due to the onset of hydrogen contamination at the shallower depth from which the SPE rate was extracted. Hence the SPE data from depths greater than 2 μm in the arsenic implanted samples represents a more accurate value for the true intrinsic hydrogen-free SPE rate. In addition, there are three independent data sets associated with the three concentrations that have data spanning a significant temperature range. The activation energies and velocity prefactors obtained from fitting these data sets are listed in Table 5.3. The high reproducibility of the SPE rates as indicated in Table 5.2 is reflected in the consistency of the values determined from the fit.

Returning to the arsenic-enhanced portions of the SPE rate data, similar measurements over the entire temperature range give the temperature dependence for each concentration. The results of such measurements are summarised in Fig. 5.14 in an Arrhenius format. The fit to the hydrogen and arsenic free data from this work (section 5.4.1) is essentially indistinguishable from the fit to the \( 1 \times 10^{19} \text{ As/cm}^3 \) data, and hence is not shown for clarity. The activation energy and velocity prefactor as determined from the fits to the data (solid lines) for each of the arsenic concentrations studied are listed in Table 5.4. A slight temperature dependence is evident from the difference in the slopes (i.e. activation energy) for each concentration.

In the treatment of the arsenic-enhanced SPE rates in germanium, the data were normalized to the undoped SPE rates to better view the temperature dependence. From Fig. 5.12, it is evident that the arsenic-enhanced SPE rates overlap with the
Table 5.4: The activation energies and velocity prefactors obtained from the various series of arsenic implanted a-Si samples studied in this work. The values obtained from the samples studied earlier that had no arsenic implants are also listed for comparison. Error values listed are from the fitting process only.

<table>
<thead>
<tr>
<th>Arsenic Concn. (/cm$^3$)</th>
<th>$E_a$ (eV)</th>
<th>$V_o$ ($\times 10^6$ m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>2.706 ± 0.009</td>
<td>4.7 ± 0.7</td>
</tr>
<tr>
<td>$1\times 10^{19}$</td>
<td>2.723 ± 0.010</td>
<td>5.8 ± 0.8</td>
</tr>
<tr>
<td>$2\times 10^{19}$</td>
<td>2.658 ± 0.013</td>
<td>2.8 ± 0.6</td>
</tr>
<tr>
<td>$5\times 10^{19}$</td>
<td>2.615 ± 0.013</td>
<td>2.4 ± 0.5</td>
</tr>
<tr>
<td>$1\times 10^{20}$</td>
<td>2.568 ± 0.009</td>
<td>1.9 ± 0.3</td>
</tr>
</tbody>
</table>

hydrogen retardation observed in the undoped samples. So, for silicon, this brings up the question of whether the arsenic-enhanced rates should be normalized to the hydrogen retarded SPE rate or to the hydrogen-free SPE rate.

Fortunately, comparison with a recent measurement by McCallum[131] provides insight into this issue. McCallum has used buried a-Si layers[51] to provide a hydrogen-free environment for measurement of the SPE rate enhancement due to arsenic. The data of McCallum provides a valuable comparison, since the same arsenic implant schedule was used, the same TRR system was employed in the measurement, and the same index of refraction was used in determining the SPE rates from the TRR data. The only significant difference between that measurement and those of this work is the use of buried layers to block hydrogen diffusion through the presence of a c-Si surface layer. Shown in Fig. 5.15 is the normalized arsenic-enhanced SPE data from McCallum along with the $1\times 10^{20}$ As/cm$^3$ data from this work. The solid lines represent fits of Eq. 5.1 to the buried layer data with $\Delta E = 0.21$ eV and $N_o = 1.2\times 10^{21}$ /cm$^3$ as reported by McCallum[131].

The arsenic-enhanced SPE data from this work is also shown in Fig. 5.15. The data is normalized against the hydrogen-free data (circles) and also normalized against the hydrogen retarded data of section 5.4.2 (triangles). The data normalized against the hydrogen-free SPE rates are essentially coincident with the buried layer data, whereas when they are normalized against the hydrogen retarded rate, the
Table 5.5: Fitting parameters to the experimental arsenic-enhanced SPE rates assuming a functional form as per Eq. 4.3. In the lowest dose case, $N_{\text{implant}}$ is sufficiently small as to allow a wide range of parameters to match the data. The reported errors are the estimated error from the fitting process.

<table>
<thead>
<tr>
<th>$N_{\text{implant}}$ (10$^{20}$/cm$^3$)</th>
<th>$\Delta E$ (eV)</th>
<th>$N_o$ (10$^{20}$/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21 ± 0.02</td>
<td>11.3 ± 2.6</td>
</tr>
<tr>
<td>0.5</td>
<td>0.21 ± 0.03</td>
<td>11.9 ± 4.4</td>
</tr>
<tr>
<td>0.2</td>
<td>0.35 ± 0.07</td>
<td>152 ± 161</td>
</tr>
</tbody>
</table>

The solid lines shown in Fig. 5.16 are fits to the experimental data assuming a functional form of

$$
\frac{V}{V_i} = 1 + \frac{N_{\text{impl}}}{N_i} \quad \text{with} \quad N_i = N_o \exp \left( -\frac{\Delta E}{kT} \right)
$$

where $V$ is the dopant-enhanced SPE rate, $V_i$ is the intrinsic SPE rate, and $N_{\text{impl}}$ is the implanted dopant concentration. The interpretation of the variables $N_o$ and $\Delta E$ varies depending on whether the fractional ionization model (section 2.4.9) or the GFLS model (section 2.4.11) is used. The $N_o$ and $\Delta E$ values determined from these fits are listed for each concentration in Table 5.5. The error values listed are those determined from the fitting process. For the lowest concentration shown, the temperature dependence is sufficiently weak so that a large range of fitting parameters can be applied. However, the values determined from the higher two

---

**Overall enhancement and temperature dependence** are clearly too strong. In particular, the comparison of the buried layer data with the thick layer data reported here suggests that for arsenic concentrations in excess of $5 \times 10^{19}$/cm$^3$, the rate-retarding role of H is effectively switched off.

Based upon this comparison, the dopant-enhanced SPE data of this work has been normalized against the hydrogen-free data instead of the hydrogen retarded data. The resulting normalized data for each of the arsenic concentrations are shown in Fig. 5.16. The temperature dependence is more evident now that the data is in a normalized fashion. As the temperature is decreased, the rate enhancement for a given concentration of arsenic is observed to increase. The temperature dependence is also observed to increase with increasing concentration.
5.5. DOPANT EFFECTS ON THE GROWTH RATE OF Si

Figure 5.15: Comparison of the normalized arsenic-enhanced SPE data from McCallum[131] with that of this work. The $1.06 \times 10^{20}$ As/cm$^3$ data (+ symbols) and $8.5 \times 10^{19}$ As/cm$^3$ data (× symbols) from McCallum have been taken from hydrogen-free buried a-Si layers. Solid lines are plots of Eq. 5.1 with the $N_0$ and $\Delta E$ values reported by McCallum. The $1 \times 10^{20}$ As/cm$^3$ data from this work is shown normalized against the H-free data (circles) and the H-retarded data (triangles).

Figure 5.16: SPE rates from arsenic implanted a-Si from this work are shown normalized against the undoped hydrogen-free a-Si data. Four different constant concentrations of As are shown. Solid lines are best fits of Eq. 5.1 to the data.
concentrations are quite consistent with each other, and also nearly identical to the 
values of $\Delta E = 0.21$ eV and $N_o = 1.2 \times 10^{21} /\text{cm}^3$ from McCallum[131]. The differ­
ence between these common values and the $\Delta E = 0.34$ eV and $N_o = 2.9 \times 10^{21} /\text{cm}^3$
reported by the Walser group[25] is most likely due to hydrogen contamination of 
the thin a-Si layers used in their experiments.

5.5.2 Doping with Aluminum

The aluminum implanted samples described in section 5.3.2 were annealed at 20 °C 
intervals from 500 °C to 660 °C on the TRR system. From Fig. 5.3, these samples 
have a constant concentration of $5 \times 10^{19} \text{Al/cm}^3$ spanning a depth region from 8000 Å 
to 12500 Å. The 1.15 µm TRR curve from the anneal of an aluminum implanted 
sample at 620 °C is shown in the upper curve of Fig. 5.17. A smaller period for the 
TRR curve is clearly evident around the 800 s point of the anneal. The lower curve of 
Fig. 5.17 shows the same TRR data with the reflected signal amplitude converted to 
a $c/a$ interface depth so that the slope of the curve gives the instantaneous SPE rate. 
The region containing aluminum has an increased slope compared to the portion of 
the curve for depths beyond $\sim 15000$ Å.

