Oxidation of relaxed Si$_{0.5}$Ge$_{0.5}$ alloy by Zhang Jing-Ping

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dedicated to my loving parents -

my mother QIN Xi-Zhen
and
my father ZHANG Jiu-Ziao

- who did not live to see this thesis
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ABSTRACT

Oxidation is a fundamental process in the fabrication of microelectronic devices and in order to promote the incorporation of SiGe into Si technology we have investigated the thermal oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy ($y$=0.5) at high temperatures (mainly 900°C and 1000°C) using Rutherford backscattering spectroscopy, infrared transmission spectroscopy and X-ray photoelectron spectroscopy. It has been observed that three distinct regions form during oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy, which are (I) a mixed oxide layer Si$_{0.5}$Ge$_{0.5}$O$_2$, (II) a pure SiO$_2$ layer and (III) a Si$_{1.25}Ge_y$ ($y$=0.5) alloy layer. These are formed during both wet and dry oxidation when the sample is not preheated, whilst only two regions (II) and (III) form when the sample is preheated in a non oxygen ambient up to the oxidation temperature prior to oxidation. Enhancement of the rate of wet oxidation of SiGe compared with bulk Si and the accumulation of Ge in region III just below SiO$_2$ layer (region II) has also been observed. This behaviour is in good agreement with other results, however, some abnormal behaviour during wet and dry oxidation has been observed. The rate of oxidation during short wet oxidations (15 minutes) of Si$_{0.5}$Ge$_{0.5}$ decreases as the oxidation temperature increases from 800°C to 1000°C for 15 minutes, which has not been previously reported. A reduced rate of oxidation of Si$_{1.25}Ge_y$ ($y$=0.5) in a dry environment has been observed and is discussed.

In order to investigate the thermodynamics of the oxidation process new experiments have been carried out which involve the synthesis of a buried oxide layer, by O$^+$ implantation followed by a high temperature anneal. The implanted oxygen atoms preferentially bond to silicon atoms and the oxygen atoms are found to bond to germanium atoms only after all of the silicon atoms are fully oxidised. Germanium tends to be rejected from the growing oxide during a subsequent higher temperature (>900°C) anneal.

The different behaviour of the Si and Ge atoms during both thermal and internal oxidations is described in terms of the thermodynamics and kinetics of the SiGe alloy system. There are three important conclusions which emerge from these analyses: (i) in order to adequately control the composition of thermal oxides (T>800°C) grown on Si$_{0.5}$Ge$_{0.5}$ material it is necessary to preheat the samples in a non oxidising atmosphere prior to oxidation. By so doing the entrapment of Ge in the near surface layer (region I) is inhibited; (ii) during the initial stage of dry oxidation the process is described by the reaction Si+O$_2$→SiO$_2$ and we suggest that the rate is controlled by the availability of oxygen atoms and is numerically the same as for bulk Si; (iii) in contrast, during the initial stage of wet oxidation, the process is described by the reaction Si+2OH→SiO$_2$+H$_2$ and the rate is controlled by the areal density of Si atoms, which we propose is high due to the weak Si-Ge binding energy and thus an enhanced oxidation rate occurs.
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LIST OF PARAMETERS

1. General parameters

T  temperature (°C)

t  time (hour or minutes)

M  atomic mass

M_1 atomic mass of the incident particle (He⁺ in this experiment)

Z  atomic number

Z_1 atomic number of the incident particle (He⁺ in this experiment)

2. Parameters for RBS

θ  scattering angle in the laboratory system (θ=180°-θ₁,θ₂)

θ₁ incident angle

θ₂ reflected angle

σ_R  Rutherford differential cross section

x  total thickness of the target (nm)

x_i the thickness from the surface to the i^th layer

(Nx) areal density (atoms/cm²)

K_M kinetic recoil factor from the element M, for example, K_O, K_Si and K_Ge represent the kinetic recoil factors from O, Si and Ge, respectively

E₀ incident energy of the incident ion (MeV or keV)

ΔE_i energy loss of the incident ion in its incoming path to a depth x_i (keV)

E_i the energy (keV) of the incident ion at the depth x_i
$E_{x,0}(M)$ scattered energy (keV) of the incident ion from element $M$ at a depth $x$, and out of the target, for example, $E_{x,0}(O)$, $E_{x,0}(Si)$ and $E_{x,0}(Ge)$ are energies of He$^+$ ion scattered from O, Si and Ge, which are located on the surface and $E_{x,0}(O)$, $E_{x,0}(Si)$ and $E_{x,0}(Ge)$ are the energies of He$^+$ ion scattering from O, Si and Ge, which are located at depth $x$ and out of the target.

$\Delta E_{x,0}(M)$ energy loss (keV) of the incident ion on its outward path after scattered from element $M$, which is located at a depth $x$.

$\Delta E(M)$ energy width (keV) of the signal in the RBS spectrum from element $M$, for example, $\Delta E(O)$, $\Delta E(Si)$ and $\Delta E(Ge)$ are used in this thesis.

$\delta E$ channel width (keV/channel)

$H$ yield-counts/channel

$H_x(E_i)$ yield, signal from element $M$ at a depth $x$, for example, $H_x(E_i)$ is the yield of the Si signal, which is located on the surface.

$A(M)$ Area - total number of counts under peak of element (M), for example, $A(O)$, $A(Si)$ and $A(Ge)$ are used in this thesis.

