Phosphorus Activation and Diffusion in Germanium

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Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

This work was done under the guidance of Professor Russell Gwilliam, at the Advanced Technology Institute within the University of Surrey.

M.A. Razali
September 2014
Abstract

Currently, the International Technology Roadmap for Semiconductors (ITRS) is targeting the 22nm technology node in accordance with Moore’s Law. The low mobility of silicon makes it inherently unsuitable as a channel material for devices at this scale, and therefore a significant amount of research is being focused at re-evaluating germanium as an alternative substrate. Germanium offers a higher mobility than that of silicon and is compatible with existing silicon device manufacturing techniques. P-type ultra shallow junction (USJ) implemented in germanium exhibit low leakage currents and low sheet resistivity, satisfying the ITRS demands. However, N-type USJ formed using phosphorus as the dopant species do not yet satisfy these requirements due to a high diffusivity and low levels of electrical activation. This is due to the fact that at high phosphorus concentrations, the difference between the equilibrium solid solubility limit and the effective solid solubility is related to the formation of phosphorus-vacancy complexes. These evolve into electrically inactive clusters, by capturing the additional phosphorus resulting in an overall reduction of the electrical activity of the phosphorus population. Another problem is phosphorus out-diffusion during annealing process. In order to overcome these problems, novel techniques are currently being research.

This thesis investigates the phosphorus activation and diffusion characteristics as a function of implant temperature and co-implantation of low dose germanium. The samples were subsequently subjected to an isochronal annealing before Hall Effect and SIMS analyses were performed to characterize the electrical activation and diffusion respectively. The results from the studies indicate that it is a non trivial process for germanium to replace silicon in order to become the next dominant substrate.
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Publications

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(2) “Point Defect engineering Study of Phosphorus Ion Implanted Germanium”

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Glossary of Terms

4pp: Four-Point-Probe
A/C interface: Amorphous/Crystalline Interface
P: Phosphorus
CMOS: Complementary Metal Oxide Semiconductor
EOR: End of Range
FLA: Flash-lamp annealing
Ge: Germanium
ITRS: International Technology Roadmap for Semiconductors
MBE: Molecular Beam Epitaxy
MIMA: Multiple Implantation Multiple Annealing
MOSFET: Metal Oxide Semiconductor Field Effect Transistor
NMOS: N-type Metal Oxide Semiconductor
Ns: Active Carrier Density
PAI: Pre-Amorphisation Implant
RHs: Hall Coefficient
Rs: Sheet Resistance
RT: Room Temperature
RTA: Rapid Thermal Anneal
RMS: Root Mean Square
SEM: Scanning Electron Microscope
Si: Silicon
SiGe: Silicon Germanium
SIMS: Secondary Ion Mass Spectroscopy
SRP: Spreading Resistance Profiling
SPER: Solid Phase Epitaxial Re-growth
TEM: Transmission Electron Microscopy
TED: Transient Enhanced Diffusion
VDP: Van der Pauw
VH: Hall Voltage
XTEM: Cross-sectional Transmission Electron Microscopy
Xj: Junction Depth
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1 Introduction

1.1 Introduction

The past four decades have seen continuous development in the field of the Silicon-based Metal-Oxide-Semiconductor-Field-Effect-Transistor (MOSFET) industry. Its evolution was based on the Moore’s Law (Figure 1), by reducing the physical dimensions of the transistors, in order to double its number on an integrated circuit for every two years [1]. Consequently, the performances of the microprocessor increased over the technology generations.

![Figure 1. Moore’s Law as expressed by the number of transistors as function of time [2]](image)

However, as the conventional silicon transistor dimensions scaling reached sub-100 nm regime, it could not continue its advantages of increasing the microprocessor performances. As a result, at every technology generation node, non-silicon elements were implemented to silicon base transistor (Figure 2) in order to maintain its traditional advantages. Strain technology was first introduced at 90 nm technology node, by implementing Silicon Germanium (SiGe) in the transistor channel. Next, at 45 nm process node, the high-K and metal gate materials were integrated. The recent development in the semiconductor industry is the tri-gate transistor, which is three-dimensional transistor architecture. Beyond the 22 nm technology node, the maximum performance achievable for the silicon base transistor would be limited due to its fundamental electronic properties. Hence, International Technology Roadmap for Semiconductor (ITRS) [3], which is an organisation that
ensure the advancement of the integrated circuit performance in the industry, has identified a number of materials that could replace the silicon channel such as germanium, III-V compounds, semiconductor nanowires, carbon nanotubes and graphene, as they show potential to enhance the performance of the CMOS circuit.

![Figure 2. Sub-100 nm CMOS technology scaling [4]](image)

1.2 Motivation

Among the alternate channel materials, germanium has drawn the greatest interest. The main reason is due to its carrier mobility and ease of integration [5]. It can be seen from Table 1 that germanium (Ge) has substantially higher bulk hole and electron mobilities, approximately four and two times higher than those of silicon (Si), respectively. At first glance, the combination of germanium for PMOS (P-type Metal-Oxide-Semiconductor) and III-V compound (GaAs) for NMOS (N-type Metal-Oxide-Semiconductor) seems to offer a large advantage for the next generation CMOS (Complementary Metal-Oxide-Semiconductor) devices as germanium has the highest hole mobility, which is P-type, while GaAs has the highest electron mobility among the materials, which is N-type. However, realizing the ‘ideal’ CMOS has many problems in terms of integration, cost and process, which may not have straightforward solutions. Other advantages of germanium are easy integration and process compatibility with silicon technology, considering that SiGe has already been integrated into the current MOSFET’s channel.

Therefore, the best choice is to use germanium as the material for both PMOS and NMOS transistors.
In recent years, several research groups have successfully demonstrated a high mobility germanium PMOS transistor [7-9]. However, forming a germanium NMOS device which is comparable with germanium PMOS device is still one of the key challenges in order to manufacture germanium base MOSFET devices. Therefore, in this thesis, more effort is spent to improve germanium NMOS device performance, in terms of increasing the dopant activation and reducing the dopant diffusion. Phosphorus (P) is the preferred dopant species for the NMOS device fabrication due to its high solid solubility in germanium [10].

In the literature, a few techniques have been reported in order to overcome the problems of phosphorus low activation and high diffusion, include: multiple implantation multiple annealing (MIMA), co-implantation of vacancy trap and donor species, laser or flash thermal processing and the use of capping layers.

In this thesis, the effect of implant temperature and co-implantation of low dose germanium towards the activation of high dose P⁺ regions are studied along with the control of diffusion of the implanted P during post-implant anneals.

### 1.3 Objectives

The objective of this work is to study the phosphorus activation and diffusion characteristics as a function of implant temperature and co-implantation of low dose germanium, respectively.

### 1.4 Novelty

The work presented in this dissertation provides a study of phosphorus electrical behaviour in germanium substrate. The effect of implant temperature with two implant energies, 30 keV and 5 keV is investigated. The effect of low dose germanium co-implant on phosphorus activation and diffusion is also studied.

<table>
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<th></th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mobility (cm²/ Vs)</td>
<td>1350</td>
<td>3900</td>
<td>8500</td>
</tr>
<tr>
<td>Hole mobility (cm²/ Vs)</td>
<td>450</td>
<td>1900</td>
<td>400</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.12</td>
<td>0.67</td>
<td>1.42</td>
</tr>
</tbody>
</table>

**TABLE 1  Bulk semiconductor properties [6]**
1.5 Thesis structure

Publications

This lists all of the publications resulting from this project, including collaborative work

Chapter 1 – Introduction

This chapter is used to indicate the objectives, novelty and overview structure of this thesis. It also presents the historical background and motivation to the work.

Chapter 2 – Literature survey

A review of the published literature for this subject is represented in this chapter. This includes an introductory background, current issues with phosphorus as a dopant in germanium as well as discussing possible solutions.

Chapter 3 – Experimental Techniques

Various experimental techniques that are used in this work are discussed in this chapter.

Chapter 4 – Results I: Temperature Dependant Study of phosphorus Ion Implantation in germanium

The first set of experiments is discussed, which investigate phosphorus activation and diffusion as a function of temperature.

Chapter 5 – Results II: Point defect engineering study of phosphorus ion implanted germanium

The experiment design for studying the effect of co-implant germanium towards phosphorus activation and diffusion is discussed and its results presented.

Chapter 6 – Conclusion and further work

This chapter concludes the thesis and also, proposes some further work in order to continue this research.

References


2 Literature Survey

2.1 Introduction

This chapter is a literature review focusing on the key aspects of improving the atomic and electric attributes of phosphorus doped germanium layers. It is partitioned into several areas; start with, Source / Drain extension engineering and junction formation. Next, understanding the challenges for Ge NMOS junction formation, which consist of problems, theory and complex mechanisms related to phosphorus doping in germanium. Furthermore, the current techniques used to improve the phosphorus layers are reviewed. It finally extends to a review highlighting the main areas to be further investigated.

2.2 Source / Drain extension Engineering

Gate length ($L_g$) is an important aspect when scaling down the size of a transistor, since the switching times for the transistor will increase as this parameter is reduced [11]. However, short channel effects will occur as the device scale down below 60 nm as the depletion-layer widths of the source and drain region is the same magnitude order with the channel length. In order to suppress these effects, the source/drain extension region (Figure 3) is necessary for reducing the maximum electric field. The key requirement for this extension region is to be very highly conductive with the junction profile as shallow and abrupt as possible in order to enhance carrier injection into the channel and minimise the resistance.

![Simplified MOSFET schematic](image)

Figure 3. Simplified MOSFET schematic
2.3 Junction formation

Ion implantation technique followed by thermal processing is widely used in the industry, to fabricate P-N junction in CMOS device. However, ion implantation creates radiation damage by displacing Ge atoms from their lattice site. It leaves behind a space called a “vacancy” which is caused by the displacement of the substrate atoms. At sufficiently high dose, this results in a complete amorphisation of the implanted layer.

Therefore, a thermal processing is required to remove the implantation damage/defects and activate the dopants by moving them onto substitutional lattice sites. In order to fabricate a good quality of P-N junction, the defects need to be removed completely during the thermal processing as the dopant activation and diffusion are influenced by the present of defects.

Phosphorus is the most popular choice of dopant for the NMOS device due to its relatively high solid solubility in germanium (see Table 2).

<table>
<thead>
<tr>
<th>Dopant Element</th>
<th>Maximum equilibrium solid solubility (at/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus (P)</td>
<td>$2.0 \times 10^{20}$</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>$8.1 \times 10^{19}$</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>$1.2 \times 10^{19}$</td>
</tr>
</tbody>
</table>

**TABLE 2 Maximum equilibrium solubility of common dopants in Ge at 600ºC [12]**
2.4 Understanding the Challenges for Ge NMOS junction formation

2.4.1 Implantation damage

When ions are ion implanted into Ge they lose energy due to two types of energy loss mechanism, which are nuclear stopping and electronic stopping [13]. Electronic stopping is the interaction between the incoming ions with the electrons of the substrate material. The process of the energy loss is the energy from the incoming ion dissipates through electron cloud, which creates thermal vibrations in the substrate.

On the other hand, nuclear stopping is a mechanism of collision between the incoming ion and target material atom, and the energy lost by the energy from the incident ion is transferred to the target atom. This will force the target atom to move away from its lattice site. As a result, lattice disorder or defects such as interstitials and vacancies will be created by the move away atom [14].

Once all the kinetic energy is lost by electronic and nuclear mechanisms, the ion becomes implanted in the substrate. Figure 4 shows the ion-solid interaction schematic presentation. Figure 5 shows that at high ion implant velocity, the energy loss is dominated by electron stopping mechanism. However, as the ion implant velocity getting slower, nuclear stopping mechanism will dominate.

Following is the equation for ion distribution (can be approximated as a Gaussian distribution) as a function of depth, where, \( R_p \) is the average depth between the positions of ion resides and the surface and \( \sigma_p \) is the standard deviation [15] :

\[
n(x) = n_0 \exp \left[ \frac{-(x-R_p)^2}{2\sigma_p^2} \right]
\] (2.1)
Figure 4. Schematic of the ion-solid interactions during ion implantation [16]
A schematic representation of the vacancy and interstitial distribution after amorphising and non-amorphising implantation, during and directly after thermal annealing are shown in Figure 6. As-implanted non-amorphising implant is shown in Figure 6(a). This implant occurs when the periodicity of the crystalline structure is not completely in a disordered form. This is due to the low implant damage from low dose implant or implantation with a light dopant species. During the annealing process, a net excess of interstitials will be produced as the vacancies (V) and generated germanium interstitials (I) recombine (6(b)). The amount of excess interstitials is about the same amount of the implanted ions. Extended defects (6(c)) will be formed from these excess interstitials and distributed over the implant distribution.

As the implant dose is increased or implantation with a heavy dopant species, an amorphising implant will occur, as shown in Figure 6(d). Following the annealing process, the SPER (Solid Phase Epitaxial Regrowth) rate occurs at a slower rate than the nucleation rate of excess interstitials into extended defects. As a result, a band of extended defects will occur at the end of the implant which is also known as End of Range (EOR) defects.