The SPE rate data obtained from the lower curve of Fig. 5.17 is shown in Fig. 5.18 
as a function of depth. The SPE rate of the plateau, associated with a constant 
concentration of $5 \times 10^{19} \text{Al/cm}^3$ is $\sim 2$ times faster than the hydrogen-free undoped 
rate. In comparison, the SPE rate associated with the same concentration of ar­
senic (Fig. 5.13) was only $\sim 1.6$ times faster than the hydrogen-free undoped rate.

As mentioned in section 2.3.5, the Walser group[22] reported that the SPE rate 
was retarded by up to $\sim 40\%$ for doping with aluminum at concentrations be­
 tween $3 \times 10^{18} /\text{cm}^3$ and $2.3 \times 10^{19} /\text{cm}^3$. From Fig. 5.3, the samples used here have 
two significant depth regions for which the concentration of aluminum lies within this 
range. The first is from 3250 Å to 5250 Å, and the second is from 15300 Å to 18000 Å. 
Yet no retardation of this magnitude is observed in Fig. 5.18. Only a slight retarda­
tion due to the onset of hydrogen contamination at depths less than 2 µm is present. 
This retardation was also observed in the undoped and arsenic implanted samples.

Similar TRR measurements were performed at 20 °C intervals between 500 °C
5.5. DOPANT EFFECTS ON THE GROWTH RATE OF SI

Figure 5.17: Upper curve shows raw TRR data from annealing of an a-Si layer containing a region with $5 \times 10^{19} \text{ Al/cm}^3$ at 620 °C. Lower curve indicates the corresponding $c/a$ interface location as a function of time as determined from the TRR curve.

Figure 5.18: The SPE rate as a function of depth for an a-Si layer containing a constant concentration of $5 \times 10^{19} \text{ Al/cm}^3$ in the region between 8000 Å and 12500 Å. Curve shown is from a direct differentiation of the lower curve of Fig. 5.17, followed by a transformation to a depth scale by applying the same curve.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

Figure 5.19: The Arrhenius behaviour of the SPE rates as measured in a-Si with $5 \times 10^{19}$ Al/cm$^3$ (stars). The aluminum-enhanced SPE rates were measured in the region containing a constant concentration of Al ($\sim$ 8000 Å to $\sim$ 12500 Å). The undoped hydrogen-free data from this work is also shown for comparison (circles).

Figure 5.20: The SPE rates for implantation doped a-Si with a constant concentration of $5 \times 10^{19}$ Al/cm$^3$, normalized against the undoped, hydrogen-free SPE rates of a-Si. The solid line is a linear fit to the data, meant only as a guide to the eye.
and 660 °C to observe if there was any temperature dependence associated with the aluminum-enhanced SPE rate. The data from these other measurements are shown in Fig. 5.19 in an Arrhenius form (stars) along with the hydrogen-free SPE data from section 5.4.1 (circles). The activation energy and velocity prefactor determined from a fit to the Al data (solid line) are 2.748 ± 0.010 eV and (1.5 ± 0.2) × 10^7 m/s respectively. The quoted error values are from the fitting process only. No temperature dependence is immediately evident from the data. The difference of ~ 0.05 eV between the slopes of the curves in Fig. 5.19 is barely perceptible.

When the aluminum-enhanced SPE data are normalized against the hydrogen-free undoped SPE data of section 5.4.1 and then re-plotted as shown in Fig. 5.20, a slight temperature dependence is observed. The solid line is a linear fit to the data. It is noted that a line with zero temperature dependence set to an offset equal to the mean of the data also lies within the error bars, and hence trying to ascribe any sort of temperature dependence based upon this data alone would be of little value.

5.5.3 Doping with Arsenic and Aluminum

The arsenic and aluminum data of the previous sections provide an accurate description of the SPE rate enhancements each dopant can cause on its own. With the individual behaviour now documented, meaningful comparisons against compensation samples containing both dopants can be performed. The samples used for this measurement were described in section 5.3.2. The net doping level resulting from the overlapping 5 × 10^{19}/cm^3 implants was previously shown in Fig. 5.4. A surplus of arsenic is present from the surface to a depth of 7500 Å and a surplus of aluminum is present from 7500 Å to beyond 15000 Å. While the net doping level is zero at only one depth, it is less than 1 × 10^{19}/cm^3 from ~ 6500 Å to ~ 9000 Å. Based upon the data of the previous sections, the enhancement associated with concentrations below this level is expected to be insignificant.

The TRR data from annealing one of these samples at 620 °C is shown in the upper half of Fig. 5.21. There are two regions in this curve where the period of the interference signal is reduced when compared to the period observed during the first 3000 s of the anneal. The interface location as a function of time determined
Figure 5.21: TRR data from the annealing of an a-Si layer containing partially overlapping $5 \times 10^{19}$ As/cm$^3$ and $5 \times 10^{19}$ Al/cm$^3$ dopant profiles at 620 °C. The upper curve shows the raw TRR data, and the lower curve gives the c/a interface location as a function of time as determined from the TRR data.

Figure 5.22: The SPE rate in compensation doped a-Si, as extracted from the lower curve shown in Fig. 5.21. The two enhancement peaks in the SPE rate are due to a significant net doping level, with the one closest to the surface being due to a surplus of arsenic and the deeper one due to a surplus of aluminum. The net doping level in the compensation region between the two peaks is less than $1 \times 10^{19}$ /cm$^3$. 
from this data is shown in the lower half of Fig. 5.21. The slope of this curve is clearly non-constant in the region containing the dopants, indicating that a SPE rate enhancement occurs in the regions with a significant net doping level.

The effect of the non-zero net doping is more easily viewed when the data of Fig. 5.21 is differentiated and then transformed to a depth scale. The resulting curve, shown in Fig. 5.22, gives the SPE rate as a function of depth so that it can be compared to the net doping profile of Fig. 5.4. Two enhancement peaks in the SPE rate are clearly evident. The peak in the SPE rate closest to the surface is due to the surplus arsenic and the larger peak is due to the surplus aluminum. The region between the two peaks corresponds to the compensation region for which the net doping level is not significant enough to give rise to an enhanced SPE rate. The overall shape of the SPE rate curve in this region for the compensation doped sample is similar to that observed previously for the hydrogen contaminated undoped a-Si layers.

It is instructive to directly compare the compensated SPE rate shown in Fig. 5.22 with the individual dopant-enhanced SPE rates for the same concentrations of arsenic and aluminum that were previously reported in sections 5.5.1 and 5.5.2 respectively. These three data sets are shown in Fig. 5.23, along with the undoped data from the 2 µm thick a-Si layers. The overlap of the individual dopant-enhanced SPE rates correlate well with the compensated SPE rate. The aluminum enhancement peak for the compensation sample just reaches the plateau rate measured in the $5\times10^{19}$ Al/cm$^3$ sample since the arsenic enhancement does not span the entire range of the aluminum enhancement plateau. However, the aluminum SPE enhancement extends through the entire arsenic enhancement plateau, and hence the arsenic enhancement peak for the compensation sample does not reach the plateau value associated with a $5\times10^{19}$ As/cm$^3$ doping level.

It is worth noting that the SPE rates shown in Fig. 5.23 for all the doped samples start to show signs of retardation due to hydrogen contamination at a slightly greater depth than the undoped sample does. The maximum depth of hydrogen penetration scales with the initial a-Si layer thickness as described in section 5.4.1, and hence this difference can be attributed to the $\sim 1$ µm thicker a-Si layer used for the
Figure 5.23: SPE rate for samples implanted with both As and Al. The implant profiles overlap so that the net dopant concentration is expected to be zero at a depth of 7500 Å. The SPE rates for samples containing the same concentration of just As or Al are shown for comparison.

Figure 5.24: SPE rates of samples implanted with both As and Al. The implant profiles overlap so that the net dopant concentration is less than $1 \times 10^{19}$ /cm$^3$ in the depth region from 6500 Å to 8500 Å and each velocity measurement was taken from within this region. The SPE rates for hydrogen-free and hydrogen contaminated undoped a-Si are also shown for comparison.
implantation doped samples.

The region between the enhancement peaks associated with a low to insignificant net doping level can be used to establish the SPE behaviour for compensation doped a-Si layers. Based upon the implantation profile of Fig. 5.4 and the SPE rate profiles of Fig. 5.23, the mean SPE rate over the region from 6500 Å to 8000 Å was taken as the SPE rate representative of compensation doped a-Si.