$[S]$ backscattering energy loss factor (eV/cm)

$\varepsilon$ backscattering stopping cross section (eV/atoms/cm$^2$)
EXPOSITION

This thesis is laid out in a logical manner with numbers being used to specify the sections, figures, tables and equations. For example, figure 4.11 is the 11th figure in chapter 4, table AI.2 is the second table in Appendix I, equation 3.24 is the 24th equation in chapter 3, section 6.1.1.2 is the section 1.1.2 in chapter 6 and equation AII.20 is the 20th equation in Appendix II. All cross referencing in this thesis will be based upon this system without explicitly specifying the Chapter or Appendix.
Silicon and germanium are two of the most useful semiconductor materials. According to the phase diagram, a solid solution of Si$_{1-y}$Ge$_y$ (0 < y < 1) can be formed with any desired composition with a band-gap which can be interpolated between the values for Si (1.1 eV) and Ge (0.7 eV) [1]. Improvements in epitaxial technology, which occurred during the 1980's, have made it possible to grow pseudomorphic SiGe alloy layers on a silicon substrate with good crystallinity and electronic properties [2,3] by using either chemical vapour deposition (CVD) or molecular beam epitaxy (MBE).

In recent years, the growth of SiGe/Si heterostructures has been extensively studied because of the desire to develop improved and novel devices such as high-frequency transistors [4], metal-oxide-semiconductor (MOS) field effect devices [5], resonant tunnelling diodes [6] and infrared photo detectors [7]. The successful introduction of SiGe material into a device fabrication process requires that structures incorporating this alloy retain many of the positive features of silicon. An important characteristic of Si is the existence of a stable high quality oxide (SiO$_2$) and in order to exploit this feature the oxidation of Si has been a topic of extensive study since the 1960's. The availability of the masking oxide, prepared by high temperature oxidation of the semiconductor, led to the development of planar technologies enabling small device structures with precisely controlled dimensions to be fabricated. Integrated MOS circuit technology is made possible because of the ease of growth and high quality of the oxide and the oxide/Si interface. In addition, the presence of an oxide film controls the electrical properties at the semiconductor surface and plays an important role in MOS field effect devices. For these reasons it would be desirable to be able to grow a good quality thermal oxide on SiGe alloy in order to fully exploit the properties of this alloy semiconductor and to facilitate its incorporation in Si based device technologies.

Some studies of the oxidation of SiGe have been published since 1987 [8-45] and all of the reports show that the oxidation is a complicated process with the behaviour very much
depending upon the composition and thickness of the alloy as well as the oxidation
temperature, time, environment (wet versus dry) and pressure. The grown structures have
been variously reported as \((\text{Si}_{1-y}\text{Ge}_y)O_2\) or \((\text{GeO}_2)^+\text{SiO}_2\) or \(\text{SiO}_2\) depending upon the
concentration of Ge in the alloy and the growth conditions.

It has been reported that the presence of small quantities of Ge in Si alters the oxidation
behaviour \([8,9,16,17,18]\). It was shown that the rate of oxidation of SiGe is higher than
that of bulk Si during wet oxidation \([8-18, 21,37]\), whereas during dry oxidation, the rate is
the same as that of bulk Si \([16, 17, 20,27]\) or even slower \([27,38]\). The enhancement of the
wet oxidation rate has been attributed to the presence of the Ge, which acts as a catalyst
\([8-18, 21,22]\). Two main mechanisms have been proposed to explain the catalytic effect of
Ge: (i) weaker Si-Ge bonds as compared with Si-Si \([8,9,18,40]\) and (ii) the presence of a
Ge rich layer at the interface of the oxide/alloy which suppresses the injection of Si
interstitials \((\text{Si}_{\text{int}})\) during wet oxidation so causing the oxidation rate to be increased
\([15,16,17]\). Other models have also been proposed which involve point defect injection
\([8,12,15]\), the creation of excess defects \([8,11,15]\) or the presence of metastable GeO
\([15,21]\). Although these and other models appear to explain some of the observed
behaviour during oxidation, it seems that the descriptions are incomplete and occasionally
ambiguous. For dry oxidation, due to the lack of experimental data, the behaviour of the
oxidation of SiGe is not yet clear.

This project involved a detailed comparative investigation of the behaviour of thick
\((>300\text{ nm})\) layers of relaxed \(\text{Si}_{1-y}\text{Ge}_y\) alloy \((y\approx0.5)\) during wet and dry oxidation at different
temperatures for various times. Internal oxidation by \(\text{O}^+\) implantation is also presented. For
reference purposes, the oxidation of bulk Si has been carried out simultaneously. The
emphasis of the experiments is to achieve an understanding of the fundamental physics
rather than demonstrating specific applications to devices. The study has served to generate
experimental results and to answer some specific questions and to provide a better insight
into the processes involved.

The analytical techniques of Rutherford backscattering spectroscopy (RBS), X-ray
photoelectron spectroscopy (XPS) and infrared transmission spectroscopy (IR) have been
used in this study.
The thesis is divided into nine chapters including this introduction. The basic concepts of Si oxidation, including the Deal Grove model [46], and ion beam synthesis of SiO₂ in bulk Si and Ge oxidation and ion beam syntheses of GeO₂ are presented in Chapter 2. A literature survey of SiGe oxidation including thermal oxidation (wet and dry), rapid thermal oxidation (wet and dry), high pressure oxidation, plasma oxidation, and ion beam oxidation is given in Chapter 3. Chapter 4 is divided into two parts. Chapter 4a describes the experimental details including sample preparation and the analytical techniques-RBS, IR and XPS. Emphasis will be placed on the interpretation of RBS data, for which the author has developed a methodology to calculate the depth profiles for a ternary system as shown in Chapter 4b. Chapters 5 and 6 show the experimental results of wet and dry oxidation, respectively. A first study of internal oxidation using high dose O⁺ implantation is addressed in Chapter 7. The kinetics and mechanisms for these three types of oxidation are discussed in Chapter 8. Finally, in Chapter 9 discussions of the conclusions presented in the Chapters 5, 6 and 7 are summarised and also some suggestions for further work are indicated. The samples used in this experiment are listed in detail in Appendix I and the basic principles of RBS are presented in Appendix II.
CHAPTER 2