Figure 5. Stopping mechanism as function of ion velocity [15]
Figure 6. Schematic representation of a non-amorphising implant and an amorphising implant. The two sequences show essentially the main differences between the two implant regimes [17]

2.4.2 Solid Phase Epitaxial Re-growth (SPER)

The re-crystallisation process of an amorphous region after ion implantation is called SPER process. It occurs when thermal energy is introduced in the material so that the atoms in the amorphous layer re-order themselves following the structure of the crystal layer, which acts as a seed, the direction of re-growth moving from the A/C interface towards the surface in the case of an amorphous layer that extends to the surface [18]. During this process, dopant atoms will be electrically activated due to the incorporation into substitutional lattice sites. A schematic of SPER process is shown in Figure 7. The main drawback of this process is the existence of left over defects below the amorphise/crystalline interface called End-Of-Range (EOR) defects.
2.4.3 Implant related damage in Ge

In Si, it is well-known that during the SPER process, the EOR defect band is formed via the agglomeration of the excess silicon self interstitials [20]. When the temperature is over 700 °C, this defect will evolve in density and size as shown in Figure 8. There are four extended defects which are perfect dislocation loops (PDLs); faulted dislocation loops (FDLs); {113}'s; and clusters (Figure 9). These defects are all from the self interstitials precipitates, and can only be dissolved by absorption of vacancies or emission of interstitials. The formation of the extended defects are dependent on anneal and implantation conditions. The extended defects will evolve from one formation to another which are in order clusters of Si atoms [21] to the well-known rod-like {113} defects [22] and eventually dislocation loops of different types [23-24].
Figure 8. TEM showing evolution of extended defect through annealing at different temperatures and times. As taken from [20]

Figure 9. TEM image of the types of defects generated in Silicon. (a) clusters (b) {113}’s (c) transformation from {113} into loops (d) PDLs and FDLs and, (e) FDLs only. As taken from [25]

The end of range (EOR) defect formation in germanium has been investigated by several authors with contrasting results. A few reports have observed the presence of small dislocation loops at the EOR, [14, 26-28] while other reports have shown that no EOR damage was observed. [7, 14, 29-31]
Koffel et. al. [28] has observed the effect of increasing the annealing time towards the EOR defect. He found that the defects increase in size while decreasing in density, which is a similar trend with silicon defect mechanism. However, this trend is observed at annealing temperature of 500 °C (Figure 10). As the annealing temperature is increased to 600 °C, the size and density of the defect are reduced as shown in Figure 11. This may have been due to the fact that vacancy is the dominant point defect in Ge rather than interstitial.

Surface erosion is not an issue for the most of silicon implantation. However, for the case of germanium, it is very significant especially for the heavy mass of dopant such as antimony. Figure 12 shows the RMS surface roughness in nm for a dose of 3x10^{15} ions cm^{-2}. However, it is observed that surface erosion is not a significant issue for phosphorus dopant that is used in this work due to the light mass. The effect of implantation with a heavy ion towards germanium surface is observed in Figure 13.

![Figure 10](image1.png)

**Figure 10.** Images showing the effect of annealing time on the population of EOR defects formed by 15 keV P⁺ and 1x10^{15} cm⁻². Samples annealed at 380 °C for 30s and then annealed at 500 °C for (a) 10s, (b) 30s and (c) 60s. As taken from [28]

![Figure 11](image2.png)

**Figure 11.** Images showing the effect of increasing the annealing temperature on a population of EOR defects formed by 15 keV P⁺ and 1x10^{15} ions/cm² implantation. Samples annealed at (a) 380 °C at 30s, followed by (b) 10s at 550 °C or (c) 10s at 600 °C. As taken from [28]
Figure 12. Root Mean Square (RMS) surface roughness values of Ge induced by implants of various ion mass using a dose of $3 \times 10^{15}$ at cm$^{-2}$[32]

Figure 13. SEM image ($x$ 150,000) of a 10 nm SiO$_2$/Ge sample implanted with $10^{15}$ at/cm$^2$ antimony (Sb) at 70 keV. As taken from [32]
2.5 Activation of P in Ge

Generally, the requirements for future MOS devices are to provide highly electrically active dopant concentrations \(10^{20}\) cm\(^{-3}\) while maintaining extremely shallow drain source extensions (less diffusion during anneal). While ultra-shallow p\(^+\) n junctions implemented in germanium exhibit high boron activation, low leakage currents and low sheet resistivity, satisfying the future MOS device demands [33], the formation of shallow n\(^+\) p junctions is still difficult.

The key bottlenecks for the germanium NMOS fabrication are forming high activation n-type layers and low diffusion. The electrical activation of high phosphorus concentrations in germanium is approximately one order of magnitude lower \((5-6) \times 10^{19}\) cm\(^{-3}\) than the equilibrium solid solubility. [34-36]. Other problems associated with phosphorus doping are related to the enhanced clustering driven by the non-equilibrium vacancies remaining from the ion implantation process.

Chui et al. [37] suggested that it is very challenging to fabricate n-type shallow junctions, while retaining the stabilization of the doped layer and to provide high doping efficiency to processing temperatures around 500-700 °C as shown in Figure 14. However, for low-dose P implants, almost 100% dopant activation has been reported [30, 38-39] after RTA, with a maximum carrier concentration below \(10^{19}\) cm\(^{-3}\).

![Figure 14. SIMS and SRP depth profiles of P in Ge after isochronal anneal at 10s at varying temperature of 500-700 °C, P was implanted at 32 keV, dose of \(8 \times 10^{14}\) cm\(^{-2}\) [37]](image-url)
Simoen et al. [38] reports that the active phosphorus concentration is limited to $5 \times 10^{19}$ cm$^{-3}$ for high dose implant by calculations based on the implant/anneal depth of 100 nm and resistance/square from the SIMS profile in figure 15. He also discovers the present of a large electrically inactive phosphorus precipitates near the peak of dopant profile after 500°C for 60s anneal, which might be the reason for low active phosphorus carrier concentration in germanium.

![Figure 15. SIMS profiles of a shallow P implant ($5 \times 10^{15}$ cm$^{-2}$ 15 keV) for the as implanted case and after 500°C anneals. The cross section view TEM micrograph shows precipitates near the peak of the implant after 500°C, 60s anneal. As taken from [38]

Beside the present of phosphorus-vacancy complexes, the other issues with anneals of high doses P resulting in out-diffusion of P, e.g. losses to gas phase or capping, in diffusion of P deeper into the sample [40]. The formation of phosphorus-vacancy cluster will be discussed in the next section.

2.5.1 Phosphorus-vacancy cluster formation (P$_2$V complexes)

Phosphorus-vacancy cluster formation is formed when a P atom binds with a PV pair [41-42]. This formation is favoured because of the Coulomb attraction between individual negatively charged phosphorus-vacancy (PV) $^-$ and singly positively charged substitutional phosphorus (P$^+_S$). Following is the reaction of the coulomb attraction (equation 2.2) [43]:

$$(PV)^- + P^+_S \leftrightarrow (P_2V)^0 \quad (2.2)$$

Where,

$(P_2V)^0$ = neutral cluster formation
2.6 Diffusion

In a semiconductor, the motion of dopant through a solid is known as diffusion. Fick’s law explains the theory behind dopant diffusion. The Fick’s first law states that the diffusion occurs due to the concentration gradient, which is in proportion to the diffusion coefficient of diffusing species. It is expressed mathematically by:

\[ J_x = -D \frac{\partial C}{\partial x} \]  \hspace{1cm} (2.3)

Where,

- \( J \) = flux (mol/m²s)
- \( D \) = diffusion coefficient (m²/s)
- \( C \) = concentration of diffusing species (mol/m³)
- \( x \) = depth (m)

Diffusion coefficient has a strong dependence on temperature and an Arrhenius equation can be used to express the diffusivity, if it happens at thermodynamic equilibrium [5]. Following is the equation for diffusivity or diffusion coefficient (equation 2.4):

\[ D = D_0 e^{\frac{E_A}{kT}} \]  \hspace{1cm} (2.4)

Where,

- \( D \) = Diffusion coefficient (cm²s⁻¹)
- \( D_0 \) = Frequency factor (cm²s⁻¹)
- \( E_A \) = Activation energy (eV or J)
- \( k \) = Boltzmann’s constant (eV/K or J/K)
- \( T \) = Temperature in K

Fick’s second law describes the diffusion process, where the concentration gradient and profile are varying with time by a differential equation. (see equation 2.5)
The following boundary conditions are used to solve equation 2.5 for the case of finite source. The initial implanted dose for the boundary condition is $Q_T$.

\[
C(x, 0) = Q_T
\]

\[
\frac{dC(0, t)}{dx} = 0
\]

\[
C(\infty, t) = 0
\]

Under these boundary conditions, the solution for equation 2.5 is a Gaussian function:

\[
C(x, t) = \frac{Q_T}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}
\] (2.6)

Following are the surface concentration depletion equation (equation 2.7):

\[
C_s = C(0, t) = \frac{Q_T}{\sqrt{\pi Dt}}
\] (2.7)

and junction depth expression (equation 2.8):

\[
x_j = \sqrt{4Dt \ln\left(\frac{Q_T}{C_B \sqrt{\pi Dt}}\right)}
\] (2.8)

Where, $C_B =$ bulk concentration.
2.6.1 Diffusion Mechanisms

The mechanisms involved for the diffusion of dopant atoms in Ge are depicted in Figure 16. For a dopant atom (red dot), diffusion is assisted by point defects (self-interstitials or vacancies). This happens via interactions of these point defects with the dopant leading to the formation of defect pairs. These diffusion mechanisms are divided into three groups, substitution/vacancy, interstitial and interstitialcy.

Figure 16. Dopant diffusion in germanium, I – Substitution/vacancy, II – Interstitial, III – Interstitialcy. As taken from [44]

Phosphorus diffusion in germanium

P atoms diffuse mainly via interstitial mechanism in silicon (type II diffusion mechanism). However, in germanium, P diffusion is attributed to \( \text{P} \text{V} \) pairs (type I diffusion mechanism) [45-47]. Werner et al. [48] conclude that in Si self diffusion, the interstitial mechanism is important, whereas in Ge self-diffusion occurs mainly via a \( \text{V} \)-mechanism [49]. This is partially due to the fact that the vacancy formation energy in Si is significantly higher compared to that in Ge [6].

The \( \text{V} \)-mediated diffusion in the Ge lattice is not a straightforward diffusion by exchanging the dopant with vacancy as the vacancy must move away from the dopant and before return back to the dopant via different way (the so-called ring mechanism for diffusion) [50]. The ring mechanism for phosphorus diffusion is presented in Figure 17. It is observed that the migration energy barriers for \( \text{PV} \) in germanium are significantly lower compared to silicon (Figure 18)
Figure 17. A schematic view of the ring mechanism of diffusion of the PV pair (P = black circles and V = squares) projected onto the (111) surface of Ge. (a) Initial configuration; (b), (d) second nearest neighbour; (c) third nearest neighbour; (e) to (f) exchange of P to V.[51]

Figure 18. The migration energy profile of the PV pair is Ge and Si. Position 1 represents the initial configuration of the PV pair (position (a) is the start and position (f) the finish) [51]
However, the phosphorus diffusion in germanium can be enhanced by a phenomenon known as concentration-enhanced diffusion.

**Concentration-enhanced diffusion**

In silicon, Transient Enhanced Diffusion (TED) phenomenon causes problems in order to achieve ultra-shallow junction for modern devices especially for boron dopant. Michel et al [52] demonstrates that the effect of TED increases by increasing the anneal time in Figure 19. This phenomenon is caused by silicon interstitial.

![Figure 19. Isothermal anneals of boron in silicon showing transient effect of TED [52]](image)

However, Simoen et al. [36] suggested that there is no significant TED phenomenon in germanium during Rapid Thermal Annealing (RTA) process. The reasons are because of the self-interstitials at the End of Range (EOR) band are in a super saturation state and also, the recovery for the defects created by the implantation is fast even at a low temperature.

Recent experimental results [53] demonstrate that the phosphorus diffusion in germanium is affected by the formation of individual negatively charged phosphorus-vacancy (PV) $^-$ pair [43]. Following is the reaction for the (PV)$^-$ formation (equation 2.9) [43]:

$$ \text{(PV)$^-$} \leftrightarrow \text{P}_S^+ + \text{V}^{2-} \quad (2.9) $$

Where,

(PV)$^-$ = individual negatively charged phosphorus-vacancy

P$_S^+$ = singly positively charged substitution phosphorus

V$^{2-}$ = doubly negatively charge vacancy
Figure 20 illustrates the concentration-enhanced diffusion phenomenon. It is observed that the junctions diffuse deeper as the phosphorus doses are increased. The reason for this is because the V$^2$ concentration in germanium will increase as the phosphorus dose increases. Hence, the formation of (PV)\(^-\) pair will also increase (from the reaction in equation 2.9), which enhance the diffusion. It can be seen from the highest dose (5 x 10\(^{15}\) cm\(^{-2}\)), a peak profile which represents phosphorus precipitates as illustrated in Figure 15 and also, significant diffusion.

Figure 20. SIMS profiles following 500°C, 60s anneal in N\(_2\) of 15 keV P implanted in Ge for doses ranging from 3 x 10\(^{13}\) to 5 x 10\(^{15}\) cm\(^{-2}\) [40]
2.7 Overcoming concentration enhanced diffusion and phosphorus-vacancy cluster formation.

The following section discusses some of the most important techniques currently being researched to overcome such deleterious effects, reviewing their advantages and disadvantages.

2.7.1 Advanced Annealing Schemes

The evolution in the anneal schemes can be seen from the slow annealing process (furnace anneals) until now, the ultra-fast annealing process (laser annealing). Even though excellent results have been achieved [55-57] by using laser annealing, this technique was never implemented as an industrial process due to integration issues [54].

Satta et al. [58] investigated flash-lamp annealing (FLA) processing in order to tackle the n-type doping problems. Using FLA they determined that there is an enhancement of phosphorus activation and shallower junction formation compared to rapid thermal annealing. However, the stability of the junction following FLA process is still a concern due to the possibility of phosphorus deactivation occurring during the subsequent processing as low-temperature post-FLA could easily drive the movement of phosphorus atoms from the lattice position.

For the duration of this study only conventional rapid thermal anneals were performed.

2.7.2 Co-implantation

2.7.2.1 Co-doping with vacancy traps

One way of stopping the interaction of vacancies with phosphorus is to find a way to trap the vacancies before they reach the phosphorus distribution. One such method was investigated by Simoen et al. [38]. They showed that when implanting nitrogen atom (N) in pre-amorphised wafers the co-implant acted as a trap for the vacancies. It was suggested that this was due to a nitrogen-vacancy cluster mechanism created during SPER. SIMS results (Figure 21) showed a significantly reduced junction depth for the sample with Pre-Amophisation Implant (PAI) and co-implant. However, this process results in a slightly higher sheet resistance than the no co-implant sample. This is due to the high concentration of nitrogen affecting the mobility of free carriers and thus limiting the conductivity.
Carbon doping is not the best way to reduce extrinsic diffusion and donor deactivation due to the low binding energy between carbon (C) and vacancy. [59-60]. The co-implant with carbon might lead towards donor deactivation due to energetically favourable to form cluster containing a carbon atom, a donor atom and vacancy.[61] Co-implantation with fluorine [62-64] might be the best way to reduce the extrinsic donor diffusion due to the large binding energy with the vacancy. However, from Duffy’s et al. preliminary results [34], fluorine co-doping combined with Ge PAI technique only gives a minor impact on reducing phosphorus sheet resistance and diffusion.