The SPE rates in this depth region for each of the temperatures studied are shown in an Arrhenius form in Fig. 5.24. The activation energy and velocity pref- actor obtained from fitting the compensation data (solid line) are 2.815 ± 0.010 eV and (1.6 ± 0.2) × 10⁷ m/s respectively. The given error values are those associated with the fitting process only. The hydrogen contaminated SPE rate data and the hydrogen-free SPE data from depths beyond 1.5 µm are also shown for comparison. The compensation data is almost identical to the hydrogen contaminated SPE data presented earlier in section 5.4.1. It is apparent from this figure that hydrogen contamination still takes place in compensation doped samples. The slight difference between the two data sets can be attributed to the shallower depth region (2500 Å to 6500 Å) over which the hydrogen contaminated SPE rates were determined.
5.6 Measurements in Silicon-Germanium Alloys

This section documents the solid phase epitaxial regrowth measurements performed on the Si_xGe_1-x alloy samples. First, the SPE behaviour for the undoped samples are reported, followed by the SPE data from samples that have been implanted to create constant concentration profiles of arsenic within the amorphous layer.

5.6.1 Undoped Material

The undoped Si_xGe_1-x samples of both alloy compositions, as described in section 5.3.1, were annealed at various temperatures within the range from 440 °C to 640 °C. The TRR data from annealing a Si_{0.79}Ge_{0.21} sample at 620 °C are shown in the upper half of Fig. 5.25. The rapid rise at the start of the signal corresponds to the loading of the sample onto the heater stage. The level of attenuation of the 1.15 µm laser in Si_{0.79}Ge_{0.21} over these depths is essentially negligible. For the Si_{0.47}Ge_{0.53} alloy samples, the attenuation in the TRR data (not shown) is significant, but not as large as it is for pure Ge samples.

The c/a interface location as a function of time as extracted from this TRR data is shown in the lower half of Fig. 5.25. Note that the point density shown is arbitrary and not representative of the overall depth resolution, since the mapping procedure of section 3.2.11 provides a 1:1 relation between the TRR data and the c/a interface location. The SPE rate, given by the slope of this curve, consists of two essentially constant regions, at depths greater than and less than ~ 8000 Å respectively. The solid lines represent two individual linear fits to each region of the data, and the dashed lines are the extrapolation of these fits into the other region. The fit to the region closest to the surface of the sample (2000 Å to 6500 Å) clearly exhibits a lower SPE rate than the fit to the region beyond 9000 Å. In comparison, the SPE rate for the Si_{0.47}Ge_{0.53} samples (not shown) was observed to be virtually constant from the near surface to the original depth of the c/a interface.

The SPE rates from measurements at other temperatures are shown in an Arrhenius form in Fig. 5.26 for both alloy compositions. For the Si_{0.79}Ge_{0.21} samples, the data extracted from both depth regions are shown. The activation energy and velocity prefactor values obtained from the fit to each data set are summarised in the
5.6. MEASUREMENTS IN SILICON-GERMANIUM ALLOYS

Figure 5.25: The raw TRR data obtained during the anneal of an amorphous Si\textsubscript{0.79}Ge\textsubscript{0.21} layer approximately 1.4 \( \mu \text{m} \) thick (upper curve). The lower curve shows the interface location as a function of time as calculated from the TRR data. Two regions of constant SPE rate are evident, separated at \( \sim 8000 \) \( \AA \). The solid lines are fits to each region, with the dashed lines being extrapolations of each fit.

Figure 5.26: The SPE rate data for both alloy compositions are shown in an Arrhenius form. For the Si\textsubscript{0.79}Ge\textsubscript{0.21} case, two data sets are shown, corresponding to the two regions of constant SPE rate observed in Fig. 5.25.
Table 5.6: The activation energies and velocity prefactors obtained from various studies of \( \text{Si}_x\text{Ge}_{1-x} \) alloys. The first three entries are from this work, and the other values are from the literature as discussed in section 2.5.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>( E_a ) (eV)</th>
<th>( V_o ) ( \times 10^7 ) m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si}<em>{0.47}\text{Ge}</em>{0.53} )</td>
<td>2.73 ± 0.09</td>
<td>30 ± 4</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.73}\text{Ge}</em>{0.21} ) ((2000 \text{ Å} - 6500 \text{ Å}))</td>
<td>2.92 ± 0.01</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.73}\text{Ge}</em>{0.21} ) ((9000 \text{ Å} +))</td>
<td>2.80 ± 0.01</td>
<td>4.1 ± 0.6</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.75}\text{Ge}</em>{0.25} ) ((\text{Shiryaev}[38]))</td>
<td>2.76 ± 0.15</td>
<td>6.7</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.79}\text{Ge}</em>{0.21} ) ((\text{Kringho}[39]))</td>
<td>2.78 ± 0.022</td>
<td>3.6 ± 1.1</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.47}\text{Ge}</em>{0.53} ) ((\text{Kringho}[39]))</td>
<td>2.59 ± 0.015</td>
<td>6.4 ± 1.4</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.80}\text{Ge}</em>{0.20} ) ((\text{Haynes}[40]))</td>
<td>2.84 ± 0.03</td>
<td>7</td>
</tr>
<tr>
<td>( \text{Si}<em>{0.47}\text{Ge}</em>{0.53} ) ((\text{Haynes}[40]))</td>
<td>2.55 ± 0.03</td>
<td>3</td>
</tr>
</tbody>
</table>

5.6.2 Arsenic Doped Material

Similar TRR measurements were performed on the arsenic implanted \( \text{Si}_x\text{Ge}_{1-x} \) alloy samples of section 5.3.2. The arsenic implant parameters were chosen to give a constant \( 1 \times 10^{20} \) As/cm\(^3\) from 3000 Å to 6500 Å for the \( \text{Si}_{0.79}\text{Ge}_{0.21} \) sample, and from 2500 Å to 6000 Å for the \( \text{Si}_{0.47}\text{Ge}_{0.53} \) sample. The TRR data from the anneal of a \( \text{Si}_{0.79}\text{Ge}_{0.21} \) sample containing arsenic at 620 °C are shown in the upper half of Fig. 5.27. The centre portion of the interference data exhibits a reduced period associated with the presence of arsenic. The SPE rate enhancement is more evident in Fig. 5.28, which shows the \( c/a \) interface location as a function of time. The solid line is a linear fit to the data for the region between 3000 Å and 6500 Å, and the slope of this line gives the arsenic-enhanced SPE rate for \( \text{Si}_{0.79}\text{Ge}_{0.21} \) at 620 °C. TRR measurements on the arsenic implanted \( \text{Si}_{0.47}\text{Ge}_{0.53} \) samples (not shown) provided the enhanced SPE rate data for the other alloy composition.

The results from the TRR measurements at all the other temperatures are plotted in an Arrhenius form in Fig 5.28 for both alloy compositions. The undoped
Figure 5.27: The raw TRR data collected during the anneal of an amorphous Si$_{0.79}$Ge$_{0.21}$ layer containing a constant concentration of $1 \times 10^{20}$ As/cm$^3$ from 3000 Å to 6500 Å (upper curve). The lower curve shows the c/a interface location as a function of time as determined from the TRR data. The slope of the linear fit to the data (solid line) over the arsenic region gives the arsenic-enhanced SPE rate.

Figure 5.28: The $1 \times 10^{20}$/cm$^3$ arsenic-enhanced Si$_x$Ge$_{1-x}$ SPE rate data in Arrhenius form. The SPE rates shown are from 3000 Å to 6500 Å for the Si$_{0.79}$Ge$_{0.21}$ samples, and from 2500 Å to 6000 Å for the Si$_{0.47}$Ge$_{0.53}$ samples. The undoped data from Fig. 5.26 is also shown for comparison.
SPE data of Fig 5.26 are also shown for comparison. The arsenic-enhanced data appear to converge slightly towards the respective undoped data at the higher temperatures. This suggests a temperature dependence similar to that observed for the arsenic-enhanced SPE rates in silicon and germanium. The activation energy and velocity prefactor values obtained from the fit to the arsenic-enhanced Si$_{0.79}$Ge$_{0.21}$ SPE data (solid line) are $2.70 \pm 0.01$ eV and $(2.0 \pm 0.3) \times 10^7$ m/s. Similarly, the values for the Si$_{0.47}$Ge$_{0.53}$ alloy are $2.56 \pm 0.01$ eV and $(5.8 \pm 0.6) \times 10^7$ m/s.