BACKGROUND - THE THERMAL OXIDE BINARY SYSTEM

2.1 Introduction

Thermal oxidation is one of the most basic process steps in the fabrication of silicon devices and consequently this subject has been investigated for almost forty years. The main features and basic mechanisms involved in the oxidation of silicon were outlined in a paper by Deal and Grove (1965) [46]. Several reviews on the oxidation of Si which contain detailed discussions with extensive references are given by Irene (1988) [47], Mott et al (1989) [48] and Stoneham (1991) [49]. Detailed accounts of the physics and technology of SiO₂ have been given by Nicollian and Brews (1982) [50] and by Balk (1988) [51]. The developments in this area have been reviewed in the proceedings of the Biennial European Conference on Insulating Films on Semiconductors (INFOS), the latest of which was edited by P Balk et al (1993) [52]. In contrast to Si, Ge oxidation has not been widely investigated because of its unfavourable properties for device manufacture.

2.2 Thermal oxidation of bulk Si

Oxidation of Si is essential to planar device processing which in turn is the foundation of silicon integrated microelectronics. Various methods of oxidising silicon produce oxides with good electronic properties and low interface state densities. The methods commonly used at atmospheric pressure are oxidation in dry O₂ (dry oxidation) and oxidation in O₂ plus steam (wet oxidation) or in steam (steam oxidation). The chemical reactions that are involved in these methods are the following [46, 53]:

\[
\text{Dry oxidation:} \quad \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \tag{2.1}
\]

\[
\text{Wet oxidation:} \quad \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2 \tag{2.2}
\]
The key physical processes in the oxidation of bulk silicon are (i) mass transport and (ii) interfacial reaction. Deal and Grove [46] proposed that the rate of growth of the first few monolayers of oxide is controlled by these reactions but as the oxide grows thicker it becomes necessary for one of the reactants to be transported through the already existing oxide. This oxidation model is shown schematically in figure 2.1. According to this model the transported species, oxygen, must go through three stages:

(i) transport from the bulk of the oxidising gas to the oxide-gas interface when the flux is $F_1$ and the concentration of oxygen is $C_0$,

(ii) transport across the oxide film towards the silicon substrate when the diffusion flux is $F_2$,

(iii) chemical reaction at the oxide/silicon interface to form further $\text{SiO}_2$ when the flux is $F_3$ and the concentration of oxygen is $C_1$.

This oxidation model was formulated by Deal-Grove in the following equations:

\[ x^2 + Ax = B (t + t_0) \]  

(2.3)
\[ x = \frac{A}{2} \left[ \left(1 + \frac{t + t_0}{A^2/4B} \right)^{1/2} - 1 \right] \]  

(2.4)

where \(x\) is the thickness of the oxide at a given time \(t\) and the quantity \(t_0\) corresponds to a shift in the time coordinate which corrects for the presence of an initial oxide layer \(x_0\) \((x = x_0, t = 0)\). \(A\) and \(B\) are constants which depend upon the particular set of oxidation conditions. It assumes two regimes for the oxidation process: (i) an initial linear regime \((t << A^2/4B)\), where the thickness \(x\) of the oxide layer is a linear function of oxidation time \(t\) and (ii) a parabolic regime for larger values of \(t\) \((t >> A^2/4B)\), where \(x\) varies with \(t^{1/2}\). The oxidation rate in the linear regime is controlled by the reaction at the Si-SiO\(_2\) interface, whilst in the parabolic regime it is controlled by diffusion of the oxidant through the oxide layer. Experiments show both the linear rate constant \((B/A)\) and parabolic rate constant \((B)\) to be temperature dependent.

Deal-Grove [46] assumed that oxidation proceeds by the inward movement of the oxidant rather than by the outward movement of a species of silicon. The moving oxidant is assumed [46] to be molecular oxygen \((O_2)\) in the case of dry oxidation and undissociated water \((H_2O)\) in the case of wet oxidation. The hydrogen is released at the Si-SiO\(_2\) interface and diffuses out of the specimen. Subsequently, Mott (1987) [54] has proposed that the diffusing species is not \(H_2O\) but a neutral pair, namely, \(H_3O^+ + OH^-\) in the case of wet oxidation. Jorgensen (1962) [55] has studied the effect of an electric field during dry oxidation. The experimental arrangement and the plot of the data obtained are shown in figure 2.2 (a) and (b). An electric field applied across the oxide layer during oxidation enhances the rate of oxidation, if the field is applied so that the silicon is positive with respect to the oxide-gas interface. Oxidation is retarded when the electric field is applied so that the silicon is negative with respect to the oxide-gas interface (as shown in figure 2.2). These observations lead to the conclusion that the diffusing species in the case of dry oxidation is the superoxide ion \(O_2^-\) described by Deal-Grove [46, 55]. Unfortunately, this experiment has been questioned by many authors [47,48,56,57]. Raleigh (1966) [56] has pointed out that the early experimental studies of Jorgensen (1962) appear to be distorted by platinum electrode effects. Later Modlin et al (1985) [57] indicated that the rate of oxidation is enhanced if the oxide is positive related to the silicon; negative voltages have
Figure 2.2 (a) The experimental arrangement for studying the effect of an electric field on the oxidation of silicon. (b) A plot of the thickness of the oxide film versus time [55].
only marginal effects.