These studies demonstrate that co-doping with vacancy traps strategies although being successful to retard the enhanced diffusion of n-type dopants under extrinsic conditions are likely not suited to establish donor activation levels close to and above $10^{20}$ cm$^{-3}$.

![Figure 21. SIMS profiles after a 40keV $10^{15}$ at/cm$^2$ P implantation, a 65keV $5 \times 10^{14}$ at/cm$^2$ N + 40keV $10^{15}$ at/cm$^2$ P implant, and a 120keV $10^{15}$ at/cm$^2$ Ge PAI + 65keV $5 \times 10^{14}$ at/cm$^2$ N + 40keV $10^{15}$ at/cm$^2$ P implant, following a RTA for 60s at 600ºC [38]](image-url)
2.7.2.2 Co-doping with donor dopant

i. Arsenic

Preliminary work on arsenic as an additional implant was undertaken by Duffy et al [34], which shows that the sheet resistance for arsenic co doping implant is higher than phosphorus mono doping implant. This preliminary result is supported experimentally by Tsouroutas et al. [65] who concluded that arsenic co implantation is not the method for enhancing phosphorus activation and also minimizing phosphorus diffusion as there is no significant difference between the results of phosphorus mono doping and arsenic co doping implant.

ii. Antimony

The activation of phosphorus in germanium over the active concentration of $1 \times 10^{20}$ cm$^{-3}$ was first demonstrated experimentally by Kim et al [66]. They were able to achieve high phosphorus activation by using antimony (Sb) as the co implant species. Spreading resistance profiling (SRP) analysis indicates high phosphorus activation (greater than $1 \times 10^{20}$ cm$^{-3}$) in the co implanted sample (see Figure 22). The implant conditions for the co-implanted sample is P dose = $1.2 \times 10^{15}$ cm$^{-2}$ at 90 keV; Sb dose = $4 \times 10^{14}$ cm$^{-2}$ at 220 keV. Then, the samples were annealed at 500 °C for 10s. P activation is strongly enhanced at region B over the conventional limit at region C and deactivated at region A (100% of implanted P is activated at region B).

Kim et al [67] suggested that the enhancement of phosphorus activation via Sb co-doping either due to Sb act as a surfactant during the SPER process or local strain compensation between the two atoms. However, the effects on donor diffusivity should be further clarified.

![Figure 22. SIMS and SRP profiles of doped Ge by co-implanted of Sb/P [67]](image-url)
2.7.3 The use of capping layers

Capping layers can be used to influence the intrinsic point defect concentration in the near surface area and to suppress donor out-diffusion.

The effect of silicon oxide as a germanium cap layer toward phosphorus activation and diffusion was first studied experimentally by Poon et al [68]. In this study, the samples were capped after the implantation process and prior to the activation annealing process. They used Hall Effect measurement and TEM analysis to confirm that the uncapped germanium sample exhibits slightly higher sheet resistance than a capped sample with silicon oxide due to surface roughness. In addition, SIMS analysis points out no significant difference in diffusion between these two samples, in terms of junction depth and dopant loss after annealing at 500°C for 60s. However, 50% dopant loss is observed in the uncapped samples after annealing at 600°C for 60s and increasing the RTA temperatures above 600°C resulted in further reduction in retained dose.

Ioannou et al. [69] introduced silicon nitride as a new capping material for germanium. According to the SIMS analysis in Figure 23, the phosphorus dose loses were determined to be 10%, 44% and 75% for the silicon nitride capped, silicon oxide capped and the uncapped sample, respectively. The cap layer was deposited on the samples after the implantation process and before the annealing process.

However, it is important to notice from Figure 23 that for the same conditions, the diffusion of phosphorus depends on the nature of the capping layer (oxide or nitride), the diffusion being enhanced for nitride capping layer compared to oxide capping layer. There are two possible causes for this difference. It is possible that there are interfacial reactions or/and change in the stress distribution into the deposited layers that could result in variations in the concentration of point defect into the substrate, and consequently to different diffusion phenomena. On the other hand, it is possible that the observed differences in the two cases might be an indirect way to conclude that silicon nitride more effectively blocks phosphorous out-diffusion. In this case, higher concentrations would be expected for the nitride-capped samples, which would lead to concentration enhanced diffusion of phosphorous. Therefore, silicon nitride is used as the cap in this work.
2.7.4 Multiple Implantation Multiple Annealing (MIMA)

This technique involves repeating step of implantations with the dose of $6 \times 10^{14}$ cm$^{-2}$ and followed by annealing process at 500 °C for 10s. The dose of $6 \times 10^{14}$ cm$^{-2}$ is chosen because the activation level of this dose is approximately equal to the activation of the dose of $1.8 \times 10^{15}$ cm$^{-2}$ (as illustrated in Figure 24).

Figure 23. SIMS analysis for uncapped, silicon oxide and nitride capped. [69]

Figure 24. SRP and SIMS profiles of the Ge substrate received P implantation with the dose of $1.8 \times 10^{15}$ cm$^{-2}$ and SRP profiles of Ge substrate received P implantation with the dose of $6.0 \times 10^{14}$ cm$^{-2}$ [70]
Kim et al [70] demonstrate the great potential for fabricating high performance n+/p junctions by using MIMA process owing to both high electrical activation and suppressed implantation-induce defects. The effect of MIMA is shown in Figure 25 and 26, where it can be seen that sheet resistance and dopant activation, respectively are significantly enhanced for the samples which received MIMA process. However, the drawback of this technique is that more steps will be required to fabricate Ge NMOS device.

![Figure 25. Variation of sheet resistance of Ge with increasing implantation doses for single implantation and MIMA [70]](image-url)
Figure 26. a) SRP profiles of Ge substrate with increasing a P MIMA cycle, b) SIMS profile of Ge substrates received $1.8 \times 10^{15} \text{P/cm}^2$ implantation and comparison of SRP profiles between single implantation and MIMA [70]
2.7.5 **Vacancy engineering**

This technique creates excess vacancies in silicon substrate via implanting silicon into silicon substrate, in order to trap the silicon interstitials as the dopant forms clusters with silicon interstitials. As a result, a highly active Si PMOS junction has been produced [71-73]. It is observed in figure 27 that the sheet resistance and active carrier density are significantly enhanced with silicon co-implantation.

For the work in this research, opposite concept will be used, which is introduced excess interstitials to trap the germanium vacancies.

![Graph showing sheet electrical measurement](image)

**Figure 27.** Sheet electrical measurement presenting the sheet resistance and active carrier density, 850°C isothermal anneal study, with and without a silicon co-implant [17]
2.8 Summary of Literature Review

Phosphorus is undoubtedly the most popular n-type dopant for the source/drain regions of the Ge NMOS device. Due to process related problems such as concentration enhanced diffusion and phosphorus clustering, the formation of highly active and shallow junctions is hindered. Therefore, in order to achieve the ITRS requirement, a technique is required to overcome the phosphorus clustering mechanism. Hence, the level of phosphorus electrical activation can be improved to a level beyond the solid solubility limit. To date is a co-doping of phosphorus and antimony, and MIMA process has been proven to achieve highly active shallow layers, to above solid solubility limit at low temperature.

Reviewing the literature survey surrounding techniques used to form n⁺ p junction in germanium has highlighted a distinct lack of research in the following areas:

• The effect of implant temperature.

• The effect of low dose germanium co-implant.
3 Experimental Theory and Techniques

3.1 Introduction

This chapter explains the methodology and theory of each experimental technique used in this work in order to obtain the data shown within chapters 4-5.

3.2 Material Fabrication

Bulk germanium was used for the initial study of this research. The method used for the growth of bulk germanium wafer is the same as bulk silicon wafer, which is Czochralski crystal pulling technique. However, due to some measurement issues, Germanium-On-Silicon (Ge-on-Si) was used for the main study of this research. These are the measurement issues with bulk germanium:

1. Create ohmic contact for Hall measurement.

   Ohmic contact is very important for Hall measurement because if the ohmic contact could not be created, the measurement is considered not valid. A few techniques were investigated such as metal evaporation and metal deposition due to the usual liquid metal contact for silicon could not be used to create ohmic contact for bulk germanium. Tin dot deposition technique was found to create the ohmic contact. However, the drawback of this technique is the process is very tedious. For Ge-on-Si substrate, the ohmic contact is created by using the same liquid metal contact for silicon substrate.

2. Inconsistency of the Hall measurement result.

   Table 3 shows the inconsistency for three days of measurement.

<table>
<thead>
<tr>
<th>Measurement (On three different days)</th>
<th>Samples (Implant Temperature)</th>
<th>Sheet Resistance (R_s) (ohm/sq)</th>
<th>Type and number of Carriers (N_s) (/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First day (two measurements)</td>
<td>RT</td>
<td>38.06</td>
<td>-5.31E+14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38.82</td>
<td>-6.45E+14</td>
</tr>
<tr>
<td>Second day (two measurements)</td>
<td>RT</td>
<td>51.22</td>
<td>+5.89E+14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.15</td>
<td>+4.02E+14</td>
</tr>
<tr>
<td>Third day (two measurements)</td>
<td></td>
<td>49.23</td>
<td>+2.21E+14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.41</td>
<td>+2.04E+14</td>
</tr>
</tbody>
</table>

**TABLE 3** Hall Effect measurement results for Silicon Nitride capping deposition after Ion Implantation study (Anneal at 500ºC for 60 seconds)
The result seem to indicate that apart from the leaky junction, there might be some contact issues between the Hall measurement probe and the surface of the sample due to unrepeatability measurement. The issues are current punch through the junction or probe penetration through the junction due to the fragility of germanium substrate, which causes the junction to break down electrically or mechanically. These problems were overcome by using Ge-on-Si substrate.

3.2.1 Germanium-On-Silicon (Ge-on-Si)

Figure 28 illustrated the fabrication flow of Ge-on-Si substrate. To begin with, a thin Ge buffer layer is deposited on Silicon at a temperature of 350 °C. Then, the temperature is increased to 600°C before deposit the thick germanium layer (about 600 nm). Finally, the wafer is cyclic annealed in a range of temperature, to reduce the Threading Dislocation Density (TDD).

The advantages of Ge-on-Si substrates over bulk germanium are greater mechanical strength, higher starting resistivity and easier to integrate with silicon processing equipment [40].
3.3 Ion Implantation

The method used for introducing dopant atoms into germanium in this work is ion implantation. In semiconductor processing, it is a key doping technique due to advantages such as:

- Isotopically pure doping due to mass selection of the ion species in the implanter
- High implantation dose reproducibility
- Precision energy implant control and hence, depth of penetrating ions
- The implantation process can be done at different temperature.

3.3.1 SUSPRE

Figure 29 shows a program called SUSPRE that simulated dopant implant profile. This program was developed by Webb [74] at the University of Surrey. This program was used in this work, in order to determine the “projected range” (Rp), which is the average depth of the implanted ions and also, the peak profile of the dopant profile. The peak profile indicates the maximum volume carrier concentration. The dopant profile is represented in figure 29 by the green line, while the red curves show the energy loss of the implanted ions due to nuclear and electronic collisions.

![Simulated implant profile using SUSPRE [74] for 30 keV P 1.3x10^{15} \text{ cm}^{-2} in Ge](image-url)
3.3.2 Ion Implanter design

The ion implanter consists of four main parts:
- Ion source
- Analysing magnet
- Acceleration tube
- Target chamber

The basic configuration of an ion implanter is shown in Figure 30.

![Plan view schematic of Surrey Ion Beam Centre’s Danfysik 1090 Ion Implanter. Implant range of 2 keV to 200 keV [17]](image)

Firstly, the ion source will break up the vapour containing the desired impurity into charged ions by using heated filament and discharge potential to generate plasma within the arc chamber from which the ions are extracted. Then, the charged ions are attracted to move out of the ion-source chamber by an extraction voltage into mass analyzer. The magnetic field of the analyzer is selected so only the ions with the desired mass and energy enter the acceleration tube. The potential difference across the acceleration tube will then accelerate the ions up to the desired final implantation energy [75].

Then, the ion beam is focused before enter the flight tube. In order to minimise energy contamination and to remove to neutralised fraction of the beam, the flight tube is steered through a 7° offset. Faraday cup is used to continually measure the implant dose at the end of the flight tube. This will ensure the reproducibility of the implant dose. Finally, the ion beam is scanned over the wafer using electrostatic or magnetic deflection plates before the target chamber.
3.4 Rapid Thermal Processing (RTP)

Even though ion implantation has lots of advantages, this technique has a few side effects. The main side effect is the damage the substrate lattice sustains caused by the energetic ion collisions. Consequently, an annealing process is used to repair the lattice and electrically activate the dopant by diffusing it to substitutional lattice sites as it is predominantly interstitial following implantation. This process is done using a suitable arrangement of temperature and time [75].

Figure 31 shows a rapid thermal processor schematic diagram. In this project, the RTP step was carried out on a Jipelec Jetstar 200ST. Before the process is started, the sample is placed on a support wafer, which is set on a wafer holder with a minimum amount of contact. Then, the chamber is evacuated to $10^{-5}$ Torr before nitrogen gas is introduced into the chamber in order to eliminate sample oxidation and also, provides inert ambient for the samples [76]. After two minutes of nitrogen purge, the sample and support wafer are heated up by the high intensity radiation generated by a bank of halogen lamps which is absorbed by the sample [77]. The lamp intensity is controlled using a PID control system with the sample temperature feedback derived from a two colour IR pyrometer. A two-step temperature process is preferred allowing the system to stabilise at 350°C prior to the fast ramp to the final temperature. Not only does this step allow the system to equilibrate but it also reduces the chance of oxidation caused by evaporating any residual moisture that was not pumped in the initial vacuum cycle. Following the anneal, the system is cooled down to room temperature under flowing nitrogen prior to a final vacuum cycle to remove any residual gases that may contain toxic materials (this is an in-built safety feature as the system is also capable of running toxic gases as used in CVD growth). The anneal cycle is illustrated in figure 32.