The normalization of the Si$_{0.79}$Ge$_{0.21}$ data brings up an issue similar to that dealt with for the arsenic-enhanced SPE rates in silicon. There are two data sets associated with the SPE rate of undoped Si$_{0.79}$Ge$_{0.21}$ that can be used for normalization purposes, although the depth range covered by the constant concentration of arsenic lies within the 3000 Å to 6500 Å region for which the slower undoped SPE rates were measured. The arsenic-enhanced Si$_{0.79}$Ge$_{0.21}$ SPE data are shown normalized against both intrinsic rates in Fig. 5.29. The temperature dependence of the enhancement is significantly greater when the data are normalized against the slower SPE rates that were taken closer to the surface of the sample. It is interesting to compare this to the arsenic-enhanced silicon data of Fig. 5:15, which were normalized against both the hydrogen retarded Si SPE rate and the hydrogen-free SPE rate. In that case, normalization against the hydrogen retarded rate indicated a larger temperature dependence than expected when compared to the relative enhancements measured in buried layer samples.

For the arsenic-enhanced SPE data collected from the Si$_{0.47}$Ge$_{0.53}$ samples, there is only one data set that can be used to normalize against, since a constant SPE rate was observed in the undoped samples. The normalized data for the arsenic doped Si$_{0.47}$Ge$_{0.53}$ samples are shown in Fig. 5.30. For both alloy compositions, the enhancement factors are in keeping with the enhancements of ~ 2 to ~ 3.5 that were observed for the same concentration of arsenic in either silicon or germanium.
Figure 5.29: The normalized SPE rates of Si$_{0.79}$Ge$_{0.21}$ containing a constant concentration of $1 \times 10^{20}$ As/cm$^3$. The arsenic lies between 3000 Å and 7000 Å, and the SPE rates have been extracted from this region. Normalization against both the intrinsic rate taken from the 2000 Å to 6500 Å region (circles) and against the intrinsic rate taken from beyond 9000 Å (triangles) are shown.

Figure 5.30: The arsenic-enhanced SPE rates in Si$_{0.47}$Ge$_{0.53}$ after being normalized against the intrinsic rate for undoped samples of the same alloy composition. A constant concentration of $1 \times 10^{20}$ As/cm$^3$ spans the depth region from 2500 Å to 6000 Å, and the SPE data were taken from within this region.
5.7 Discussion

In this section, the results presented earlier in the chapter are considered, along with the current solid phase epitaxial regrowth theories and solid phase epitaxial regrowth data from previous studies. In particular, the hydrogen contamination and the dopant effect measurements are discussed, followed by a consideration of the results from the silicon-germanium alloy samples.

5.7.1 Hydrogen and SPE in a-Si

Olson and Roth[14, 19, 20] have reported that the effect of hydrogen on SPE in silicon is limited to the absolute rates measured, and that the activation energy for SPE remains unchanged. In terms of normalized velocity plots, this is the same as indicating that there is no temperature dependence. However, the work of this study (Fig. 5.10) indicates that the mean rate reduction varies from 20% to 40% within the temperature range of 480 °C to 660 °C. The rate reduction monotonically decreases with increasing temperature. It is interesting to note that the enhancement in the SPE rate due to arsenic is also greatest at the lowest annealing temperatures.

If the hydrogen is presumed to reduce the SPE rate by making sites unavailable for crystallization, as proposed by Roth et al.[20], then there are two possible ways to interpret the temperature dependence. Firstly, a lower concentration of interfacial hydrogen at the higher temperatures could explain the difference. Roth et al.[20] have reported that the SPE rate reduction increases linearly with H concentration[20]. Thus, a similar percentage change in the H concentration between the lowest and highest annealing temperatures would be expected if this were the case. The second possibility involves a relatively constant concentration of hydrogen, combined with an increase in the number of available growth sites with increasing temperature. Of course, there is no reason why these possibilities need to be considered as mutually exclusive, since it could be a combination of both that gives rise to the observed temperature dependence. SIMS measurements of the hydrogen concentration in samples partially annealed at the extrema of the temperature range studied may make it possible to discern between the two effects. However, such measurements have yet to be performed.
5.7. DISCUSSION

5.7.2 Doped Si as Extrinsic and Nondegenerate

The issue of whether it is valid to treat the implantation doped silicon samples of this work as extrinsic and nondegenerate follows the same lines as the discussion in section 4.7.3. The main differences between the treatment for Ge and Si arise from the smaller band gap for Ge which results in a higher intrinsic carrier concentration, and the different effective mass values (Table 2.2) which give different density of states concentrations for these two elements.

Consideration as Extrinsic

For the silicon to be treated as extrinsic, the number of active carriers resulting from doping must be significantly greater than the intrinsic carrier concentration. From Fig. 2.4, the intrinsic carrier concentration for silicon in the temperature range of interest is always less than $4 \times 10^{17} / \text{cm}^2$. Even if the fractional ionization for the $1 \times 10^{19} \text{As/cm}^3$ case was as low as 50%, the number of ionized donors would still be more than ten times the number of intrinsic carriers, and hence the treatment as extrinsic is valid.

Nondegeneracy and Density of States

A comparison of the conduction band density of states for germanium and silicon indicates that the Si value is about three times as large as the Ge value for a given temperature (Fig. 2.3). Hence, for n-type doping, germanium will require a degenerate treatment for lower concentrations than for silicon. Following the treatment of section 4.7.3, the ratio of active carriers ($N_c$ or $N_h$) to the density of states ($N_c$ or $N_v$) can be used to determine the maximum concentration for which a nondegenerate treatment will be valid. For a 2 kT gap between the Fermi level and the conduction band, the maximum $N_c$ is determined from solving $N_c/N_c = \exp(\eta)$ with $\eta = -2$. With an $N_c$ value of $1.1 \times 10^{20} / \text{cm}^3$ at 480 °C, a limiting value of $N_c \sim 1.5 \times 10^{19} / \text{cm}^3$ is obtained. This indicates that a nondegenerate treatment will be valid for an n-type doping level of $1 \times 10^{19} / \text{cm}^3$, but a doping level of $2 \times 10^{19} / \text{cm}^3$ will be close to the limiting case if a fractional ionization of $\sim 0.75$ is assumed.
The case for p-type doping is considerably worse, since the valence band density of states, as shown in Fig. 2.3 is significantly smaller than the conduction band value. At 480 °C, \( N_v \) is only \( 4.4 \times 10^{19} \) /cm\(^3\) (Fig. 2.3) which gives \( N_h \sim 6 \times 10^{18} \) /cm\(^3\). For the \( 5 \times 10^{19} \) Al/cm\(^3\) samples, a fractional ionization value as low as only 15% would still imply that a fully degenerate treatment is required.

### 5.7.3 Fermi Levels in Doped Silicon

The calculation of the Fermi level in c-Si for the various doping levels used is essentially the same problem as treated for c-Ge in section 4.7.4, except that different parameters apply for silicon. The parameters of the equation to be solved (Eq. 4.7 for n-type doping or Eq. 4.8 for p-type doping) that are different for Si are \( N_e \) and \( N_v \) due to the effective masses (Table 2.2), \( E_e \) due to the larger band gap (Fig. 2.2), the temperature range and finally the dopant energy level (\( E_d \) or \( E_a \)). For arsenic in silicon, \( E_d = 49 \) meV, and for aluminum in silicon, \( E_a = 57 \) meV.

When these different parameters are all substituted into the neutrality equation for n-type doping, the Fermi level for each arsenic concentration can be calculated. These are shown in Fig. 5.31, in conjunction with a curve marking a 2 \( kT \) boundary below the conduction band edge. Only the band gap narrowing (BGN) due to temperature[64] has been included in the calculation, since the magnitude of dopant-induced BGN at typical SPE temperatures is unclear[66, 67].

The individual Fermi levels shown in Fig. 5.31 indicate that a nondegenerate treatment is adequate for the \( 1 \times 10^{19} \) As/cm\(^3\) case, and that the \( 2 \times 10^{19} \) As/cm\(^3\) case is bordering on requiring a fully degenerate treatment, as deduced earlier in section 5.7.2. Both the \( 5 \times 10^{19} \) As/cm\(^3\) and the \( 1 \times 10^{20} \) As/cm\(^3\) cases have their respective Fermi levels lying within 2 \( kT \) of the conduction band edge and hence require a degenerate treatment. In contrast, a concentration of only \( 1 \times 10^{19} \) As/cm\(^3\) in germanium was sufficient to put the Fermi level within 2 \( kT \) of the conduction band edge as shown in Fig. 4.42.

The Fermi level calculated from the neutrality equation for p-type c-Si (Eq. 4.8) doped with \( 5 \times 10^{19} \) Al/cm\(^3\) lies between 0.71 \( kT \) and 0.82 \( kT \) of the valence band edge (not shown). Thus, this material is also degenerate, in agreement with the
5.7. DISCUSSION

Figure 5.31: Fermi levels as a function of temperature for various concentrations of arsenic doped silicon. The conduction band edge, $E_c$, which is equal to the band gap energy when the valence band edge is taken as the zero reference, and the boundary associated with a $2kT$ window below the conduction band are also shown.