Experimentally it has been found that the presence of water vapour greatly increases the rate of oxidation by as much as an order of magnitude, compared with dry oxidation. There are two main reasons for this phenomenon: firstly, the activation energy of diffusion is in the range of 0.7-0.78 eV for H$_2$O [58] whilst it is ~1.2 eV for O$_2$ [59] and, thus, H$_2$O diffuses more rapidly than O$_2$. Secondly the bond energy of H-O (110.6 kcal/mol) [60] is weaker than that of O-O (298 kcal/mol) [60] and, thus, the reaction of H$_2$O with Si as expressed in equation 2.2 is easier than that of O$_2$ with Si, described in equation 2.1. Although several models have involved other moving species of oxidant a full understanding of the details of the oxidation of silicon is still lacking.

2.3 Ion beam synthesis of SiO$_2$ in Si

An alternative method of forming SiO$_2$ by ion beam synthesis is now being successfully employed to form buried dielectric SiO$_2$ layers. The technology is known by the acronym SIMOX (Separation by IMplanted OXygen) [61-63]. Preparation of SIMOX substrates is a two stage process; firstly, a high dose of O$^+$ ions is implanted of the order of $10^{18}$O$^+$cm$^{-2}$ to synthesise the buried layer of oxide and then a very high temperature anneal is used to annihilate lattice defects and achieve segregation of oxygen and the formation of the buried layer of SiO$_2$ with abrupt Si/SiO$_2$ interface. Hemment et al [61] have reported that with high dose O$^+$ implantation and optimum annealing temperature it is possible to achieve a buried dielectric (SiO$_2$) layer with very abrupt Si/SiO$_2$ and SiO$_2$/Si interfaces, which can be used for device applications. There are many published works discussing SIMOX. Recent review papers on this topic can be found in references 62 and 63. The behaviour of implanted metallic impurities in SIMOX has been studied by several authors [64,65] who have proposed that the observed segregation of the metallic impurities is due to a thermodynamic driving force arising from differences in the enthalpies of formation of the relevant oxides. Kilner (1990) [65] found that those elements with a large positive enthalpy of formation with respect to SiO$_2$ are strongly segregated. A plot of the enthalpies of formation of several oxides is shown in reference 65. The data is normalised to the value per oxygen molecule, with the heat of formation of SiO$_2$ (7.3 eV) set to zero. This relative
plot is shown in figure 2.3 where it can be seen that the elements with large positive enthalpies relative to SiO\(_2\), such as copper, palladium and silver are the strongly segregating elements in Si. In contrast, the elements with a comparable enthalpy of formation to that of SiO\(_2\), like boron or titanium, do not appear to be segregated. In a related experiment Celler et al (1988) [66] have demonstrated that precipitation of dopants implanted into SiO\(_2\) is common for group V elements, as represented by phosphorus, arsenic and antimony. Germanium, a representative of group IV, also precipitates but boron from group III probably does not.

2.4 Oxidation of bulk Ge (thermal and internal)

Oxide films of GeO\(_2\) and GeO grown on the surface of germanium are interesting due to their optical properties. In contrast to SiO\(_2\) thermal germanium oxide GeO\(_2\) is very hygroscopic and readily dissolves in water. Albers et al (1966) [67] have produced an amorphous oxide film with a composition of approximately GeO\(_2\) at around 500°C. A dielectric layer of composition GeO\(_2\) was grown by Canina et al (1960) [68] using anodic oxidation at room temperature and these authors found that at higher temperatures the film tends to become oxygen deficient. Sladkova (1968) [69] has studied the growth of Ge oxide on a germanium substrate at temperatures ranging from 450°C to 600°C. This author demonstrated that at temperatures above 525°C, the thickness of the oxide film increases linearly with the square root of time. The oxide produced on germanium at temperatures exceeding 600°C is a white-grey film upon which ellipsometric measurements are impossible to perform. The same white-grey film also found for longer oxidation times when lower temperatures were employed. Although Ge, unlike Si, does not have a stable dioxide, Crisman (1982) [70] and Grigory et al (1986) [71] reported that it was possible to form GeO\(_2\) by diffusion of oxygen at high pressures (>100 atm) and elevated temperatures (500°C-600°C). A different approach has been used by Hymes et al (1988) [72]. They grew a germanium oxide layer by thermal oxidation at 600°C which was subsequently nitrided in flowing ammonia NH\(_3\) at the same temperature. The resulting oxynitride films are insoluble in water.