The advantages of RTP are shorter time of annealing compared to the conventional annealing process [78].
After the annealing process, the samples are now ready to be characterised. The purpose of characterising the samples is to observe the effect of the annealing process towards the samples. These characterisation methods will be discussed in the following section.
3.5 Electrical Characterisation

The purpose of electrical characterisation is to investigate the number of carriers, resistivity and mobility of the sample. Three measurements techniques have been used; these are respectively four point probe (4PP), Sheet Hall and resistivity technique and Hall profiling using the Van der Pauw geometry described in 3.5.2.

3.5.1 Four Point Probe Measurement (4PP)

Four Point probe measurement is an easy and quick method for measuring sheet resistance and usually used for measuring the initial sheet resistance results.

**Sheet resistance ($R_s$)**

Sheet resistance is a ratio between material resistivity, $\rho$ and thickness of the layer, $t$. From equations 3.1 to 3.3, it shows that sheet resistance is inversely proportional to the electrical conductivity. Therefore, high dopant activation gives low sheet resistance

Therefore, $\rho = R_s t$ (3.1)

Since, $\sigma = \frac{1}{\rho}$ (3.2)

Then, $\sigma = \frac{1}{R_s t}$ (3.3)

**Equation 3.1 to 3.3 Relation between electrical conductivity and sheet resistance derivation**

Where,

- $R_s$ – sheet resistance ($\Omega/\square$)
- $\rho$ – Resistivity ($\Omega$-cm)
- $\sigma$ – Electrical conductivity (Siemens/cm)
- $t$ – Sample thickness (Å)
Description of equipment

Figure 33 presents the diagram of Four Point Probe measurement setup. There are two parts of Four Point Probe, which are current carrying probes (outer probes) and voltage measuring probes (inner probes). A constant current is injected through the two current carrying probes into the sample, and the two inner probes will measure the voltage.

![Diagram of 4PP measuring](image)

Since wafers are finite in size, a combination of correction factors (CF) must be added into the equation [79]. The correction factor is the explanations for shape, the sample size (L/W ratio), probe spacing (s) and thickness (t) of the sample. Therefore, the equation (equation 3.4) for calculating sheet resistance is:

\[
R_s = \frac{\rho}{I} = \left(\frac{V}{I}\right) \cdot CF_1 \cdot CF_2
\]

(3.4)

Where:

\( R_s \) – sheet resistance (Ω/□)
\( \rho \) – Resistivity (Ω-cm)
\( V \) – Voltage (V)
\( I \) – current (A)
\( t \) – Sample thickness (Å)
\( CF_1 \) – Sheet resistance correction factor 1 (L/W ratio)
\( CF_2 \) – Sheet resistance correction factor 2 (t/s ratio)

\( CF_1 \) is determined by the shape of the sample and \( CF_2 \) is dependent on the thickness of the conducting layer and the probe spacing.
A disadvantage of this method is the possibility of the probe head penetrating the sample below the implanted region, resulting in a measurement of the substrate. This is a particular problem for ultra shallow implants and soft substrate materials. However, this method is used to get a quick value of sheet resistance for a sample. As a solution, Van der Pauw Hall effect method has been used in this project to give the accurate sheet resistance.

3.5.2 Van der Pauw Measurements

In 1958, a problem of the distribution of potential in a thin layer of arbitrary shape was solved by Van der Pauw. With this solution, the Hall Effect technique in terms of sheet resistance measurement is improved. In this method, the most interesting attribute is for the sheet carrier concentration or sheet resistance calculation, no dimension is required to be measured. Due to its convenience, today, in the semiconductor industry, this method is widely used. To use this method, there are a few conditions to be satisfied. The conditions [80] are:

i. The contacts are placed at the edge of the sample.

ii. The contacts are as small as possible.

iii. The sample layer is continuous.

iv. The sample is uniform in thickness.

Figure 34 shows the illustration of a flat uniform sample of an arbitrary shape that satisfies the condition for Van der Pauw method. The first condition, which is the contacts are placed at the edge of the sample is the most challenging to do in practice. Besides, if the condition is not met, it will lead to serious errors in Hall voltage measurement. However, Van der Pauw [80] had discovered a solution to overcome this problem. He found that by using a pattern such as the clover leaf (see Figure 35), the errors in Hall voltage measurement will be drastically reduced and it is easy to fabricate the pattern.

![Figure 34. Illustration of a sample for Van der Pauw method](image-url)


**Sheet Resistance**

The sheet resistance is measured using Van der Pauw geometry as shown in Figure 36.

![Sheet Resistance Diagram](image)

**Figure 36. Calculating sheet resistance using Van der Pauw geometry[44]**

The sheet resistance is calculated by the following relations:

\[
R_{12,43} = \frac{V_{43}}{I_{12}} \quad R_{23,14} = \frac{V_{14}}{I_{23}}
\]

**Equation 3.5 Clover Leaf Pattern Contact Resistance (Ω) [80]**

Where the contact points on the samples are represent as the subscripts 1,2,3,4.
The values from equation 3.5 are used to establish the Rs calculations:

\[
\exp\left(-\frac{\pi}{R_S} R_{12,43}\right) + \exp\left(-\frac{\pi}{R_S} R_{23,14}\right) = 1
\]

Equation 3.6 Van der Pauw Sheet Resistance [80]

Rs can be solved as equation 3.7, by assuming \( R_{12,43} = R_{23,14} \), where, there is a line of symmetry through contacts 3 and 1.

\[
R_S = \frac{\pi}{\ln(2)} R_{12,43}
\]

Equation 3.7 Symmetrical Case Rs (Ω/sq) [80]

However, equation 3.7 couldn’t be used for the general Rs calculation. The solution for general Rs can be expressed as in Equation 3.8:

\[
R_S = \frac{\pi}{\ln(2)} \times \frac{R_{12,43} + R_{23,14}}{2} \times f
\]

Equation 3.8 Rs general case (Ω/sq) [80]

Where, \( f \) is a correction factor.

The correction faction is determined by function of the ratio \( Q = \frac{R_{12,43}}{R_{23,14}} \). The correction factor indicates poor contact or uneven layer when the value is higher than 1.5.

Hall carrier mobility is also possible to measure by using the same sample via Hall Effect measurement.

**Hall Effect**

The Hall Effect was discovered by Edwin H. Hall in 1897. He found that a transverse voltage is created perpendicularly across a metal strip when a current is applied through the metal strip in a magnetic field [81]. Lorentz force is the principle behind this theory, which is given by (equation 3.9):-
Where,  

\[ F = -q \nu_d X B \]  

\[ (3.9) \]

\( F \) – Force (N)  
\( q \) – Elementary charge \((1.602 \times 10^{-19} \text{ C})\)  
\( \nu_d \) – drift velocity (m/s)  
\( B \) – The magnetic field (T)

The equation explains how an electron moves towards a force which is acting normal to both directions of the electron flow while the electron is moving along a direction perpendicular to an applied magnetic field.

When a magnetic field is applied perpendicular to the current flow, the carrier, will move to one side of the metal. As a result, a transverse electric field will be created and then, a steady state will be reached [81]. Therefore, Hall Voltage (\( V_{Hi} \)) is the resulting voltage drop across the sample (Figure 37).

![Figure 37. Hall Effect](image-url)
A sample with Van der Pauw pattern is used to measure the Hall voltage as shown in Figure 38.

Figure 38. Van der Pauw geometry for measuring Hall voltage[44]
Hall voltage is measured across the contact points of 2 and 4, while a current is passing through diagonally via contact points of 1 and 3. The Hall coefficient \( R_{HS} \) can be calculated using the equation 3.10, after the Hall voltage is measured.

\[
R_{HS} = \frac{V_H}{I \times B}
\]

**Equation 3.10 Hall coefficient with respect to \( V_H \) (m²C⁻¹)**

Then, using the following equation, the sheet carrier concentration \( N_S \) can be calculated:

\[
R_{HS} = \frac{r}{q \times N_S}
\]

**Equation 3.11 Hall coefficient (m²C⁻¹) with respect to \( N_S \)**

Where ‘r’ is the Hall scattering factor,

In the work presented within, the scattering factor of unity is used.
The Hall mobility can be calculated using equation 3.13, once sheet resistance and hall coefficient have been obtained:

\[ \mu_H = \frac{R_{HS}}{R_S} \]

Equation 3.13 Hall mobility (cm²V⁻¹s⁻¹)

In the next section, the sample preparation steps in order to carry out the Hall measurement will be described.

**Van der Pauw pattern fabrication**

Photolithography and etching are the two techniques to fabricate the Van der Pauw pattern.

i. **Photolithography**

Photolithography is a technique to create a pattern onto the wafer surface. The pattern is created via a mask. The pattern is transferred from the mask to the wafer surface by using ultra violet (UV) light. The photolithographic process consists of a few steps, which are:-

1. The first step is 3-stage clean. At the first stage of cleaning, the samples were boiled in Acetone for about 30 seconds at 100ºC. Then, the samples were transferred into Methanol and also boiled for the same temperature and time. After that, the samples were moved into IPA at room temperature for about 30 seconds. Next, the samples were rinsed with water and finally dried with nitrogen gas. The purpose of this procedure is to make sure the surface of the sample is sufficiently clean before the VDP pattern is generated on the surface.

2. The second step is photo resist application. In this step, a spinner is used to coat photo resist onto the sample. A photoresist is applied on the sample after the sample is placed onto the spinner. Then, the spinner is spun at ~5000 rpm for 60 seconds to produce a film thickness of 2.8µm on the sample. In this experiment, a positive photoresist S1828 is chosen as the photo resist because this photoresist is optimized for UV light (436nm). Though, this photo resist can be used for a range of 350nm and 450nm.

3. Then, the sample is soft baked at 100ºC for 80 seconds to skin the photoresist to avoid sample sticking to the photo-mask during the UV exposure process.

4. For the UV exposure step; after the soft bake, the sample is placed on a flat plate with the mask aligner which is located on a moveable platform. Then, the platform is pushed inside the machine. Finally, the mask pattern is centred on the sample and the sample is exposed to UV light for 15 seconds. The polymer bonds in photoresist are broken by the
UV light, to produce a pattern on the sample.

5. Next, the sample is transferred and submerged into a solution known as MF-319 developer for the pattern development step. After a clear clover leaf pattern can be seen, the sample is rinsed off with water and dried with nitrogen gas. MF-319 developer is used for the pattern development because this solution has been formulated for use with S1800 series resist.

6. Lastly, the Van der Pauw pattern on the sample is checked under a microscope. If there are any anomalies in the pattern on the sample, the sample has to be cleaned again and the photolithographic process steps have to be repeated again. However, if the pattern on the sample is good, the sample is placed on a thin plate. After all the samples completely finished the photolithographic process steps, the samples are hard baked at 120ºC for one hour to increases the physical and chemical stability of the resist for upcoming process which is etching.

ii. Etching
A mesa structure of phosphorus doped layer is important to obtain accurate Hall Effect measurement results. Therefore, in order to achieve this, the phosphorus doped layer must be completely electrically isolated by a uniform etch deeper than n⁺ p junction.

An isotropic wet etch was chosen for etching in this experiment. Nitric acid (HNO₃), buffered Hydrofluoric acid (buffered HF) and DI water (H₂O) mixture is used in this wet etching. In this experiment, the solution ratio for Germanium etching is:-

$$20 \text{[HNO}_3\text{]} : 34 \text{[H}_2\text{O]} : 2 \text{[buffer HF]}$$

The etch rate for this recipe is 171 nm per minute.

The steps involved in the etching process are:-

1. The sample is submerged in etch solution for 5 minutes.
2. Rinse the sample in DI water.
3. Dried the sample with nitrogen gas.
4. Remove the photoresist on the sample with acetone.
Measurements

Figure 39 shows the equipment of Hall Effect measurement. The left picture is the HL5500 Accent machine and the right picture is the sample mounting compartment. This measurement is done after the Van der Pauw pattern is fabricated on the samples. In order to measure the samples, each corner of the pattern must be placed a metal contact. The metal contact is called Indium Gallium Eutectic. A very fine paintbrush is used to paint the metal contact on each corner of the pattern. After the metal contact is completely painted, the sample is located in the sample mounting compartment and four tiny probes are placed on the metal contact. Then, the lid is closed and the measurement can be started.

![Figure 39. Pictures of the Hall equipment (left) HL5500 Accent Machine, and sample mounting compartment (right)](image)

3.6 Differential Hall Profiling

This technique determines the sheet resistivity and Hall voltage as a function of depth in order to calculate carrier concentration, Hall mobility and resistivity [82-84]. The SIMS profiles can be compared with the carrier concentration profiles measured using this technique in order to determine the activation of phosphorus after annealing process.
3.6.1 Measurement and Calculation

Figure 40 illustrated the layer of removal thickness for the measurement with two values of conductivity, which are before ($\sigma_{s1}$) and after the removal ($\sigma_{s2}$).

![Figure 40. Schematic representation of depth profiling](image)

The expression for the difference in conductivity ($\delta\sigma_s$) before and after layer removal:

$$\delta\sigma_s = \sigma_{s1} - \sigma_{s2}$$

Equation 3.14

The mobility of the removed layer can be expressed as:

$$\mu = \frac{\delta(R_H^2\sigma_s^2)}{\delta\sigma_s}$$

Equation 3.15

The expression for the carrier concentration of the removed layer:

$$N = \frac{1}{q\mu} \frac{\delta\sigma_s}{\delta x}$$

Equation 3.16
The effects of surface depletion and inherent noise in the system are the two main problems with the differential Hall technique [85]. Figure 41 taken from Yeo et al [85] shows a distorted carrier profile because of the decreasing of carrier concentration with the increases of the surface depletion region width. This is due to the trapped carriers in the surface depletion region states do not contribute towards conductivity and more carriers will be trapped in the surface states as the width of the region increases.

Figure 41. Apparent and real carrier profiles highlighting the effect of surface depletion

Hall scattering factor “r” is used to adjust the Hall measurement as the drift mobility differs from the measured Hall mobility. This is due to the scattering of carriers differs in an electric field compared to a magnetic field.

In the work presented within, the Hall scattering factor is maintained at 1 which may produce errors in absolute value allows for good relative comparisons between samples.
3.6.2 Differential Hall Measurement Procedure

Accent HL5900PC Hall profiling tool is used for this measurement. The inside of the Hall profile machine is shown in figure 42.