Figure 5.32: Fractional ionization of arsenic and aluminum atoms in silicon as a function of temperature. The values were calculated from Eq. 2.18 and the Fermi levels shown in Fig. 5.31. The fractional ionization for aluminum is lower than for the same concentration of arsenic primarily due to the difference in the effective mass of electrons and holes.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

Table 5.7: The net ionized dopant concentration for the gross arsenic and aluminum concentrations used in the SPE measurements of this work. The ranges of values listed correspond to the temperature range covered by this study.

<table>
<thead>
<tr>
<th>Dopant Concentration (/cm³)</th>
<th>Arsenic: $N_d^+$ (/cm³)</th>
<th>Aluminum: $N_a^-$ (/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{19}$</td>
<td>(0.77–0.82)×10^{19}</td>
<td>–</td>
</tr>
<tr>
<td>$5 \times 10^{19}$</td>
<td>(2.45–2.86)×10^{19}</td>
<td>(0.87–1.09)×10^{19}</td>
</tr>
<tr>
<td>$1 \times 10^{20}$</td>
<td>(3.76–4.49)×10^{19}</td>
<td>–</td>
</tr>
</tbody>
</table>

5.7.4 Fractional Ionization in Doped Silicon

With the Fermi level for each of the dopant concentrations used now explicitly determined, the fractional ionization of each can be calculated with Eq. 2.18 to compare with the full ionization approximation made by some of the SPE models. Fig. 5.32 shows the calculated fractional ionization levels as a function of temperature for the various arsenic concentrations used, along with the $5 \times 10^{19}$ Al/cm³ case. The low fractional ionization level for aluminum is primarily due to the fact that the effective mass of a hole is only about half that of an electron. Table 5.7 summarizes the ranges of ionized concentrations for each dopant concentration.

These values reveal that the full ionization approximation is not valid for the concentrations associated with dopant-enhanced SPE enhancement measurements. For the lowest concentration of arsenic ($1 \times 10^{19}$ /cm³) used in this work there was no significant SPE rate increase over the hydrogen-free value, as shown in Fig. 5.16. Yet, for the same concentration, the full ionization approximation would result in a ~ 20% error in the dopant introduced carrier concentration at SPE temperatures. For the arsenic concentrations of $5 \times 10^{19}$ /cm³ and $1 \times 10^{20}$ /cm³, the ionized fraction lies between 37% and 58%. With an aluminum concentration of $5 \times 10^{19}$ /cm³, the ionized fraction is only between 17% and 22% for the temperature range of these SPE measurements.
5.7. DISCUSSION

5.7.5 Dopant Enhanced SPE and Nondegenerate Models

The calculation of the Fermi level and the fractional ionization associated with the dopant concentrations used reveals the same problem that was observed for germanium in section 4.7.6. From Fig. 5.16, the concentration at which a significant SPE rate enhancement is observed corresponds to a degenerately doped semiconductor. Hence, any model that predicts a SPE rate enhancement based on the Fermi level shift introduced by doping must include a degenerate treatment to be of any practical value for comparing to the experimental SPE enhancement data. Unfortunately this typically precludes the feasibility of an analytic treatment, as discussed in section 4.7.6.

Doped Silicon and the GFLS Model

The generalized Fermi level shifting (GFLS) model of of Lu et al.[11] as discussed in section 2.4.11 has the same two problems that it did for germanium. As shown in section 2.4.11, to get the final velocity enhancement ratio of Eq. 2.46, both the full ionization approximation and nondegenerate semiconductor statistics were used. Yet the calculations of sections 5.7.3 and 5.7.4 have shown that the full ionization approximation is invalid and that a degenerate treatment is required at these concentrations and temperatures.

To compare the experimental doped Ge SPE rate enhancement data to those predicted by Fermi level shifting (FLS) models, the basic expression of Eq. 2.32 was used. This equation encapsulates the basic premise of FLS models without making any ionization approximations or restrictions to nondegenerate material. To reiterate, the velocity enhancement ratio is given by

\[ \frac{v}{v_i} = \frac{1 + g \exp \left( \frac{E_f - E_k}{kT} \right)}{1 + g \exp \left( \frac{E_{fi} - E_k}{kT} \right)} \]  

(5.2)

where \( E_k \) is the donor level introduced by the defect that is assumed to control SPE, \( g \) is the degeneracy of that level, and \( E_f, E_{fi} \) are the extrinsic and intrinsic Fermi levels respectively. This equation simply states that the SPE enhancement is given by the concentration enhancement of the controlling defects caused by the Fermi level shift.
The comparison to the experimentally determined velocity enhancement ratios for doped Ge was performed by leaving \( E_k \) and \( g \) as fitting parameters, and by using the calculated Fermi level values from Eq. 5.2. The same can also be done with the arsenic-enhanced Si SPE data of Fig 5.16. With both \( E_k \) and \( g \) free to vary, the data can be fitted extremely well, as shown in Fig. 5.33. However, the values determined from fitting the two highest concentrations are \( g \sim 40 \) with \( E_k = 1.12 \) eV, and \( g \sim 46 \) with \( E_k = 1.11 \) eV for the \( 5 \times 10^{19} \) As/cm\(^3\) and \( 1 \times 10^{20} \) As/cm\(^3\) SPE enhancement data respectively. A degeneracy between 40 and 50 does not seem realistic, and a defect level of 1.1 eV is above the conduction band edge.

The large degeneracy value and defect energy above the conduction band edge are properties shared with the values determined from fitting the Ge data. In that case, the degeneracy was then fixed at a more plausible value of four to determine what sort of predictions the FLS equation (Eq. 5.2) would make for the defect level, based upon the experimental data. The fits to the experimental data associated with \( g = 4 \) and \( E_k \) as a fitting parameter are shown in Fig. 5.34. The energy levels from these fits for the \( 5 \times 10^{19} \) As/cm\(^3\) and the \( 1 \times 10^{20} \) As/cm\(^3\) case are 0.94 eV and 0.96 eV respectively. For comparison, the conduction band edge (Fig. 2.2) varies between 0.91 eV and 0.98 eV over the temperature range of the SPE measurements.

**Comparison to the Extended GFLS Model**

Both the kink site model and the GFLS model start from an expression for the SPE rate enhancement that relies on the energy level of an introduced defect and the Fermi level of the bulk crystalline material. In section 4.7.6, an extension of these models was proposed in which the band structure at the interface was considered instead of the band structure of the bulk crystalline material. The band bending that occurs in a \( p-n \) junction (Fig. 4.48) was used to establish a similar band structure for the \( c/a \) interface (Fig. 4.49). The exact interface location within the region containing band bending was then left as a fitting parameter.

For the germanium case, the treatment of this extension was reasonably straightforward, since there is a paucity of data available on the band structure of a-Ge. In light of this, the extension as detailed in section 4.7.6 assumed that the width
Figure 5.33: Fits to the arsenic-enhanced SPE data of this work as per the degenerate generalized Fermi level shifting (GFLS) model. Both the energy level and the degeneracy of the proposed defect controlling SPE have been left free to vary as fitting parameters.

Figure 5.34: Fits to the arsenic-enhanced SPE data of this work as per the degenerate generalized Fermi level shifting (GFLS) model. The energy level of the proposed defect controlling SPE has been left free as the only fitting parameter, while the degeneracy of the defect has been fixed at a value of four.
of the band gap was the same in the c-Ge and the a-Ge, and furthermore, that the energy level of the introduced defect remained at a constant offset from the band edges. The proposed band structure of the c/a interface in germanium based on these assumptions was shown earlier in Fig. 4.49.

For the silicon case, there is recent data available on the band structure of the amorphous material, and hence it is included in this treatment. In particular, Stolk et al.[132] have performed extensive measurements on both relaxed and as-implanted a-Si samples. From these measurements, they reported a band gap of 1.58 eV for relaxed a-Si. They also found that the centroid of the defect band was at 0.97 eV below the conduction band, and placed the Fermi level of the a-Si material at the centre of this defect band.

Based upon this information, a more complete representation of the proposed band structure at the c/a interface for silicon can be formed. Shown in Fig. 5.35 is a quantitative representation of this proposed band structure, based upon the c-Si parameters of this work and the a-Si parameters of Stolk et al.[132]. The c-Si Fermi level shown in Fig. 5.35 was calculated for a doping level of $1 \times 10^{20}$ As/cm$^3$ and at 500 °C. It has been assumed that the band gap narrowing due to temperature in a-Si is the same as that observed for c-Si[64], and that the doping of the a-Si does not cause a Fermi level shift since most of the arsenic will be fully coordinated and electrically inactive. However, it is noted that Coffa and Poate[133] suggest that Fermi level shifts in a-Si may take place when the doping concentration is similar to the defect density, as is the case for the concentration regime in which dopant-enhanced SPE has been found to occur in this work.