The first synthesis of Ge oxide by oxygen ion implantation into single crystal Ge was by
Figure 2.3 Values of standard enthalpy changes for impurity oxides relative to that of SiO₂ (in eV/oxygen molecule) [65].
Stein in 1974 [73] who was attempting to obtain a stable insulating GeO$_2$ film. However, the ion doses were not enough to form a stoichiometric oxide layer. Sjoreen et al (1988) [74] have subsequently reported that Ge samples implanted with O$^+$ to a dose of up to $2 \times 10^{18}$ cm$^2$ show no change during anneal temperatures up to 550°C. At a higher temperature (650°C) the buried layer was annihilated and all that remained was a damaged Ge substrate with little or no oxygen. The formation of GeO$_2$ glasses by ion implantation of oxygen into Ge at an energy of 180 keV with a dose of $2 \times 10^{18}$ cm$^2$ has been reported by Ravindra et al (1990) [75]. They found that oxygen implantation into Ge at 250°C leads to the formation of a buried layer of GeO$_2$. These authors believed that the heating of the Ge wafer under these implantation conditions could possibly supply the necessary heat for the formation of the GeO$_2$. Zhang et al (1990) [76] have stated that a stoichiometric oxide GeO$_2$ layer could be formed using O$^+$ ion implantation at 45 keV with a dose of $1.5 \times 10^{18}$ cm$^2$ at a temperature of about 400°C. Reflectivity measurements indicate that this Ge implanted material shows potential as an efficient solar cell.
CHAPTER 3

LITERATURE SURVEY OF PUBLISHED WORK
RELEVANT TO THIS PROJECT

3.1 Introduction

It is highly desirable to be able to grow a high quality dielectric on SiGe for incorporation in semiconductor devices and consequently there have been many investigations of the oxidation of SiGe. The first reported study was on (111) bulk SiGe by Balk [77] in 1971, but very few reports can be found covering the period 1972-1986 [78,79]. With the development of new layer growth techniques such as MBE and CVD it is now possible to grow epitaxial alloy layers of good crystallographic quality and, as a consequence in recent years, there has been an increasing number of studies made of the oxidation of SiGe using several different oxidation methods. These methods include thermal (dry and wet) [8-18, 22-28, 34-42], rapid thermal (dry and wet) [20,21], high pressure [14,24], plasma [19,35], and ion beam [29-33,41,46] oxidation. In this literature survey the emphasis will be placed on publications appearing since 1987, as these are the most relevant to the experiments described in this thesis.

3.2 Previous studies of SiGe oxidation

The first group of experiments [8,9] were carried out using steam oxidation of Si (100) substrates at 900°C and 1000°C for various times, which were implanted with Ge⁺ ions to achieve various alloy compositions. The thicknesses of the oxide layers were in the range of 80 nm to 400 nm. The oxidation rate of the implanted samples started at the same rate as observed for bulk (non-implanted) Si and then increased with increasing Ge content. The authors proposed that the effect was due either to a decrease in the constant A or an increase in the value of B/A in the Deal-Grove model (equation 2.3). The formation of a Ge rich layer beneath the advancing oxidation front, but with no uptake of Ge in the oxide, was observed by RBS measurements [8,9]. Based on a calculation of the amount of silicon consumed during the oxidation process these authors suggested that one full monolayer of
Ge was "snowploughed" by the oxidation front. They proposed that the increased oxidation rate was related to the lower binding energy of Si-Ge, which is expected to be comparable with the Ge-Ge binding energy of 42 kcal/mol [8], which is much lower than the Si-Si binding energy (76 kcal/mol) [8]. A further study of Ge implanted Si by Srivatsa et al. (1989) [18] confirmed the above results during steam oxidation and showed that the enhancement of the oxidation rate is more pronounced at 900°C than at 1000°C. These authors supported the speculation that the increase in the oxidation rate is due to the lower energy required to break Si-Ge bonds compared to Si-Si bonds. Details of the temperature-time (T-t) profile during oxidation was not reported by these researchers.

Steam oxidation of strained epitaxial (100) Si$_{1-y}$Ge$_y$ ($y = 0, 0.06$ and $0.12$) layers at 800°C was investigated by Patton et al. (1988) [11]. A large difference in oxidation behaviour between samples containing 0 and 6% Ge was found whilst only a small difference was observed between 6% and 12%. Several interesting features were reported in their study. These include an initial enhancement of the oxidation rate, an absence of Ge in the oxide and the accumulation of Ge in front of the moving oxide/SiGe interface. These authors attributed the absence of GeO$_2$ to the difference in the energy of formation of SiO$_2$ and GeO$_2$. It was also proposed that the accumulation of Ge at the interface might inhibit Ge oxidation and might influence the oxidation rate. When this Ge rich layer was fully formed, little further enhancement of the Si oxidation rate was found. Patton [10] pointed out that the reduction of the enhancement of the rate was difficult to explain if the rate was controlled by the weak binding energy of Si and Ge, as proposed by Holland et al. [8,9]. Patton et al. [10] suggested more complex phenomena to explain the enhancement of the oxidation rate of SiGe, namely strain enhanced diffusion, modified interface conditions and electronic effects.

A comparison of dry O$_2$ and steam oxidation of Si$_{1-y}$Ge$_y$ (for $y \leq 0.20$) using rapid thermal processing has been investigated by Nayak et al (1990) [19,20]. For oxidation in dry O$_2$ at 905°C and 1010°C they found that the oxidation rate was indistinguishable from that of bulk Si. For wet oxidation at 870°C, it was found that the oxidation rate of the alloy was significantly higher than that of bulk Si, particularly in the initial phase of oxidation. The oxidation rate was found to increase with the Ge concentration. It was also found that the
enhancement of the oxidation rate decreased with oxidation time. These authors proposed that Ge acted as a catalyst in that it was neither oxidised nor incorporated into the growing SiO₂ film. They proposed that the Ge promoted the decomposition of H₂O or Si-OH molecular bonding during wet oxidation. The GeO formed in this process was less stable than SiO₂ and was subsequently replaced by Si to form Ge and SiO₂. The formation of SiO₂ via the catalytic action of Ge went in parallel with the formation of the SiO₂ by the direct reaction of Si with the oxidant (as in bulk Si). The catalytic effect increased the reaction rate of Ge with H₂O, but not with O₂. These authors disagreed with the idea of a weaker binding energy causing the observed enhancement during wet oxidation because the dry oxidation rate of SiGe did not show a similar behaviour.