![Hall profile machine](image)

Figure 42. Inside of the Hall profile machine showing carousel and etch, wash and drying pots, compressed air is delivered to the sample next to the drying pot.[86]

Firstly, the sample needs to be mounted on the holder with silicone rubber. Next, silver dag is used to connect the contacts with the holder. Finally, the whole holder and sample are covered with silicon rubber except the centre of the sample as shown in Figure 43. The reasons for this are to protect the holder from the etch solution and to ensure that only the middle of the sample is etched.

![Sample mounted](image)

Figure 43. Sample mounted onto holder and insulated with silicone rubber [86]

The process flow is as follows:

1. The Hall coefficient and resistivity of sample is measured.
2. Layer removal in etch solution.
3. Washing in the water pot.
4. Finally, rinse in isopropyl-alcohol and drying with air before re-measuring.
This process is then repeated until the machined starts to measure the P-type substrate. This means that there are no more active N-type carriers. The final step is to measure the depth of the total layer removal by using Talystep. The real etch rate can be achieved by dividing the total depth with the number of etch steps. Therefore, the correction of the measured profile can be done by replacing the initial assumed etch rate with the real etch rate.

3.7 Secondary Ion Mass Spectrometry (SIMS)

In order to obtain the phosphorus depth profiles in germanium, dynamic SIMS technique will be used in this project. The principle for this technique is that the surface of the sample will be bombarded with an energetic primary ion beam. This will lead towards the emission of both charged and neutral particles. Mass spectrometer will analyse the emitted secondary ions, which are extracted by an electrical potential.

Figure 44 illustrates the schematic of SIMS instrument.

![Double Focusing Magnetic Sector Mass Spectrometer](image.png)

Figure 44. Schematic of a Double Focusing Magnetic sector SIMS instrument [87]
There are three parts in this instrument:

i. Primary Sources

There are three types of primary sources which are inert, reactive and liquid metal ion sources. Inert sources like argon will act as electron impact sources, while liquid metal ion sources such as gallium create the best lateral imaging resolution and the smallest primary beam spot size. Caesium and oxygen are the examples for the reactive sources. These sources are used to boost negative and positive secondary ion yields.

ii. Mass Analyzers

Double focusing magnetic sector, time-of-flight and quadrupole are the three main types of mass analyzers. In order to choose the appropriate mass analyzer for the analysis, a few things need to be considered such as mass range detectable, mass resolution, cost, switching speed and transmission efficiency.

iii. Detectors

The two common detectors for this instrument are Faraday cup or electron multipliers detectors.

Figure 45(a) shows a raw data for SIMS measurement of phosphorus in a silicon matrix. In order to convert the raw data into depth profile, the SIMS analyst uses a profilometer to measure the crater depth, in order to convert the time into depth for the horizontal axis. Moreover, the following expression (equation 3.17) is used to convert the vertical axis from ion counts to concentration [17]:-

\[
C_e = RSF \times \frac{I_e}{I_M} \quad (3.17)
\]

Where,

- \(C_e\) = Concentration.
- RSF = Relative Sensitivity Factor
- \(I_e\) = Negative secondary ions
- \(I_M\) = Matrix current

Figure 45(b) illustrated the converted SIMS profile in terms of concentration for vertical axis and depth for horizontal axis.
3.7.1 Methodology

All of the SIMS carried out in this work were made at the ‘Frondazione Bruno Kessler’ in Trento, Italy.

3.8 Transmission Electron Microscopy (TEM)

TEM is a standard technique used to analyse and visualise the image defects in semiconductor material. This technique can provide the information about the morphology and crystallographic of a sample. In this work, cross-sectional view is used for defect imaging.

A TEM works similar way as a slide projector, the main difference between this two is the source, where TEM uses electrons rather than electromagnetic radiation. For the sample preparation, the sample needs to be milled down to a few nanometres thick first before the sample is placed onto the sample holder.

The sample is fired with an electron beam, which will diffract off the defects and atoms in the sample. Then, the diffract atoms and defect impinging on an array of photo detectors or a fluorescent screen. The image of the defect can be obtained from the electron “photograph”.

3.8.1 Methodology

The TEM for this work was carried out at University of Florida in Florida, U.S. The schematic diagram is shown in Figure 46.
Figure 46. Schematic of TEM [16]
3.9 Rutherford Backscattering (RBS)

Rutherford Backscattering is named for this technique after Ernest Rutherford, who was the first to suggest the concept of atoms having nucleus surrounded with negative electron based on collisions between atomic nuclei.

In this technique, the sample is bombarded with an ion beam (typically $1.5\text{MeV} \ ^4\text{He}^+ \ )$. The ion beam will enter the sample via inelastic collisions with electrons. Some of the incident atoms are backscattered to be detected and losing its energy via inelastic collisions with electrons. Then, the detected atoms will be shown as an energy distribution. The energy distribution can be converted into a target atom mass spectrum as the incident ion and target atom interaction is governed by Coulomb repulsion and also, can be described by two body collisions.

This technique is used to analyse to the information of the single crystal material structure. There are two modes in RBS, channelling and random. From these two modes, quantitative information on level of damage and structure can be obtained. The channelling occurs as the backscattering probability is very low. On the other hand, random occurs when the orientation of the crystal lattice is not aligned with the incident ion beam, where the backscattering probability is very high. Therefore, random spectrum is used as reference spectra in order to determine the level of damage.

Figure 47 (a) shows the output spectra for the perfect crystal with no defect. Where, in a disordered lattice having defects, the output spectra is shown in Figure 47 (b).
Figure 47. Comparison of aligned (channelled) and random spectra from a perfect (a) and disordered (b) crystal substrates. Illustrating how a combination of spectra can be used to examine the quality and level of disorder of the crystal structure [76]
3.10 Experimental Errors

This section addresses the errors associated with the experimental techniques used in this work.

1. Ion implantation:

The phosphorus and germanium implants carried out by Surrey Ion Beam Centre are shown to have an error in uniformity across the 4” wafer of less than 1% with metrology tools such as four point probe wafer mapping techniques and ThermaWave [88]

2. Annealing:

Proportional Band, Integral, Derivative (PID) settings are used to minimise the over / under shoot for each anneal temperature cycle. Combined with the error from the pyrometer, the subsequent error in annealing temperature is estimated to be ±1%.

3. Hall Effect Measurements:

The electrical measurements were performed on Accent HI5500 system. Smith [17] carried out a study using samples with low temperature fluctuations sensitivity and determined 4%, 4% and 8% errors for carrier concentration, sheet resistance and mobility respectively. The measurements of eliminating the spurious voltages, which are carried out by the Hall software, influence the electrical measurement’s error.

4. Differential Hall Measurement:

The errors in this measurement are determined by the etch rate variation throughout the measurement, which is estimated to be ± 10%. Additional error is from the measurement of etch depth after the measurement finish, which is about ±5 nm

5. SIMS:

Mixing of layers within material and variation in sputter rate are the errors factor for this technique as it can cause incorrect element concentration and depth distribution, respectively. Therefore, the primary and secondary ion beams are measured and the sputter rates are predicted using accurate theoretical model before the measurement starts in order to minimise or avoid these errors.

The error for the reproducibility of the measurement is estimated to be < 1% and the depth measurement error using Profilometer is about ±1%.
6. **Rutherrford Backscattering Spectroscopy:**

Table 4 summarised the errors in RBS analysis, which is studied by Jeynes et al [89], who found the total error to be in the order of ±2.55%.

<table>
<thead>
<tr>
<th>Uncertainty Components</th>
<th>IBM detector (%)</th>
<th>Cornell detector (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counting Statistics, a-Si signal</td>
<td>0.94</td>
<td>2.89</td>
</tr>
<tr>
<td>Scattering angle</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>Electronic gain</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Relative uncertainty</td>
<td>1.10</td>
<td>2.93</td>
</tr>
<tr>
<td>Relative uncertainty of average of two detectors</td>
<td></td>
<td>1.57</td>
</tr>
<tr>
<td>Beam Energy</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>Rutherford cross-section</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>Si stopping power</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td><strong>Total combined standard uncertainty</strong></td>
<td><strong>2.55</strong></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4 RBS uncertainty budget**
4 Temperature Dependant Study of phosphorus Ion Implantation in germanium

4.1 Introduction

This section and the subsequent sections discuss the experimental details and the results from this study to date, with the goal of studying the effects of using germanium as the replacement for silicon substrate. Study of phosphorus implantation focuses on activation and diffusion as a function of implant temperature, in order to give maximum benefits and thus form a highly activated Ge NMOS transistor.

The advantages of the hot implant technique have been observed in silicon processing [90-92]. The interest of using the hot implant technique for this project is to maintain the germanium crystallinity during the ion implantation process. Therefore, the accumulation of point defects could be reduced. As a result, higher phosphorus activation could be achieved.

Another popular technique for silicon processing is the cryogenic implant. The benefits of this technique are the containment of the defect distribution and the mobility of point defects is reduced [93-94]. These benefits could result in enhanced phosphorus activation due to the reduction of phosphorus-vacancy complex formation.

The focus of this chapter is to investigate the effect of three different implant temperatures, cold (-200 °C), hot (500 °C) and at room temperature, towards phosphorus activation and diffusion. The secondary objective is to investigate the implant temperature effect at lower implant energy in order to meet the requirements of the International Technology Roadmap for Semiconductor (ITRS).

4.2 Process Steps

Phosphorus was implanted at three different temperatures using the ion implantation technique and the samples were annealed using RTA at different temperatures. Details of these experimental conditions can be found in Table 5. Subsequent to implantation and annealing the samples were analysed using the Hall Effect measurements to determine carrier density (Ns), Hall mobility (Us) and sheet resistivity (Rs), whereas RBS and ion channelling were used to evaluate the amorphous depth prior to annealing and its subsequent re-growth during annealing. SIMS was used to determine the depth distribution of the dopant atoms after implantation and how they diffused and clustered during annealing. The differential Hall profiling technique was used to determine the electrically active fraction of the dopant. The structure of substrate after implantation was investigated by XTEM in order to verify the RBS and ion channelling results.
4.3 Experimental details

P-type (100) germanium on silicon (Ge-on-Si) wafers, grown at University of Warwick, UK, with a starting resistivity of about 16 ohm-cm was used in this study. After the implantation, the samples were capped with 50 nm silicon nitride, deposited using the PECVD process at a temperature of 300°C. The wafers were subjected to phosphorus-ion implantation at 30 keV with a dose of 1.3x10^{15} cm^{-2} at room temperature (RT), liquid nitrogen temperature (cold) which is about –200°C, and at a temperature of 500 °C (hot). In order to minimise channelling, the implantations were performed under 7° tilt angles.

Rutherford Backscattering Spectrometry channelled in the (100) direction (RBS-c) measurements were used to monitor the germanium substrate damage. The amorphous depth was measured using a 1.1 MeV ^4He- beam at a glancing angle of 45° to the sample, and the resulting spectra were analysed using the IBA DataFurnace software [95] developed at the University of Surrey.

RTA steps were done using a Jipelec Jetstar 200ST, in a 10s isochronal scheme from 500 °C to 800 °C. The cap layer was stripped using a buffered HF solution before characterisation. Hall measurements were performed using an Accent HL5500 on 1 cm² samples using the Van der Pauw (VDP) geometry to extract the number of carriers (Ns), corresponding sheet resistance (Rs) and their mobility (μ). The VDP structures were created using standard photolithography and wet chemical etching. Differential Hall profiling measurements were done using an Accent HL5900 after the Hall measurement in order to measure the electrically active dopant. XTEM and SIMS were carried out in University of Florida, US and Minalab –Center for Materials and Microsystems, FBK, in Trento, Italy, respectively.

4.4 Implant matrix Experiment I

Table 5 summarises the implantation details for the first batch of wafers. It lists the implant species, energy, dose and implant temperature. The phosphorus dose of 1.3 x 10^{15} cm^{-2} is chosen in order to obtain the maximum volume concentration slightly higher than the theoretical solid solubility limit as shown in Figure 48. The maximum volume concentration for this work is 2.9 x 10^{20} cm^{-2} where the theoretical maximum solid solubility limit is 2 x 10^{20} cm^{-2}.

<table>
<thead>
<tr>
<th>Implant</th>
<th>Dose (cm^{-2})</th>
<th>Implant Energy (keV)</th>
<th>Implant Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phosphorus</td>
<td>1.3 x 10^{15}</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Phosphorus</td>
<td>1.3 x 10^{15}</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Phosphorus</td>
<td>1.3 x 10^{15}</td>
<td>30</td>
</tr>
</tbody>
</table>

**TABLE 5 Implant details for Implant Batch I**
The amorphisation check was carried out by using the RBS technique in order to observe the effect of implanting phosphorus at different temperatures. Figure 49 shows the ion channelling spectra for samples implanted at RT, cold and hot temperature along with a virgin sample and at a random spectrum for comparison and reference, respectively. A selected portion of the RBS-c spectra (channel 240 to 285) was chosen to show and emphasize the germanium damage peak.

The implantation damage is clearly visible in the samples implanted at cold and RT as the dechannelling yield for both samples, which have a similar trend, is far higher than the virgin sample. It can be seen that the surface peak, which represents implantation damage for cold and RT samples are nearly to the random spectra. This would suggest that the surfaces of the samples are amorphous. An equivalent amorphous germanium (a-Ge) layer thickness of 53 nm and 63 nm are formed for RT and cold implants, respectively. The Data Furnace program was used to calculate the thickness of the amorphous layer. The sample implanted at the hot temperature shows very little dechannelling yield, indicating marginal residual damage following the implantation. As expected,
the channelling spectra indicates that with increasing implantation temperature, the degree of germanium amorphisation is reduced

![Figure 49](image)

**Figure 49.** This RBS spectra of a virgin (line) germanium structure in comparison to corresponding channelling spectra after 30 keV, $1.3 \times 10^{15}$ cm$^{-2}$ phosphorus implantation at RT (triangle), cold (square) & hot (circle).

During implantation at cold temperature, dynamic annealing is not present. Therefore, the damage is agglomerated to form a continuous amorphous layer. However, the implantation at RT results in a narrower amorphous region than the cold implant due to some recombination process that occurs during the implantation process. In the case of the phosphorus implantation at hot temperature, most of the associated displacement damage will recover by the mutual recombination of self-interstitial atoms and vacancies.