From Fig. 5.35, it is evident that the energy spacing between the conduction band and the Fermi level increases dramatically when crossing from the c-Si side to the a-Si side. Small horizontal shifts of the vertical line marking the interface within the region of band bending result in significant variations of the Fermi level location with respect to the band edges. When applying these shifts to Eq. 5.2 for the germanium case, only the numerator needed to be considered, since the Fermi level location with respect to the band edges and the band gap magnitude have been assumed to be constant across a c/a interface in intrinsic material. However, the
Figure 5.35: Proposed band gap structure at the c/a interface for silicon doped with $1 \times 10^{20}$ As/cm$^3$ at $500^\circ$C. The Fermi level is constant across the interface and hence band bending is expected to take place.

Figure 5.36: Band gap structure as per Fig. 5.35 but for intrinsic material. The difference between the magnitude of the band gap for c-Si and a-Si implies that band bending still takes place even in undoped material.
CHAPTER 5. SPE OF AMORPHOUS SI AND SI-GE ALLOYS

band structure of a c/a interface in intrinsic silicon, as depicted in Fig. 5.36, clearly indicates that this is not the case. Hence, any lateral shifts of the interface location within the region of band bending must also be applied to the calculation of the denominator of Eq. 5.2 as well.

At this point it was necessary to make some assumptions about how the energy level of the defect controlling SPE behaves in the band gap. For the germanium case, it was sufficient to say that the defect energy level remained at a constant fraction of the band gap, since that was equivalent to saying it tracked either band edge due to the constant band gap width across the interface. The case of the defect level remaining at a constant amount from the conduction band is treated here for silicon. Similar considerations are required for the temperature dependence of the Fermi level location in the a-Si material. In the germanium case, the Fermi level of intrinsic c-Ge was used, placing it near mid-gap for all temperatures. In this case the defect band containing the Fermi level is assumed to remain at a constant fraction of the band gap since the temperature dependence of the Fermi level location has not been reported. It is also possible that it remains at 0.98 eV below the conduction band edge, in accordance with the value given by Stolk et al. [132]. However, combining this with the temperature dependence of Thurmond et al. [64] would then mean that the Fermi level in a-Si progressively heads towards the valence band with increasing temperature. This is in conflict with the general understanding that the Fermi level remains near mid-gap in a-Si.

With these considerations in place, the modified GFLS model can be fitted to the experimental data with the weighting factor that represents the interface location within the region of band bending. A weighting factor of $W = 1$ corresponds to the c/a interface being at the left of the band bending region in Fig. 5.35, indicating that the Fermi level at the interface is equal to the bulk crystalline value, which in turn gives the same result as considered in Fig. 5.34. A value of $W = 0.5$ implies equal band bending in both phases, as schematically indicated in Fig. 5.35. Finally, a value of $W = 0$ is equivalent to having the Fermi level at the interface equal to the a-Si value, with all the band bending taking place in the crystalline phase.

A value of $W = 0.5$ improves the quality of the fit over that of Fig. 5.34, and at
DISCUSSION

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{As/cm}^3 & W = 0.45 & W = 0.35 & W = 0.30 & W = 0.25 & W = 0.20 \\
2 \times 10^{19} & 0.62 \text{ eV} & 0.54 \text{ eV} & 0.50 \text{ eV} & 0.45 \text{ eV} & 0.41 \text{ eV} \\
5 \times 10^{19} & 0.53 \text{ eV} & 0.45 \text{ eV} & 0.40 \text{ eV} & 0.35 \text{ eV} & 0.29 \text{ eV} \\
1 \times 10^{20} & 0.48 \text{ eV} & 0.39 \text{ eV} & 0.34 \text{ eV} & 0.28 \text{ eV} & 0.18 \text{ eV} \\
\hline
\end{array}
\]

Table 5.8: The defect levels \(E_k\) calculated from the fitting of the modified degenerate Fermi level shifting model to the experimental arsenic-enhanced Si SPE data of this work. The \(W\) values indicate the relative interface location within the region of band bending, or equivalently, the fraction of band bending that takes place in the amorphous phase. Values corresponding to a range of interfacial location weighting values are shown.

\(W = 0.25-0.20\), the fit is essentially identical to that shown in Fig. 5.33, while still maintaining a degeneracy of four, which is more reasonable than a value of \(\sim 40\). The value of \(E_k\) determined from such fits is dependent on the particular concentration and the \(W\) value used. The behaviour of the defect energy level \(E_k\) with respect to doping concentration and the weighting factor \(W\) is indicated in Table 5.8.

There is a clear decrease in \(E_k\) associated with a decrease in \(W\). The \(E_k\) values determined from the fit are also observed to increase with decreasing doping concentration for a given \(W\) value. In the context of the model, this would imply that the energy level of the defect is not independent of doping concentration, or that some other factor which depends on the doping concentration is not properly accounted for in the model. It is also noted that for \(W \sim 0.15\), the resulting fit makes a transition from positive to negative curvature, and reasonable fits to the experimental \(1 \times 10^{20} \text{ As/cm}^3\) data are no longer obtainable. However, the indication that \(\sim 80\%\) of the band bending takes place in the crystalline phase is in keeping with the model's result for the germanium data as detailed in section 4.7.6.

Due to the paucity of information on the band structure of a-Si at these doping levels and temperatures, this extension of the degenerate FLS model only serves to show that plausible results can be obtained by considering possible band bending effects. Further improvements in the understanding of a-Si, or some independent means of identifying the defect levels would be needed before these fitted parameters can be seriously considered.
5.7.6 SPE Measurements in Compensation Doped Silicon

When the net doping level was less than $1 \times 10^{19} / \text{cm}^3$, the silicon samples containing overlapping profiles of arsenic and aluminum exhibited a SPE rate very close to the hydrogen retarded rate observed in undoped samples over the same depth region. This indicated that the hydrogen rate retardation effect was not suppressed by the presence of both dopants.

A calculation of the Fermi level from Eq. 4.14 and the parameters used in section 5.7.3 for $5 \times 10^{19} / \text{cm}^3$ of both arsenic and aluminum was performed. This indicated that the Fermi level in the compensation region was 0.045 eV to 0.052 eV above the intrinsic level over the temperature range from 480 °C to 660 °C. For comparison, the width of the band gap over the same temperature range is 0.98 eV to 0.91 eV. The fact that the Fermi level had shifted slightly towards the conduction band indicated that the fractional ionization of the arsenic was greater than the aluminum over this temperature range. The calculation of the actual fractional ionization values gave 99.7% to 98.3% for arsenic, and 99.6% to 97.9% for aluminum. This small difference translates into a surplus of ionized arsenic ranging from $(0.2-2.0) \times 10^{17} / \text{cm}^2$, which is small when compared to the doping levels required to cause enhanced SPE rates.

5.7.7 SPE Measurements in Si$_x$Ge$_{1-x}$Alloys

The measurements of the SPE rate in the undoped Si$_{0.79}$Ge$_{0.21}$ alloy samples revealed that there were two distinct depth regions that had a constant SPE rate, with the division between the two being at $\sim 8000$ Å. The SPE rate for the region beyond this point was significantly faster than the SPE rate taken from the region between 2500 Å and 6500 Å. Since the alloy layers were 1 to 1.5 µm thick, and a graded buffer layer 2 µm thick lay below that, one would not expect to observe SPE rate changes associated with a variation in the alloy composition at depths less than $\sim 1.5$ µm.

Based upon the observations from the silicon SPE measurements, the slower SPE rate in the region closer to the surface of the Si$_{0.79}$Ge$_{0.21}$ samples was most likely due to hydrogen contamination. Measurements involving regrowth of several
microns of a-Si have clearly indicated the difference between the SPE rate of the hydrogen contaminated Si surface layer and the SPE rate of the remaining hydrogen-free Si material. Unfortunately, these samples had already been amorphized to the maximum useful depth possible. The use of thicker alloy layers, combined with SIMS measurements on partially annealed samples would be required to fully establish whether hydrogen contamination is responsible for the lower SPE rate in the region closest to the sample surface.