A very thorough study, using an extremely thin (5 nm) epitaxial Si₀.₅Ge₀.₅ layer as a marker, was carried out by LeGoues et al (1988, 1989) [15,16,17] who investigated the mechanism of the oxidation of SiGe alloys. Again, different oxidation rates during dry and wet oxidation were observed and, in addition, it was found that in both processes the concentration profile (but not the position) of Ge remained completely unchanged during oxidation. Ge did not diffuse into the substrate but moved in front of the oxide/alloy interface. The marker experiment was also performed in wet N₂ when an enhanced rate and some loss of Ge was observed during the initial stage of oxidation. Oxidation of alloy material was also carried out in wet N₂, further diluted with N₂, in order to achieve an oxidation rate typical of dry oxidation. Under these circumstances equal growth rates of oxide were found for the alloy and pure Si. These authors were against the idea that the lower strength of the Si-Ge bond caused the fast wet oxidation rate. LeGoues et al [15,16,17] speculated that the Ge rich layer suppressed the formation of Si interstitials during oxidation and thus enhanced the oxidation rate. Since dry oxidation was slower than wet oxidation, the suppression of interstitial formation would only affect the wet oxidation process whilst during dry oxidation the formation and diffusion of interstitials would not be the rate limiting factor. In support of their hypothesis LeGoues et al [15,16] proposed that the existence of Ge suppressed the observed oxidation enhanced diffusion of boron in Si, where Si interstitials are known to play an important role.

Using a UHV system LeGoues et al (1989) [16] also studied the initial phase of the
oxidation of clean surfaces. Enhancement of the rate was observed when 1 nm of oxide was obtained. Again they proposed that the enhancement of the wet oxidation rate was due to the suppression of the injection of interstitials by the presence of Ge.

A study of ultraviolet ozone induced oxidation of epitaxial (111) Si$_{1-y}$Ge$_y$ ($y = 0$, 0.06, 0.22, 0.5 and 1) has been reported recently by Agarwal et al (1993) [40]. They indicated that the rate of UV/ozone-induced oxidation at room temperature increased by a factor of ~2 even in the absence of Ge segregation. Agarwal et al attributed this increased oxidation rate to a locally increasing Ge concentration coupled with the relative ease of breaking Si-Ge bond compared to Si-Si bond, which supported the proposal made by Holland et al [8,9].

The oxidation of SiGe alloy with higher compositions (25% to 75%) was studied by Eugene et al (1991) [23] who found a thinner oxide layer on Si$_{0.75}$Ge$_{0.25}$ alloy than that on bulk Si after wet oxidation for 8 hours. For a shorter time (45 minutes) oxidation was faster for Si$_{0.75}$Ge$_{0.25}$ alloy than for bulk Si. For samples of composition Si$_{0.50}$Ge$_{0.50}$ and Si$_{0.25}$Ge$_{0.75}$ the oxidation rate was about 1.6 and 6 times that of bulk Si, respectively. In these two alloys both Ge and Si oxide were formed during the initial period when a mixed oxide layer was obtained. During shorter oxidation times no Ge pile up was observed but during prolonged oxidations, the oxidant supply was sufficiently slow (diffusion limit) to allow only the oxidation of Si. In this case, a second layer formed consisting of pure SiO$_2$ with Ge accumulation below the oxide layer. Eugene [22] pointed out that the oxidation behaviour of thin films of SiGe alloy was strongly related to the balance between oxidation kinetics and diffusion kinetics. At low Ge concentrations, the rate of oxidation was enhanced by the presence of Ge and enough Si could be provided to the interface resulting in fast initial oxidation and the formation of pure SiO$_2$. In alloys containing 50% to 75% Ge atoms, the rate of diffusion of Si to the oxide/alloy was slower than the rate of oxidation with the consequence that Ge was trapped in the oxide layer.

The above mentioned balance between diffusion and oxidation implies that when the oxidation rate is speeded up there will be a certain temperature when both Ge and Si will be oxidised and Ge accumulation will be prevented. This was observed during high pressure oxidation by Pain et al (1991) [25]. They studied the oxidation of approximately 200 nm
thick alloy layers of Si$_{1-y}$Ge$_y$ ($y = 0.05, 0.116$ and $0.17$) in O$_2$ at 550°C and at a pressure of 680 atmospheres and found that Ge was incorporated in the oxide with a reduction or elimination of Ge accumulation at the interface. A similar effect was found by Vancauwenbergh (1991) [26] during the oxidation of Si$_{1-y}$Ge$_y$ ($y=0.20$) alloy by O$^+$ implantation and during oxidation in an electron cyclotron resonance oxygen plasma by Li (1992) [35].

Liu et al (1992) [36,37] have studied the wet oxidation of Si$_{1-y}$Ge$_y$ ($y = 0.36$ or $0.28$) at 700°C and 1000°C. Before oxidation the samples were preheated in flowing nitrogen. It was found that a pure SiO$_2$ layer is formed and Ge piles up at the oxide/alloy interface during oxidation at 1000°C. However, at 700°C the oxide layer included Ge and consisted of a mixed oxide SiO$_2$+GeO$_2$. They suggested the reason for the different oxidation formation at 700°C and 1000°C was due to the balance between the oxidation rate and diffusion rate of Ge and Si. At a higher temperature (1000°C) the diffusion of Ge and Si was faster than the oxidation velocity. They pointed out that as thermodynamics control the reaction only SiO$_2$ is formed. At lower temperatures Ge and Si are relatively immobile compared to the motion of the oxidation front when Ge and Si are uniformly oxidised.