### 4.6 TEM

In order to investigate the surface structure in more detail, the samples which are implanted at different temperatures were examined by the TEM technique. Figure 50 shows three images of the surface after implanted at three different temperatures. The images confirm the amorphous thickness for the cold implant is 63 nm and 53 nm for the room temperature implant. Also, no amorphous layer is observed for the hot implant.
4.7 Isochronal Anneal Study

In this section the electrical results are shown and discussed in terms of the implant temperature effect after isochronal anneal.

4.7.1 Anneal Time Study

For the initial study of this research, 60s is chosen as the anneal time. However from the initial SIMS result as shown in Figure 51, it is observed that the phosphorus diffuses very far away from the junction depth of 91 nm to 500 nm. Therefore, it seems that 60s is not the optimum time for annealing as the aim of the research is to form shallow junction.

Figures 52-54 show the isothermal anneals study with the anneal time of 1s, 5s and 10s in order to determine the optimum anneal time. Figure 52 shows that the sheet resistance for Phosphorus with shorter time than 10s are higher for the temperature range investigated. This is coincidental with the lower activation of sheet carrier concentration and slightly higher mobility as observed in Figure 53 and 54.

In summary, it seems that shorter time than 10s has not more advantageous and 10s is the optimised anneal time.
Figure 51. SIMS profiles P cold implant as implanted and after 800 °C for 60s annealing

Figure 52. Sheet resistance for cold implant after 500, 600, and 750°C annealing for 1, 5 and 10s
Figure 53. Sheet carrier concentrations for the cold implant after 500, 600, and 750°C annealing for 1, 5 and 10s

Figure 54. Hall mobility for the cold implant after 500, 600, and 750°C annealing for 1, 5 and 10s
4.7.2 Electrical Measurement

Sheet resistance

Figure 55 shows a graph of sheet resistance versus implant temperature for samples implanted with P species in germanium annealed 10s at temperatures ranging from 500 to 800 °C. The interconnecting lines between the data points here and further on are used to guide the eye.

Figure 55. Sheet resistance after being annealed for 10s at 500, 600, 750, 775 and 800 °C

The P implants into germanium at room temperature shows sheet resistance of 66.6 ohms/square when annealed at a temperature of 500 °C, which is lower than the sheet resistance of the cold and hot implants. However, as the anneal temperature increases, the sheet resistance for the samples implanted at cold and hot temperature are constantly lower than the samples implanted at room temperature. This is essentially due to the increased phosphorus incorporation and solubility during SPER. From these two implant temperatures; the cold implant exhibits the lowest sheet resistance value.

The effect of the cold implant can be described being due to lack of dynamic annealing at low temperature. Therefore, Frenkel pairs remain within close proximity to one another and annihilate
easily during annealing. This again leads to a situation of low levels of complex thermally stable defects and hence, good activation.

Even though, very low levels of damage remain following implantation at the hot temperature and it is expected that from this low damage level starting point, good activation of phosphorus is achieved due to the low level of stable defect complexes. However, the hot implant exhibits a higher sheet resistance value than the cold implant. The reason may be due to the out-diffusion mechanism during implantation process (see figure 58). As for the RT implant, due to the dynamic annealing, more complex defect structures form resulting in the thermally stable defects, which are thought to bind the phosphorus in an electrically inactive state.

Carrier Concentration

The active sheet carrier concentration is shown in Figure 56.

![Carrier Concentration Graph](image)

**Figure 56.** Sheet carrier concentrations after being annealed for 10s at 500, 600, 750, 775 and 800 °C

The values mirror the Rs results, where higher sheet resistance corresponds to lower carrier concentration and vice versa. Activation is the highest for P implants at LN$_2$ temperature between 600 and 800 °C. The lower activation for the cold implants at lower anneal temperatures could be attributed to the unrecovered implantation damage.
Mobility

Figure 57 shows a plot of Hall mobility versus implant temperature for P implants into germanium.

![Graph showing Hall mobility versus implant temperature for P implants into germanium.](image)

Figure 57. Hall mobility after 500, 600, 750, 775 and 800 °C annealing for 10s

Hall mobility increases as the annealing temperature increases for all the implants. The values of electron mobility increase, which may have been due to the reduction of implantation damage as the anneal temperature increase.

At temperatures above 750 °C, the Hall mobility for P implants at room temperature is the highest. This high mobility corresponds to the decrease in carrier concentration. The ionised impurity scattering is the primary mechanism, which affects mobility. Therefore, a higher number of electrically active dopant atoms results in lower mobility.

4.7.3 SIMS

In order to further investigate the activation behaviour of phosphorus, temperatures of 600 °C and 750°C were chosen for SIMS analysis, as they correspond to low and high annealing temperatures, respectively. The as-implanted profiles are discussed first, in order to establish the initial conditions prior to thermal processing. The profiles for P implanted at RT, cold and hot are shown in Figure...
Figure 59 shows the retained dose and junction depth for As-implanted SIMS profiles for P at three different temperatures.

**Figure 58.** As-implanted SIMS profiles for P at three different temperatures

**Figure 59.** Retained dose and junction depth for As-implanted SIMS profiles for P at three different temperatures
From the obtained results, one can see that the profile of hot implant differ noticeably from the RT implant. The peak of the distribution is deeper than the other two temperatures and the dopant tail penetrates far deeper. This may have been due to out-diffusion during the implantation process couple with in-diffusion. Furthermore, this also may have been due to some channelling due to the retention of the crystalline phase as the sample also anneals during the implant as a result of the elevated temperature. For the cold implant, no significant differences are shown in terms of the peak of the profile. However, the depth of the profile is reduced from 96 nm (RT implant) to 92 nm. It might due to the present of thicker amorphise layer in the cold implant compared to the RT implant. In order to verify the amount of dopant present, the retained dose was calculated by integrating under the curves ignoring the surface peak. The surface peak is not well characterised due to the presence of a surface oxide. The surface oxide will corrupt the surface data, until the sputter rate is normalised. Table 6 provides a summary of the retained dose for each implantation temperature.

<table>
<thead>
<tr>
<th></th>
<th>Implant</th>
<th>As-implanted</th>
<th>After being anneal at 600 °C</th>
<th>After being anneal at 750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RT</td>
<td>$1.3 \times 10^{15}$ cm$^{-2}$</td>
<td>$5 \times 10^{14}$ cm$^{-2}$</td>
<td>$4.75 \times 10^{14}$ cm$^{-2}$</td>
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<tr>
<td>2</td>
<td>Cold</td>
<td>$1.3 \times 10^{15}$ cm$^{-2}$</td>
<td>$4.65 \times 10^{14}$ cm$^{-2}$</td>
<td>$6.1 \times 10^{14}$ cm$^{-2}$</td>
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<tr>
<td>3</td>
<td>Hot</td>
<td>$9 \times 10^{14}$ cm$^{-2}$</td>
<td>$4.4 \times 10^{14}$ cm$^{-2}$</td>
<td>$4.9 \times 10^{14}$ cm$^{-2}$</td>
</tr>
</tbody>
</table>

**Table 6 Retained dose calculated for P implant at three different temperatures**

Figure 60 shows SIMS profiles for as-implanted and after being annealed for 10s at 600 and 750 °C for the P implant at RT. Figure 61 shows retained dose and junction depth for RT implant, as – implanted and after being anneal for 10s at 600 and 750 °C.
Figure 60. SIMS profiles for P at RT implant, as–implanted and after being anneal for 10s at 600 and 750 °C.

Figure 61. Retained dose and junction depth for RT implant, as–implanted and after being anneal for 10s at 600 and 750 °C.
The results reveal that P redistributed during the annealing and some diffusion has occurred. The as-implanted P only shows a junction depth of about 96 nm (measured at $3 \times 10^{18}$ cm$^{-3}$), which is shifted to 165 and 252 nm after being annealed at 600 and 750 °C, respectively. The retained dose for this implant was calculated to be 38.5 % and 36.5 % for samples annealed at 600 and 750 °C, respectively, indicating some dopant loss to the surface when increasing the anneal temperatures.

These results provide a benchmark for the comparison for the diffusion of hot and cold implants, and germanium co-implant, which are discussed together in the next chapter. The SIMS profiles are observed to have a same trend with Chui et. al. [37] work.

Figure 62 shows SIMS profiles for P following the hot implant, as-implanted and after 10s anneal at 600 and 750 °C. Figure 63 shows retained dose and junction depth for P at hot implant temperature, as-implanted and after 10s anneal at 600 and 750°C.

Figure 62. SIMS profiles for P at hot implant temperature, as-implanted and after 10s anneal at 600 and 750°C.
Figure 63. Retained dose and junction depth for P at hot implant temperature, as-implanted and after 10s anneal at 600 and 750°C.

The junction depth for the as-implanted profile occurs at 150 nm, shifting to 155 nm and 250 nm after annealing at 600 and 750 °C respectively. The SIMS profiles after 600 °C anneal shows enhanced diffusion beyond the depth of 164 nm, which is the location of the junction depth (measured at 3 X 10^{18} cm^{-3}). This may have been due to the defects located at the end of range of the implant gettering the P as vacancies can enhance P diffusion [96] and trapping it at defect sites. High Hall mobility at 600 °C (see figure 57) compared to the RT and cold implants, indicating enhanced diffusion. The mobility is a function of the defect density and the carrier density. At these concentrations the carrier mobility is dominated by ionised impurity scattering so the higher the volume carrier density the lower the mobility. If there are defects in the crystal that scatter the carriers as well, this will further degrade the mobility. So, in the case of a diffused profile, the sheet carrier density will be distributed over a greater distance which means the volume carrier density will be lower and hence you would have a higher mobility.

However, when annealed at 750 °C, the SIMS profile exhibits no such kink because at this temperature, the defects have been dissolved. Integrating under the curve for 600 and 750 °C, annealed samples showed 48.9 % and 54.4 % retained dose, respectively. Interestingly, sample annealed at 750 °C have a higher retained dose. This may be due to the fact that P has diffused past the enhanced diffusion region or the defects have been dissolved at this temperature, which may have effectively reduced the out-diffusion to the surface.

Figure 64 shows SIMS profiles for P at cold implant temperature, as implanted and after 10s anneal at 600 and 750 °C. Figure 65 shows retained dose and junction depth for P at cold implant temperature, as implanted and after 10s anneal at 600 and 750 °C.
Figure 64. SIMS profiles for P at cold implant temperature, as implanted and after 10s anneal at 600 and 750 °C.

Figure 65. Retained dose and junction depth for P at cold implant temperature, as implanted and after 10s anneal at 600 and 750 °C.
35.8 % and 46.9 % was calculated as the retained dose for samples annealed 600 and 750 °C respectively. The reason for a higher retained dose at 750 °C might due to a higher recovery of implantation damage at high temperature coupled with the greater in diffusion into the sample reducing the diffusion gradient at the surface. Therefore, more phosphorus is active. The junction depth moves from 92 nm to 161 nm and 267 nm after 600 and 750°C annealed respectively.

Figure 66 shows SIMS profiles for P implant at three different temperatures after being annealed at 600 °C. Figure 67 shows retained dose and junction depth for P implant at RT, cold and hot temperatures after 10s anneal at 600 °C.

![Figure 66. SIMS profiles for P implant at RT, cold and hot temperatures after 10s anneal at 600 °C](image-url)
Figure 67. Retained dose and junction depth for P implant at RT, cold and hot temperatures after 10s anneal at 600 °C

The junction depth of P implant at RT occurs at 165 nm (measured at 3x10^{18} cm^{-3}). As for the hot and cold implant, the junction depths have been reduced by just a few nanometres to 164 and 161 nm, respectively. The formation of box-like profile is observed for the cold and RT implants.

In terms of the retained dose, the hot implant exhibits the highest, 48.9% followed by RT, 38.5% and finally, the cold implant, 35.8%. The higher retained dose for the hot implant is as a result of the lower retained dose following implant compared to the RT and cold implants (see Table 4), which in turn reduces the dopant loss at the surface due to a reduced P gradient thus reducing the dopant loss during annealing. In fact, actually, all three samples have a very similar retained dose as the hot implant showing greater diffusion in the tail of the distribution where clearly the dopant has diffused off the back of the almost box-like profile.

The behaviour of dopant at this point can be seen in Figure 68 which shows SIMS profiles for P at RT, cold and hot temperatures after 10s anneal at 750 °C. Figure 69 shows retained dose and junction depth for for P implant at RT, cold and hot temperatures after 10s anneal at 750 °C.
Figure 68. SIMS profiles for P implant at RT, cold and hot temperatures after 10s anneal at 750 °C

Figure 69. Retained dose and junction depth for P implant at RT, cold and hot temperatures after 10s anneal at 750 °C
The junction depth for the RT and hot implant are almost the same, measuring at 250 nm. However, the cold implant seems to diffuse deeper than the other samples. At this temperature, the dose loss has increased for the RT implant, showing the retain dose of 36.5%. However, for the cold and hot implants, the retained dose has increased to 46.9% and 54.4%, respectively. The increment of retained dose for cold and hot implants is mainly due to the recovery of the implantation damage and annihilation of point defects at high temperatures, respectively.

4.7.4 SIMS and Differential Hall measurements

In this section, the carrier concentration as a function of depth obtained using the Differential Hall technique is compared with the SIMS results in order to compare the electrically active fraction of the dopant profile with atomic distribution of P.

Figures 70-72 show the Differential Hall and SIMS profiles for P, implanted at three different temperatures after being annealed for 10s at 600°C. Figure 73 shows retained dose and active dopant fraction for for P, implanted at three different temperatures after 10s anneal at 600 °C.

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**Figure 70.** SIMS and Differential Hall profiles for P, implanted at room temperature after 10s anneal at 600 °C
Figure 71. SIMS and Differential Hall profiles for P, implanted at hot temperature after 10s anneal at 600 °C

Figure 72. SIMS and Differential Hall profiles for P, implanted at cold temperature after 10s anneal at 600 °C
Figure 73. Retained dose and active dopant fraction for P, implanted at 3 different temperatures after 10s anneal at 600 °C

The differential Hall profiles are compared to the SIMS results so that the fraction of electrically active and inactive P can be determined. It is observed from all of the profiles in figure 65, in the near-surface region, the differential Hall profile is lower than the SIMS profile, indicating that the activation of phosphorus is low in this region. A.R. Peaker et al [97] suggested that the phosphorus deactivation is due to the presence of excess vacancies near to the surface region. However, as the differential Hall profile move deeper into the samples, it starts to follow the shape of the SIMS profiles, showing maximum phosphorus activation in this region.