The depth region containing the implanted arsenic was within the region exhibiting the slower SPE rate. Hence, it would have seemed logical to normalize the arsenic-enhanced Si$_{0.79}$Ge$_{0.21}$ SPE data against the slower rate. However, in the silicon case, a comparison with the buried layer data indicated that normalization against the faster rates obtained from the hydrogen-free region was appropriate. When the thick layer arsenic-enhanced Si SPE data was normalized against the hydrogen retarded SPE rates, the temperature dependence of the enhancement was too large in comparison to the buried layer data. The normalization of the Si$_{0.79}$Ge$_{0.21}$ data (Fig. 5.29) against the slower rates showed a larger temperature dependence than when normalized against the faster SPE rates associated with regrowth beyond 8000 Å. This further suggests that hydrogen contamination may also play a role in SPE measurements involving silicon-rich Si$_x$Ge$_{1-x}$ alloys.
5.8 Conclusions

Measurements of the SPE rates for a-Si layers on (100) Si verified the existence of a retardation effect extending to depths up to 2 µm. The SPE rate associated with hydrogen-free material as calculated from depths beyond this point was found to follow an Arrhenius form with an activation energy and velocity prefactor of $2.70 \pm 0.01$ eV and $(4.6 \pm 0.7) \times 10^6$ m/s respectively. These values are in good agreement with the only other SPE measurements of thick a-Si layers reported in the literature. The SPE rate reduction associated with the maximum hydrogen concentration was found to be temperature dependent, with the maximum retardation effect being observed at the lowest annealing temperatures.

The SPE rate enhancements for doping with arsenic and aluminum were then investigated. A comparison of the relative enhancement for arsenic in the hydrogen contaminated surface amorphous silicon layers of this study with similar data obtained from hydrogen-free buried a-Si layers was performed. This comparison showed good agreement between the temperature dependence of the SPE rate enhancements in both the surface a-Si layers and buried a-Si layers relative to the hydrogen-free SPE rate, and not relative to the hydrogen retarded rate, even though in the surface a-Si layers, the dopant resided in the depth region which exhibited retardation in undoped samples.

The relative enhancement for doping with arsenic was observed to be temperature dependent, with the greatest enhancements occurring at the lower annealing temperatures. When the arsenic-enhanced SPE data was plotted in an Arrhenius fashion, this temperature dependence could be represented by a reduction of $\sim 0.13$ eV in the activation energy for doping with $1 \times 10^{20}$ As/cm$^3$. The SPE rate enhancement for $5 \times 10^{19}$ Al/cm$^3$ was observed to be greater than the enhancement for the same concentration of arsenic. In addition, the enhancement for aluminum doping did not exhibit any significant temperature dependence.

Samples containing overlapping profiles of $5 \times 10^{19}$/cm$^3$ arsenic and aluminum were also studied. The region of overlap lay within the region that exhibited a hydrogen retarded SPE rate in undoped samples. The SPE rate associated with this region was found to return to a value nearly identical to the hydrogen contaminated
5.8. CONCLUSIONS

The enhancements in the SPE rate due to the significant net doping level on either side of the compensation region agreed well with the SPE rate profiles taken from samples containing only one of the two dopants.

Semiconductor statistical calculations of the Fermi level in c-Si at SPE temperatures and at the doping levels used were performed. These revealed that the concentrations used corresponded to degenerately doped layers, and that models using a nondegenerate approximation would not be valid in the doping regime for which significant SPE rate enhancements are observed. Furthermore, these calculations indicated that the full ionization approximation used in some models is inappropriate at these dopant concentrations.

A fully degenerate treatment of the Fermi level shifting model was performed so that the predicted relative SPE rate enhancements could be compared to the experimental data. Fitting the model to the arsenic-enhanced Si SPE data resulted in an implausible degeneracy value for the proposed defect that is responsible for governing the SPE rate. Requiring a small degeneracy value resulted in the model predicting too strong a temperature dependence when compared with the arsenic-enhanced silicon SPE rate data. These results are similar to those found from performing similar comparisons with the arsenic-enhanced Ge SPE rate data.

The extension to the Fermi level shifting model involving consideration of the Fermi level at the c/a interface through band bending arguments was shown to produce plausible results. However, the lack of information about the band gap structure of amorphous silicon at typical SPE temperatures and doping levels prevents serious consideration of the quantitative results provided by the model.

Measurements on undoped Si\textsubscript{0.79}Ge\textsubscript{0.21} samples revealed that the SPE rates at depths beyond \( \sim 8000 \) Å were significantly faster than the rates observed at shallower depths. This suggested that silicon-rich (\( \geq 80\% \) Si) alloy materials may also suffer hydrogen contamination and subsequent retardation of the SPE rate during annealing. The alloy samples containing \( \sim 50\% \) Si did not show any similar variation in the SPE rate with depth. The first measurements involving dopant-enhanced SPE rates in Si\textsubscript{x}Ge\textsubscript{1-x} alloy samples indicated that the presence of arsenic also enhances the SPE rate in this material. The magnitude of the enhancement was similar to that
observed in arsenic doped silicon and germanium samples. Furthermore, the relative enhancement increased with decreasing temperature, giving the same general temperature dependence that was observed in the silicon and germanium samples.
Chapter 6

Summary and Conclusions
6.1 Germanium

Multiple-energy implants were used to create constant concentration dopant profiles in a-Ge. Time Resolved Reflectivity measurements on these samples have provided new data on the solid phase epitaxial regrowth rate enhancement for known concentrations of arsenic and aluminum at various temperatures.

The treatment of implantation doped germanium in Chapter 4 revealed an important result regarding the various models that relate dopant-enhanced SPE rates to Fermi level shifting. Calculations indicated that the minimum doping levels that still gave rise to an enhanced SPE rate resulted in the crystalline phase being degenerately doped at SPE temperatures. The existing SPE rate enhancement models based on Fermi level shifting arguments have been developed using nondegenerate approximations in the semiconductor statistical calculations. These approximations are no longer valid in the degenerate regime for which enhanced SPE rates have been observed. These models were also shown in Chapter 2 to assume that the dopant was fully ionized in the crystalline material. However, similar calculations demonstrated that this assumption was also no longer valid at the temperatures and dopant concentrations associated with enhanced SPE measurements. A concentration of $1 \times 10^{19}$ As/cm$^3$ in Ge resulted in only a slight SPE rate enhancement, and yet the fractional ionization of the arsenic was already down to 71% even at the highest temperature studied. The worst case was for a concentration of $1 \times 10^{20}$ Al/cm$^3$ in Ge, with the fractional ionization being only a mere 13% at the very lowest annealing temperature.

In Chapter 2, the Fermi level shifting models were shown to all start from a shared expression for the SPE rate enhancement ratio written in terms of the Fermi level shift, the introduced energy level of the defect that controls SPE, and the degeneracy of the introduced level. This expression provides a sufficiently general basis to develop an expression for the enhanced SPE rate in degenerately doped material since, in the existing treatment, the approximations associated with assuming a nondegenerate semiconductor with full ionization are applied later. In particular, these approximations are used to transform the velocity ratio so that the explicit Fermi level dependence is replaced with the doping concentration and the
temperature, as they are the experimentally determined quantities. A numerical treatment of this expression was performed so that the predicted SPE rate enhancements could be compared to the experimental data without having to use either of these approximations.

Only the arsenic data was compared to the predicted rate enhancement since the aluminum-enhanced SPE rates showed no significant temperature dependence. In contrast, the enhancement due to the highest concentration of arsenic studied here increased significantly with decreasing temperature. If both the defect level and the defect degeneracy were left free as fitting parameters, then the predicted enhancement could be fitted to the experimental data. However the degeneracy value obtained from the fit appeared to be too large to be plausible. If the degeneracy was fixed to a reasonable value then the temperature dependence predicted by the model became too large.

Since previous studies have shown conclusively that the SPE rate is controlled at the c/a interface and not by the bulk, a modification based on this was considered. The Fermi level used in the common expression for the velocity enhancement ratio has always been taken as that of the bulk crystalline phase, which will be near one of the band edges for the dopant concentrations used in SPE enhancement measurements. Yet, it is generally accepted that the Fermi level is pinned at or near the middle of the band gap in the amorphous phase. This suggests that the placement of the Fermi level with respect to the band edges at the c/a interface will be some sort of a compromise between the two.

When this extension is added, the model is able to fit the experimental data without requiring an unreasonably large degeneracy, and the extension suggests that the positioning of the Fermi level at the interface is slightly dominated by the amorphous phase. However the unavailability of information on the band structure of a-Ge precludes one from drawing any more substantial conclusions.

Germanium samples containing both arsenic and aluminum within the same depth range exhibited essentially complete compensation with the SPE rate returning to a value quite near the undoped SPE rate. One of the strong points for Fermi level shifting models is that the Fermi level returns to the intrinsic value when equal
concentrations of both n-type and p-type are present and hence dopant compensation follows naturally.