Munukutla et al (1991) [27] have observed a very different behaviour during dry oxidation of strained and relaxed Si$_{0.8}$Ge$_{0.2}$ films at 800°C. They found that the oxidation rate of a strained film is 10 - 20% faster than that of bulk Si whilst for a relaxed film the oxidation rate decreases by 60%. The reason for this unexpected result is not clear though these authors do suggest that it may be related to the strain in the thick alloy. It is noted that we have reported the retard oxidation rate during dry oxidation of thick Si$_{0.5}$Ge$_{0.5}$ (1992) [38] and further experimental data will be shown in sections 6.1.1 and 6.2.1.

Hall et al (1989) [19] have reported oxidation by plasma-anodisation of SiGe alloys. The results were rather different from thermal oxidation at low temperature (525°C or 550°C). Using Auger they found a large Ge concentration at the top surface of the oxide film. The Ge concentration within the oxide was below the sensitivity limit of the technique and no significant Ge pile up at the interface of oxide/alloy was observed. These authors suggested that Ge reached the surface of the oxide as a positive ion driven by the electric field which
is present during anodisation. The state of the bonding of this Ge was not identified. This phenomenon supports the idea that the oxidation can be affected by an electric field [55].

In a recent paper Tsutsu et al (1994) [45] investigated wet oxidation of poly-SiGe alloys with a Ge concentration ranging from 5% to 30% at temperatures from 700°C to 1000°C. They reported that oxidation of poly-SiGe films differs from that of single crystal SiGe in the following ways: (i) at 800°C or above, the oxide thickness is almost independent of Ge concentration; (ii) Ge piles up below the oxide due to the rejection of Ge from the oxide during the oxidation, which suggests that Ge diffuses into poly-SiGe layer; (iii) during a 700°C oxidation, Ge is rejected from the oxide layer for low concentration films (≤15% Ge) whilst for high Ge concentration films (>20% Ge), some Ge is incorporated in the oxide at an atomic concentration considerably lower than the Ge concentration in the original poly-SiGe. Their explanation is that the oxidation rate is controlled by the diffusion of the oxidising species through the oxide. The more rapid diffusion of Ge along grain boundaries away from the oxide/poly-SiGe interface limits the amount of Ge incorporated into the oxide to a lower value than is found in oxidised single crystal SiGe.

Rai et al (1992) [37] reported a study of the wet oxidation of amorphous SiGe layers at 800°C and 900°C. They found that Ge is rejected from the growing oxide and the amorphous structure crystallises to form an epitaxial SiGe layer at 900°C. When oxidation was performed at 800°C, Si and Ge were incorporated into the oxide and no epitaxial SiGe was observed.

Most of the above mentioned studies were based on thermal oxidation. In general, it has been found that thermal oxidation of SiGe alloy has the same oxidation mechanism as bulk Si, namely oxygen diffuses through the oxide layer where it reacts with the substrate at the oxide/alloy interface. Therefore, the oxidation rate is not only dependent upon the particular set of oxidation conditions but also varies with the composition of the alloy. As a consequence it is difficult to define unique values to the growth constants (linear constant B/A and parabolic constant B), unlike bulk Si. However, although several models have been reported to explain the behaviour during oxidation it seems that a complete description of the oxidation of the SiGe system is not yet available.
CHAPTER 4a
EXPERIMENTAL DETAILS

This chapter contains detailed information about the experiments. The sample structures and the preparation of the samples are described in section 4.1 whilst thermal oxidation (wet and dry) and internal oxidation are presented in sections 4.2 and 4.3, respectively. A complete list of all wafers and specimens together with experimental conditions are included in table 4.1. Complete details of the specimens used for the oxidations are given in tables AI.1, AI.2 and AI.3, respectively.

4.1 Layer growth and sample preparation

The relaxed Si$_{1-y}$Ge$_y$ (y=0.5) layers used in this study were specified by the author and were grown on 3 inch diameter (100) Si n-type (ρ=5-20 Ω-cm) substrates by colleagues in the Department of Physics, University of Warwick using a VG Semicon V80 Molecular Beam Epitaxy (MBE) instrument. Growth was carried out at 570°C [80], being measured by a thermocouple placed behind the sample in a conventional vacuum system, with a base pressure of 2x10$^{-11}$ Torr. Silicon and germanium were evaporated from an electron gun evaporator and effusion cell, respectively, and the beam flux in both cases was monitored using a quartz crystal oscillator. Four alloy wafers have been used in this research, as listed in table 4.1. Firstly, wafer #1 consisted of a 300 nm Si buffer layer upon which Si$_{0.5}$Ge$_{0.5}$ material was grown to form an essentially relaxed layer of thickness 320 nm. Secondly, wafer #2 consisted of a Si buffer layer with 900 nm of Si$_{0.5}$Ge$_{0.5}$ and a 75 nm Si cap. Thirdly, wafer #3 consisted of a Si buffer layer with 435 nm of Si$_{0.45}$Ge$_{0.55}$ alloy. The last wafer #5 consisted of a Si buffer layer with 570 nm of Si$_{0.57}$Ge$_{0.43}$ alloy. The thickness x and composition y of the alloy were determined by RBS analysis as described in Appendix II. Wafer #4 was a bulk (100) Si n-type wafer (ρ=5-20 Ω-cm) and was used as a control.