The percentage of active dopant could be achieved by calculating the ratio of the calculated SIMS retained dose and the sheet carrier density after annealing. The active dopant fraction in this case was calculated to be 93 %, 85 % and 78% for RT, hot and cold implant, respectively. At this temperature, for all samples, the maximum level of P becomes electrically active is about 4 x 10¹⁹ at/cm³ which is about the same value as the effective solid solubility in the literature [45]. The reason for the low activation is because there is a large amount of dopant loss during the annealing process for all of the samples and also, may have been due to the formation of phosphorus-vacancy complexes.

Figures 74-76 shows SIMS and Differential Hall profiles for P, implanted at 3 different temperatures after 10s anneal at 750 °C. Figure 77 shows retained dose and active dopant fraction for P, implanted at three different temperatures after 10s anneal at 750 °C.
Figure 74. SIMS and Differential Hall profiles for P, implanted at room temperature after 10s anneal at 750 °C

Figure 75. SIMS and Differential Hall profiles for P, implanted at hot temperature after 10s anneal at 750 °C
Figure 76. SIMS and Differential Hall profiles for P, implanted at cold temperatures after 10s anneal at 750 °C

Figure 77. Retained dose and active dopant fraction for P, implanted at three different temperatures after 10s anneal at 750 °C
At 750 °C, the RT implant shows an active dopant fraction of 84 %, whereas the hot and cold implants resulted in an active dopant fraction of 76 % and 89 %, respectively. In terms of the maximum level of P becoming electrically active, cold implant exhibits one magnitude higher (3 x 10^19 cm^-3) than the RT and hot implants. This may have been due to the phosphorus atoms that had fallen out of the germanium solid solution as it approaches its equilibrium state. However, for the cold implant, it contains the phosphorus in the amorphous layer and at this temperature, the contain phosphorus move into the lattice site.

It could be observed the apparent contradiction between the differential Hall and SIMS profile at some depth. It seems possible that these results are due to the variation of etch rate through the differential Hall measurement. The etch rate increase in the region of high P concentration and this would remove more material and hence more P carriers. As a result, the carrier density in the regions of faster etch rate would be over estimated by the etch rate error. However, this error does not affect the percentage of active dopant result as it is a ratio of the calculated SIMS retained dose and the sheet carrier density after annealing. Apart from the error, these results have a similar trend with results obtained by Peaker et. al. [97] (Figure 78) and Bennett et. al. [98] (Figure 79)
Figure 78. SIMS and SRP measurements of $10^{16}$ cm$^{-2}$ 150 keV phosphorus implant into Ge annealed at 600 °C for 60s [97]

Figure 79. Electron concentration profile as a function of depth for P-doped Ge measured using the differential Hall technique annealed at 600°C for 100s [98]
4.8 Implant matrix Experiment II

For experiment II, the implant energy has been changed from 30 keV to 5 keV in order to examine the implant temperature effect for shallower implants. The conditions of the implant batch II for the phosphorus species implanted in Ge-on-Si are shown in Table 7. The implantation dose was reduced to $3.25 \times 10^{14}$ cm$^{-2}$ to maintain the same maximum volume dopant concentration as for the higher energy implants. This is verified by the SUSPRE profile shown in Figure 80.

<table>
<thead>
<tr>
<th>Implant</th>
<th>Dose (cm$^{-2}$)</th>
<th>Implant energy</th>
<th>Implant Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phosphorus</td>
<td>$3.25 \times 10^{14}$</td>
<td>5 keV</td>
</tr>
<tr>
<td>2</td>
<td>Phosphorus</td>
<td>$3.25 \times 10^{14}$</td>
<td>5 keV</td>
</tr>
<tr>
<td>3</td>
<td>Phosphorus</td>
<td>$3.25 \times 10^{14}$</td>
<td>5 keV</td>
</tr>
</tbody>
</table>

TABLE 7 Implant details for Implant Batch II

Figure 80. Simulated implant profile for 5 keV P $3.25 \times 10^{14}$ cm$^{-2}$ in Ge
4.9 Isothermal 10s anneal study

4.9.1 Electrical measurement

Figure 81 to 83 show sheet resistance, carrier concentration and Hall mobility, respectively for P implants at 5 keV for different implant temperatures and were annealed at 500, 600, 650, 700 and 750°C for 10s.

![Graph showing sheet resistance vs implant temperature](image)

**Figure 81.** Sheet resistance after 500, 600, 650, 700 and 750 °C annealing for 10s
Figure 82.  Carrier concentrations after 500, 600, 650, 700 and 750 °C annealing for 10s

Figure 83.  Hall mobility after 500, 600, 650, 700 and 750 °C annealing for 10s
At lower anneal temperature (500 °C and 600 °C); the sheet carrier concentration is higher than the implant dose, which cannot be possible because the sheet carrier concentration should be always lower than the implant dose. Besides that, the Hall mobility is very low. This could be due to the contribution of the substrate towards the Hall measurement results. In other words, the junction formation is low quality or leaky n/p junction; therefore, during the measurement, the current will move in both ways, which are the substrate (p-type) and the top n-type layer (Illustrated in Figure 84). As a result, the exact measurement will take the total carrier of p-type and n-type. This is proving as the 500°C implant exhibits p-type result; even though it should have exhibits n-type result when anneal at 500°C. However, as the anneal temperature increases, the junction formation gradually become better, which in turn reduces any substrate leakage currents and with good junction isolation. As a result, n type activity is measured and the measured sheet carrier concentration is within the implanted dose range.

From the literature, it was found that shallow dopant implant activation characterisation in germanium is almost impossible when using the conventional Hall Effect and four-point probe technique. This is due to high junction leakage as the band gap in Ge is smaller compared to silicon. Therefore, techniques and instruments have been developed to overcome this problem. Recently, the Micro Hall Effect (MHE) and micro four-point probe (M4PP) have successfully demonstrated the characterization of active shallow dopants in Ge [8, 99].

![Figure 84. Illustration of leakage current in this experiment](image-url)
4.10 Summary

The electrical activation and diffusion of phosphorus as a function of implant temperature was investigated using RBS, XTEM, Hall, Differential Hall and SIMS techniques following isochronal anneals between 500 and 800 °C.

In experiment I, no significant difference has been observed between the three implant temperatures at 600 °C anneal. For the hot implant, enhanced diffusion occurs at the end of range (EOR) region, while the cold implant exhibit the same behaviour as the RT implant. However, at 750 °C, the cold implant exhibits a higher retained dose with high active dopant fraction and exhibit a higher maximum level of P becomes electrical active. Despite that, a deeper profile for the cold implant was observed. Hot implant has the highest retain dose for 750 °C. However, the hot implant does not show any significant difference in terms of junction depth and maximum level of P becomes electrical active with a lower active dopant fraction.

In experiment II, it has been shown that it is very challenging to characterise the shallow implant in germanium using the convensional Hall technique due to the leaky junction formation.
5 Point defect engineering study of phosphorus ion implanted germanium

5.1 Introduction

In this chapter, a point defect engineering method will be investigated for the first time in order to enhance the electrically active concentration of phosphorus in germanium. This is achieved by introducing an excess of point defects by Ge⁺ ion implantation prior to the phosphorus implantation. These excess of point defects or Ge interstitials are expected to bind with the vacancies in the germanium substrate. As a result, highly active Ge NMOS would be achieved as less phosphorus-vacancy complexes are produced. This method is inspired by a method called vacancy engineering, which is described in section 2.7.5.

Various characterisation techniques (Van der Pauw, Hall Effect, Differential Hall profiling and SIMS) were used in order to determine the electrical and compositional properties of the P implants in germanium. Samples from these wafers were then annealed isochronally in order to carry out activation and diffusion studies.

5.2 Experiment Details I

The actual implant parameters are listed in Table 8, indicating the implant species, dose and implant energy. All implants were performed at room temperature. The corresponding projected ranges (Rp) selected for the Ge implants were 15 nm and 60 nm. The germanium dose chosen is below the amorphisation threshold, as indicated by Darby et al. [100]. The simulation of the germanium implant profiles are shown in Figure 85 and 86. After Ge implant, the germanium wafers were then implanted with P. In order to minimise channelling, the implantations were performed under 7° tilt angles.
Figure 85. Simulated implant profile for 25 keV Ge $2 \times 10^{13}$ cm$^{-2}$ in Ge

Figure 86. Simulated implant profile for 135 keV Ge $2 \times 10^{13}$ cm$^{-2}$ in Ge
TABLE 8 Implant specifications for the implants in experiment I

<table>
<thead>
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<th>Process step</th>
<th>Implant</th>
<th>Dose (cm$^{-2}$)</th>
<th>Implant Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Germanium (Ge then P)</td>
<td>$2 \times 10^{13}$</td>
<td>25 keV</td>
</tr>
<tr>
<td></td>
<td>Phosphorus</td>
<td>$1.3 \times 10^{15}$</td>
<td>30 keV</td>
</tr>
<tr>
<td>2</td>
<td>Germanium (Ge then P)</td>
<td>$2 \times 10^{13}$</td>
<td>135 keV</td>
</tr>
<tr>
<td></td>
<td>Phosphorus</td>
<td>$1.3 \times 10^{15}$</td>
<td>30 keV</td>
</tr>
</tbody>
</table>

5.3 Process step

The wafers were cleaved into samples of 1 cm x 1 cm then annealed to see the effects of temperature on the electrical and compositional properties of the samples. The temperature range here was 600 – 800 ºC for anneal times of 10s. In order to measure the sheet resistance of the samples, a four point probe method (4pp) was employed. Next the Hall measurement with Van der Pauw technique was used in order to find \( R_{\text{HIS}} \) and from these the carrier density and mobility are calculated. Consequently, differential Hall is carried out in order to determine to the active dopant fraction. Finally, SIMS was used to study the diffusion of the P implant with increasing annealing temperature.
5.4 Isochronal Anneal study

5.4.1 Electrical measurement

Sheet Resistance

Figure 87 shows isochronal sheet resistance following anneal temperatures between 600-800 °C for samples implanted with P into germanium with and without the Ge co-implant.

![Figure 87. Sheet resistance after 600, 700, 750, 775 and 800 °C annealing for 60s.](image)

In the case of the phosphorus layer with the germanium co-implant there is a clear reduction of Rs for samples annealed above 750 °C, whereas Rs is higher for samples thermally treated at 600 and 700 °C. Moreover, the germanium co-implant energy does not significantly affect the sheet resistance.

It was showed by Markevich et al. [53] that Frenkel point defect or interstitials-vacancy pairs in germanium, behave as acceptor states in the band gap. Hence, Kim et al. [66] suggested that the residual implantation damage that could not be recovered by the RTP step and hence these would contribute towards acceptor level defect creation in the band gap and can compensate the donor activation. In the germanium co-implant case, lower annealing temperatures could not recover the residual implantation damage created by the germanium co-implant. This leads toward higher Rs values than the sample without co-implant. The germanium co-implant shows that the sheet resistance is reduced only at higher annealing temperature. This trend does not show any significant of
adding interstitials into the substrate but only adding more damage via germanium implantation and the damage recover at higher annealing temperature is not via interaction with the interstitials. Therefore, this technique might be a damage engineering technique which is similar to cold implant technique not point defect engineering.

Hall measurements were carried out in order to have a better understanding of the activation mechanism as single Rs measurements only show the inverse product of the mobility and sheet carrier concentration. These two values can be separated by Hall measurements. Figure 88 and 89; represent the corresponding active carrier concentration (Ns) and Hall mobility, respectively.

**Carrier concentration.**

![Figure 88. Sheet carrier concentrations after 600, 700, 750, 775 and 800 °C annealing for 10s](image)

The results show that dopants with germanium co-implant display higher activation at higher anneal temperatures. Comparing the level of activation at 800 °C, it can be seen that with the germanium co-implant, the number of active phosphorus atoms is of the order of $8 \times 10^{14}$ cm$^{-2}$, compared to $6.75 \times 10^{14}$ cm$^{-2}$ in the control sample (0 keV). However, 800 °C is not a good choice for processing germanium as the dopant will diffuse deeper into the sample (see figure 51) even though high activation is achieved.
Figure 89. Hall mobility after 600, 700, 750, 775 and 800°C annealing for 10s

The mobility for P implant with germanium co-implant reduces from the mobility of the control sample. This decrease in mobility corresponds to the phosphorus activation increase due to an increase in the number of ionized impurities which dominates the scattering process.

5.4.2 SIMS measurement

In order to understand the behaviour of P and also to verify whether either the dopant interacts with excess germanium interstitials or not, SIMS analysis is carried out. The temperatures of 600 and 750 °C were chosen for the SIMS analysis. The as-implanted profiles for P species with and without the germanium implant energy are shown in Figure 90. Figure 91 shows retained dose and junction depth for as-implanted SIMS profiles for P at two different co-implant energies.
Figure 90. As-implanted SIMS profiles for P at two different co-implant energies

Figure 91. Retained dose and junction depth for As-implanted SIMS profiles for P at two different co-implant energies

From the obtained results, one can see that there is no significant different between the co-
implant and the RT implant in term of profile peak. However, the co-implant profiles exhibit shallower profile probably as a result of slightly reduced channelling due to the addition damage in the sample resulting from the Ge pre-implant. Table 9 provides a summary of the calculated dose.