To obtain experimental velocity enhancement ratios, the SPE rate associated with undoped a-Ge on (100) Ge had to be determined first. The variation between the values reported in the literature were not sufficient for providing an accurate normalization of the dopant-enhanced SPE data. Measurements over a large temperature range of the SPE rate for undoped a-Si layers on various (100) Ge substrates indicated that the SPE rate could be accurately represented by an Arrhenius equation with an activation energy and velocity prefactor of 2.15 ± 0.04 eV and (2.6 ± 0.5) × 10^7 m/s respectively.

A retardation effect has been reported for SPE measurements in a-Si, associated with the absorption of hydrogen into the a-Si layer. The SPE rate can be retarded by up to 40% and the retardation can reach depths in excess of 2 µm. The hydrogen is thought to result from dissociation of water vapour during oxide formation at the surface of the sample. Experiments on a-Ge layers were performed to look for a similar effect in germanium. Layers of a-Ge in excess of 3 µm thick exhibited a constant SPE rate to within a few thousand angstroms of the sample surface, indicating that the hydrogen contamination does not occur in amorphous germanium samples to the same extent as observed in silicon. When hydrogen was implanted into a-Ge a similar SPE rate reduction was observed, indicating that the lack of a retardation effect was due to the lack of hydrogen in the a-Ge layer. SIMS measurements of the hydrogen content in partially annealed samples confirmed this. It was concluded that the instability of the native oxide of germanium was responsible for the lack of hydrogen contamination during annealing.

6.2 Silicon and Silicon-Germanium Alloys

Similar measurements involving constant concentration profiles of arsenic and aluminium in a-Si on (100) Si substrates were performed. The temperature dependence of the SPE enhancement was observed to be very similar to what was observed in germanium. The SPE enhancement due to aluminum showed no significant temperature dependence, whereas the arsenic-enhancement showed an increase as the
temperature was decreased. Comparison of the normalized SPE rates in the hydrogen contaminated samples of this study with those of the hydrogen-free buried layer measurements showed good agreement when the dopant-enhanced hydrogen contaminated data were normalized to the hydrogen-free SPE rates, and not to the hydrogen retarded rates, suggesting that when the dopant concentration significantly exceeds the hydrogen concentration, the normalization should be with respect to the hydrogen-free rates.

Numerical calculations of the Fermi level once again revealed that significant SPE rate enhancements in Si were only observed when the dopant concentration reached or exceeded the threshold associated with degenerate doping. Furthermore, the full ionization approximation was shown to be no longer valid, with the fractional ionization for the aluminum doped sample being as low as 17%.

Application of the fully degenerate statistical treatment to the arsenic-enhanced silicon SPE data resulted in similar problems to those uncovered when it was applied to the arsenic-enhanced germanium SPE data. In particular, a large degeneracy for the defect controlling SPE resulted from fitting the model to the experimental data, and if the degeneracy was fixed at a plausible lower value, the temperature dependence predicted by the model was once again too strong.

The extension of the degenerate Fermi level shifting model to consider the Fermi level at the c/a interface instead of the bulk crystalline Fermi level was then applied to the arsenic-enhanced silicon SPE data. With this in place, the model can be fitted to the experimental data, but the lack of sufficiently detailed data describing the band structure in a-Si again makes the actual values determined from the fit of minimal value.

Measurements of the SPE rate in undoped a-Si on (100) Si substrates were also performed for the purpose of normalizing the dopant-enhanced SPE data, and to compare with the reported hydrogen contamination problem. The growth of hydrogen-free intrinsic a-Si was found to follow an Arrhenius form with an activation energy and velocity prefactor of $2.70 \pm 0.01$ eV and $(4.6 \pm 0.7) \times 10^6$ m/s respectively. These values are in good agreement with the values previously reported in the literature. The SPE data associated with the hydrogen contaminated region
indicated that the rate reduction due to the hydrogen was temperature dependent, with the largest retardation being observed at the lowest temperatures.

Measurements involving SiₓGe₁₋ₓ alloys have shown that the SPE rates were also enhanced by a concentration of 1×10^{20} \text{As/cm}^3. The relative enhancement was of a similar magnitude as observed for the same concentration of arsenic in both silicon and germanium. The temperature dependence of the arsenic enhancement was also similar to that observed in both silicon and germanium, with the greatest enhancements being observed at the lowest temperatures. The measurements on the undoped Si₀.₇₉Ge₀.₂₁ samples exhibited slower SPE rates in the last ~ 8000 Å of regrowth, suggesting that hydrogen contamination may also play a role in SPE measurements involving silicon-rich SiₓGe₁₋ₓ alloys.

6.3 Further Work

Germanium has proven to be a useful host material for performing SPE rate enhancement experiments since the hydrogen contamination problem appears to be limited to the first few thousand angstroms below the sample surface. However, amorphous layers exceeding 2 \text{μm} in thickness can be troublesome due to the explosive crystallization problem. In hindsight, the use of a 1.5 \text{μm} laser for TRR measurements in Ge would appear to a better choice than the 1.15 \text{μm} laser if the depth of interest exceeds 0.5 \text{μm}. Use of the longer wavelength would have most likely increased the quality of the aluminum-enhanced germanium SPE data by a significant amount.

In germanium, a given concentration of arsenic was observed to enhance the SPE rate more than the same concentration of aluminum. Yet, in silicon, the exact opposite is observed, with aluminum providing a larger enhancement. The fact that essentially complete compensation occurs when both are present simultaneously tends to rule out any gross errors in the concentration measurements. In addition, the arsenic-enhanced SPE rate shows a clear temperature dependence, whereas the aluminum enhancement appears essentially independent of the temperature, for both silicon and germanium. It would be useful to perform similar constant concentration TRR measurements involving boron and phosphorous in a-Ge so that a better overall
picture of the temperature dependence and enhancement efficiency for each dopant could be obtained.

Unfortunately the current models do not provide the reasons why this dopant-specific behaviour is observed. In particular, without any knowledge of the band gap narrowing due to doping at typical SPE temperatures, the only parameter related to the dopant species that appears in the Fermi level shifting models is the donor or acceptor energy level introduced into the band gap by the dopant. Measurements of the band gap narrowing and variations in the introduced dopant level with temperature and doping concentration could provide insight into why the two species exhibit different enhancement behaviour. However, performing such measurements at the elevated temperatures used during SPE measurements is considerably more difficult than performing similar measurements at room temperature.

The nature of how the aluminum is incorporated into the semiconductor is another area where further measurements should prove useful. In the case of arsenic, previous measurements in the literature have indicated that the arsenic is essentially 100% substitutional and electrically active. However, there is substantially less information of a similar nature available for aluminum, since its use as a dopant is relatively uncommon.

The consideration of the Fermi level at the c/a interface instead of the bulk crystalline Fermi level was shown to provide plausible results when applied to the degenerate Fermi level shifting model. However, the primary problem with this extension is that it requires a qualitative knowledge of the band structure in the amorphous material at SPE temperatures and at the doping levels used in SPE enhancement measurements. If such measurements are performed on amorphous layers on crystalline substrates, then the measurement is complicated by the regrowth of the amorphous layer that will take place during the measurement.

There are several other areas in which the results of this work have revealed the need for additional research. SIMS measurements of partially annealed a-Si layers at low and high temperatures should give information on the temperature dependence of the hydrogen contamination effect in silicon. Further comparisons between
the thick layer and buried layer SPE enhancement data would be required to verify whether the presence of arsenic effectively turns off the hydrogen retardation. Dopant measurements involving depths beyond the hydrogen contamination region would also prove useful. The compensation measurements in germanium suffered from the fact that an individual dopant concentration of $5 \times 10^{19}$/cm$^3$ does not produce a very large enhancement to begin with. With this knowledge now in hand, further compensation measurements in germanium involving higher concentrations and possibly larger regions of dopant overlap would be useful. The measurements of the dopant enhancement associated with arsenic in Si$_x$Ge$_{1-x}$ alloys presented in this work have only scratched the surface. Measurements involving other concentrations and other dopant species are required before a clear picture will be obtained of how the SPE rates in Si$_x$Ge$_{1-x}$ are altered by doping. In addition, SIMS measurements involving partially annealed silicon-rich Si$_x$Ge$_{1-x}$ alloy samples would help to ascertain whether hydrogen contamination is an issue in these materials.

In closing, the work presented in this thesis has provided new data on the solid phase epitaxial regrowth of semiconductor materials, and dopant enhancements of the SPE rate. Calculations based upon this data and the available semiconductor parameters have revealed significant shortcomings in the current models used to explain dopant-enhanced SPE rates. It is felt that a better understanding of the SPE process taking place at the crystalline-amorphous interface will ultimately require a better understanding of the properties of the amorphous phase.
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