<table>
<thead>
<tr>
<th>Co-Implant</th>
<th>As-implanted</th>
<th>After 600 °C annealed</th>
<th>After 750 °C annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 No coimplant</td>
<td>1.3 x 10^{15} cm^{-2}</td>
<td>5 x 10^{14} cm^{-2}</td>
<td>4.75 x 10^{14} cm^{-2}</td>
</tr>
<tr>
<td>2 25 keV Ge Co-implant</td>
<td>1.3 x 10^{15} cm^{-2}</td>
<td>4.7 x 10^{14} cm^{-2}</td>
<td>5.44 x 10^{14} cm^{-2}</td>
</tr>
<tr>
<td>3 135 keV Ge Co-implant</td>
<td>1.3 x 10^{15} cm^{-2}</td>
<td>4.34 x 10^{14} cm^{-2}</td>
<td>5.1 x 10^{14} cm^{-2}</td>
</tr>
</tbody>
</table>

Table 9 Retained dose calculated for P implant

Figure 92 shows SIMS profiles for P with 25 keV Ge co-implant, as implanted and after 10s anneal at 600 and 750 °C. Figure 93 shows Retained dose and junction depth for P with 25 keV Ge co-implant, as implanted and after 10s anneal at 600 °C and 750 °C

Figure 92. SIMS profiles for P with 25 keV Ge co-implant, as implanted and after 10s anneal at 600 °C and 750 °C
Figure 93. Retained dose and junction depth for P with 25 keV Ge co-implant, as implanted and after 10s anneal at 600 °C and 750 °C

The junction depth for the as-implanted profile occurs at 93 nm, shifting to 159 nm and 248 nm after annealing at 600 and 750 °C respectively. Integrating under the curve for 600 and 750 °C annealed samples showed 36 % and 42 % retained dose, respectively.

Figure 94 shows SIMS profiles P with 135 keV Ge co-implant, as implanted and after 10s anneal at 600 and 750 °C. Figure 95 shows retained dose and junction depth for P with 135 keV Ge co-implant, as implanted and after 10s anneal at 600 °C and 750 °C.
Figure 94. SIMS profiles for P with 135 keV Ge co-implant, as implanted and after 10sec anneal at 600 °C and 750 °C

Figure 95. Retained dose and junction depth for P with 135 keV Ge co-implant, as implanted and after 10s anneal at 600 °C and 750 °C
33.4% and 39.2% was calculated as the retained dose for samples annealed 600 and 750 °C respectively. The junction depth moves from 91 nm to 159 nm and 240 nm after 600 and 750 °C annealed respectively.

The behaviour of dopant at this point can be seen in Figure 96 which shows SIMS profiles for P with or without Ge co-implant after 10s anneal at 600 °C. Figure 97 shows retained dose and junction depth for P implant for two different Ge co-implant energies after 10s anneal at 600 °C.

Figure 96. SIMS profiles for P implant for two different Ge co-implant energies after 10s anneal at 600 °C
Figure 97. Retained dose and junction depth for P implant for two different Ge co-implant energies after 10s anneal at 600 °C

At this temperature, no-coimplant, 25 keV Ge and 135 keV Ge exhibit 38.5%, 36% and 33% retained dose respectively. The junction depths for the co-implant samples are reduce from 165 nm (no coimplant) to 159 nm.

Figure 98 shows SIMS profiles for P implant with or without Ge co-implant after 10s and 750 °C anneal. Figure 99 shows retained dose and junction depth for two different Ge co-implant energies after 10s anneal at 750 °C
Figure 98. SIMS profiles for P implant for two different Ge co-implant energies after 10s anneal at 750 °C

Figure 99. Retained dose and junction depth for two different Ge co-implant energies after 10s anneal at 750 °C
In term of retained dose, 25 keV Ge co implant exhibits the highest, 42% followed by 135 keV Ge co implant, 39.2% and lastly, no co implant, 36.5%. Interestingly, it is observed for the 135 keV Ge co implant sample, the junction depth is reduced from 251 nm (0 keV sample) to 240 nm. This is probably as a result of slightly reduced diffusion due to the deeper damage in the sample resulting from the Ge pre-implant.

5.4.3 SIMS and Differential Hall

Figures 100-102 show Differential Hall and SIMS profiles for P, implanted at 3 different temperatures after 10s anneal at 600°C. Figure 103 shows retained dose and active dopant fraction for P, implanted with two different Ge co-implant energies after 10s anneal at 600 °C.

Figure 100. SIMS and Differential Hall profiles for P, implanted with no co-implant after 10s anneal at 600 °C
Figure 101. SIMS and Differential Hall profiles for P, implanted with 25 keV Ge co-implant energy after 10s anneal at 600 °C

Figure 102. SIMS and Differential Hall profiles for P, implanted with 135 keV Ge co-implant energy after 10s anneal at 600 °C
Figure 103. Retained dose and active dopant fraction for P, implanted with 2 different Ge co-implant energies after 10s anneal at 600 °C

The active dopant fraction in this case was calculated to be 93 %, 89.5 % and 83.5% for no, Ge 25 keV and Ge 135 keV implant, respectively. At this temperature, for all samples, the maximum level of P activity is about $4 \times 10^{19}$ at/cm$^3$ which is about the same as the effective solid solubility in the literature

Figures 104-106 show SIMS and Differential Hall profiles for P, implanted at 3 different temperatures after 10s anneal at 750 °C. Figure 107 shows the retained dose and active dopant fraction for P, implanted with 2 different Ge co-implant energies after 10s anneal at 750 °C
Figure 104. SIMS and Differential Hall profiles for P, implanted with no Ge co-implant after 10s anneal at 750 °C

Figure 105. SIMS and Differential Hall profiles for P, implanted with 25 keV Ge co-implant energy after 10s anneal at 750 °C
Figure 106. SIMS and Differential Hall profiles for P, implanted with 135 keV Ge co-implant energy after 10s anneal at 750 °C.

Figure 107. Retained dose and active dopant fraction for P, implanted with 2 different Ge co-implant energies after 10s anneal at 750 °C.

At this high temperature, the no co-implant shows an active dopant fraction of 84 %, where Ge 25 keV and 135 keV co-implant resulted in 89.6 % and 83 %, respectively. In terms of the maximum level of P become electrically active, Ge co-implant samples exhibits one magnitude higher (3 x 10¹⁹ cm⁻³) than no co-implant sample.
Figure 108 and 109, show comparison between cold implant and Ge co-implant sample at anneal temperature of 600 and 750 °C, respectively.

**Figure 108.** Comparison between cold implant and Ge co-implant sample at anneal temperature of 600 °C

**Figure 109.** Comparison between cold implant and Ge co-implant sample at anneal temperature of 750 °C
5.4.3.1 Discussion

From figure 108 and 109, it is observed that there are lots of similarity between this technique and the cold implantation technique, which are discussed in the previous chapter.

In term of retained dose, both techniques shows lower retained dose at 600 °C annealing temperature and higher retained dose at 750 °C. However, the cold implant technique exhibits higher retained dose compared to this technique.

For the case of diffusion, both techniques have a reduction in junction depth for as-implanted and 600 °C annealing process. Similar trends have been seen for both techniques in reference to the active dopant fraction and maximum level of phosphorus electrical activity at low and high annealing temperatures.

From this observation, it can be concluded that this technique is not a point defect engineering technique but it is a damage engineering technique as it shows similar behaviour with the cold implant techniques. The only difference is that cold implant fully amorphised the samples and for this technique, it is only partially damaging the substrate.

Even though this technique has similarities with the cold implant technique, it also has advantages compared to the cold implant. The advantages are at higher temperature, where the retained higher dose with shallower junction depth is beneficial. This advantage is observed only for the 135 keV Ge co-implant. It might due to deeper implant damage than the phosphorus amorphous layer compared to the 25 keV Ge co-implant, where damage is contained inside the phosphorus amorphise layer.
5.5 Experiment Details II

The hypothesis of the experiment II is that the excess germanium could break the phosphorus vacancy complex formation and release the phosphorus from the vacancy bonding. Therefore, more phosphorus could be activated. Firstly, the germanium wafers were then implanted with P and annealed at 500°C for 60s, in order to activate the phosphorus. After the annealing process, germanium wafers were then implanted with germanium at two different projected ranges (15 nm and 60 nm). The implantation details for experiment II are summarise in Table 10.

<table>
<thead>
<tr>
<th>Implant</th>
<th>Dose (cm²)</th>
<th>Implant Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus (P, then anneal at 500C for 60s follow by Ge)</td>
<td>1.3 x 10¹⁵</td>
<td>30 keV</td>
</tr>
<tr>
<td>Germanium</td>
<td>2 x 10¹³</td>
<td>25 keV</td>
</tr>
<tr>
<td>Phosphorus (P implant, then anneal at 500C for 60s follow by Ge)</td>
<td>1.3 x 10¹⁵</td>
<td>30 keV</td>
</tr>
<tr>
<td>Germanium</td>
<td>2 x 10¹³</td>
<td>135 keV</td>
</tr>
</tbody>
</table>

TABLE 10 Implant specifications for the implants in experiment II

5.6 Isochronal Anneal Study

5.6.1 Electrical measurements

In this section electrical results are shown and discussed in terms of comparison between single P and P with Germanium co-implant in germanium after isochronal anneals. This approach is used in order to investigate the hypothesis of this experiment as stated in the section 5.5.

Figure 110 shows that the sheet resistance for Phosphorus with germanium co-implant cases is higher than the control sample for the temperature range investigated. This is coincidental with the lower activation of sheet carrier concentration and higher mobility as observed in Figure 111 and 112, respectively.
Figure 110.  Sheet resistance after 750, 775 and 800 °C annealing for 10s

Figure 111.  Sheet carrier concentrations after 750, 775 and 800 °C annealing for 10s
Figure 112. Hall mobility after 750, 775 and 800 °C annealing for 10s

The lower activation of sheet carrier concentration could be explained; as when adding germanium species in the substrate after the annealing process, the damage in the substrate is accumulate and it becomes harder to recover the damage. As a result, the P activation is reduced. This experiment confirming that this is not a point defect technique as stated in the main hypothesis (refer section 5.1) but it is a damage engineering technique.

5.7 Summary

The electrical activation and diffusion of Phosphorus as a function of Germanium co-implant energy was investigated using the Hall, Differential Hall and SIMS techniques following isochronal anneals between 500 and 800 °C.

In experiment I, no significant different have been observed between the sample with and without Ge- implant at temperature of 600 °C except for the shallower junction depth for the Ge co-implant samples. However, at 750 °C, the Ge co-implant samples exhibit a higher retained dose with a high active dopant fraction and also, higher maximum level of P becomes electrical active, which is a similar trend with the cold implant, a type of damage engineering technique. From this observation, it is determined that this technique is not a point defect technique.

In experiment II, it has confirmed that this is a damage engineering technique.
6 Conclusion and Further Work

6.1 Conclusions

This research investigated the phosphorus activation and diffusion characteristics as a function of implant temperature and co-implantation of low dose germanium in order to deal with the challenges of creating highly active, n-type ultra shallow source/drain extension region for future Ge-based transistor. The implementation of this region by using ion implantation encountered fundamentals difficulties, such as phosphorus-vacancy complexes and concentration enhanced diffusion, which hinder the high activation of phosphorus and enhanced P diffusion. Currently, techniques such as co-implantation of antimony and MIMA technique have shown a promising solution for n-type source/drain extension fabrication in germanium.

Returning to the objectives at the beginning of this research, it is now possible to state the effects of implant temperature and low dose germanium co-implant toward P activation and diffusion. The following conclusions can be drawn from the studies.

6.1.1 Effect of implant temperature on P activation and diffusion

Experiment I – Phosphorus implant energy of 30 keV

1. It has been shown that the effect of low annealing temperature (600 °C) has no significant different between these three implant temperatures in terms of junction depth and phosphorus activation.

2. For High temperature (750 °C) isochronal anneals, it was shown that the cold implant exhibits the highest P electrical activation with high active dopant fraction. In spite of that, a deeper profile for cold implant was observed. Whilst, hot implant shows the highest retained dose. However, the hot implant does not show any significant differences in terms of junction depth and the maximum level of P that becomes electrically active with lower active dopant fraction.

The results of this experiment indicated that the cold and hot implants techniques are not suitable for Ge NMOS processing. The reason being is that the Ge NMOS processing requires a low temperature processing.
Experiment II – Phosphorus implant energy of 5 keV

The main findings that emerge from this experiment are:

1. High leakage junctions are formed for shallower implant energy.
2. High annealing temperature is required to repair the leaky junction.

The results of this study support the fact that conventional Hall Effect and Four Point Probe measurement is not suitable for shallow dopant implant activation characterisation in germanium.

6.1.2 Effect of low dose germanium co-implant on P activation and diffusion

Experiment I – Implant germanium before P implantation

1. The results of the investigation show that the advantage of this technique is it retained high dose with shallow junction depth at high anneal temperature.
2. The findings of this experiment suggest that in general, the outcomes are similar to cold implant techniques.

Experiment II – Implant germanium after P implantation

1. The major finding of this experiment is that the activation gets lower after germanium implant.

The evidences from this study showed that low dose germanium co-implant is not a technique for point defect engineering as stated in section 5.1. It is concluded that this technique is a type of damage engineering technique.

Overall, the findings of the studies suggest that it is a nontrivial process to switch the NMOS channel from silicon to germanium.
6.2 Further work

This section presents several possible directions to take in order to follow on from this work.

6.2.1 Switching Co-Implant Species

The technique of co-implant in germanium could be further investigated by changing the species type. There are two promising species that can be used, which are nitrogen (N₂) and Tin (Sn). Tin might have a significant impact on phosphorus activation and diffusion due to the effect of strain. Further reduction of diffusion could be observed by using N₂ than N due to more formation of vacancy trap. The crucial part of using co-implant technique is to determine the dose and implant energy.

6.2.2 Optimising the Experimental Technique

1. Capping the sample before implantation process

   It was shown that hot implant has the highest out diffusion during the implantation process. Therefore, it is suggested that the substrate is capped before the implantation process in order to avoid out diffusion. As a result, higher activation could be observed with the hot implant.

2. Using ultra fast and high temperature anneal

   For the cold implant, it is suggested to use ultra fast and high temperature anneal such as laser or flash lamp annealing. This is because at high annealing temperature and shorter time; higher phosphorus activation and minimum diffusion could be achieved from the cold implant technique.

3. Optimise the implant temperature

   A suggested experimental study is to implant phosphorus at several elevated temperature. Consequently, optimum implant temperature could be determined in order to get higher phosphorus activation.

4. Using Micro Hall Effect (MHE) and micro four-point probe (M4PP)

   These instruments need to be used in order to characterise the dopant with shallow implant energy as it was proved that the conventional Hall measurement could not characterise it.

6.2.3 Alternative Substrates

Germanium-Alloy on Silicon substrate is alternative substrates due to higher carrier mobility [101-102] than the carrier in the Germanium on Silicon substrate. Therefore, this research could be further investigated using this alternative substrate.
References


[86] "Accent HL5900PC Hall profiler system, user manual, issue 2.0, 2001."