Samples were cleaved from the wafers into about 5x5 mm$^2$ or 6x12 mm$^2$ pieces using a diamond scribe. After cleaving, each sample was cleaned in acetone and isopropyl alcohol.
Table 4.1 Description of samples and methods of oxidation

<table>
<thead>
<tr>
<th>Wafer number</th>
<th>Structure (y)</th>
<th>Thickness (x) of SiGe layer (nm)</th>
<th>Method of oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Si&lt;sub&gt;1.5&lt;/sub&gt;Ge&lt;sub&gt;y&lt;/sub&gt; &lt;br&gt; Si&lt;sub&gt;sub&lt;/sub&gt; -</td>
<td>320 &lt;br&gt; -</td>
<td>Wet and dry</td>
</tr>
<tr>
<td>#2</td>
<td>Si&lt;sub&gt;1.3&lt;/sub&gt;Ge&lt;sub&gt;y&lt;/sub&gt; &lt;br&gt; Si&lt;sub&gt;sub&lt;/sub&gt; -</td>
<td>75 &lt;br&gt; 900 &lt;br&gt; -</td>
<td>Wet and internal (O&lt;sup&gt;+&lt;/sup&gt; implantation)</td>
</tr>
<tr>
<td>#3</td>
<td>Si&lt;sub&gt;1.5&lt;/sub&gt;Ge&lt;sub&gt;y&lt;/sub&gt; &lt;br&gt; Si&lt;sub&gt;sub&lt;/sub&gt; -</td>
<td>435 &lt;br&gt; -</td>
<td>Dry</td>
</tr>
<tr>
<td>#4</td>
<td>Bulk Si &lt;br&gt; Si -</td>
<td>-</td>
<td>Wet and dry</td>
</tr>
<tr>
<td>#5</td>
<td>Si&lt;sub&gt;1.5&lt;/sub&gt;Ge&lt;sub&gt;y&lt;/sub&gt; &lt;br&gt; Si&lt;sub&gt;sub&lt;/sub&gt; -</td>
<td>570 &lt;br&gt; -</td>
<td>Internal oxidation &lt;br&gt; (RBS Ternary system analysis)</td>
</tr>
</tbody>
</table>

in an ultrasonic bath then thoroughly rinsed in distilled and deionised water. Before thermal treatment the samples were dip etched in 10% HF for 10 seconds and rinsed thoroughly in distilled and deionised water. Finally, 99.99% purity flowing nitrogen gas was used to dry the samples.

4.2 Thermal treatment and thermal oxidation

The thermal treatments were carried out using a horizontal open tube furnace in the Microfabrication Laboratory, University of Surrey. The temperature of the furnace was measured using a Pt-Rh (13%) thermocouple. The small samples were placed side by side on a 2 inch clean Si wafer, which was then placed in a quartz carrier. When the equilibrium temperature of the tube furnace was reached, the gas (nitrogen from BOC with a purity of 99.99%) was introduced into the tube with a flow rate of 1 litr/minute and after a further 5 minutes the samples were inserted into the hot zone. The carrier was pushed smoothly into the furnace in ~1 minute. At the end of the thermal treatment the carrier was removed from the hot region in ~30 seconds. The time for a sample to reach the equilibrium
temperature at 1000°C has been measured as 7~8 minutes.

Both wet and dry oxidation were carried out using oxygen gas from BOC with a purity of 99.99%. The wet oxides were grown at 700°C, 800°C, 900°C and 1000°C during times ranging from 5 minutes to 1 hour whilst dry oxides were grown only at 900°C and 1000°C for 1 hour to 24 hours. The wet ambient was achieved by passing oxygen gas, with a flow rate of 1 litre/minute at atmospheric pressure, through water heated to a temperature of 95°C and then into the wet oxidation furnace tube. Dry oxidation was carried out in flowing dry oxygen, also with a flow rate of 1 litre/minute at atmospheric pressure, in an adjacent tube dedicated to dry oxidation. The oxygen flow was turned on for 5 minutes and then the samples were pushed into the furnace in a time estimated to be 3 seconds. At the end of oxidation the samples were quickly pulled out of the centre of the hot zone and completely withdrawn in 30 seconds. Full details of the oxidation temperatures and times are shown in tables AI.1 (i) and (ii) for wet oxidation and AI.2 (i) and (ii) for dry oxidation experiments.

Preheating

Selected samples were preheated in a non oxidising ambient (flowing nitrogen) for 15 minutes at the oxidation temperature prior to wet or dry oxidation. After the 15 minutes preheat, when the samples had reached the (pre-set) equilibrium temperature, the oxygen gas was turned on whilst the nitrogen flow was turned off. At the end of the oxidation time the samples were withdrawn as described above.

4.3. Internal oxidation - O⁺ ion implantation

In the case of internal oxidation, the capped alloy wafers #2 and #5 were used for all of the experiments when a buried oxide layer was formed by O⁺ ion implantation using the 500keV Heavy Ion Accelerator in the D.R.Chick Accelerator Laboratory, University of Surrey. The oxide layers were synthesised using 400 keV O₂⁺ ions, which disassociated to give 200 keV atomic ions, with doses of 0.6x10¹⁸ O⁺/cm², 1.2x10¹⁸ O⁺/cm² and 1.8x10¹⁹O⁺/cm², hereafter referred to as low, medium and high doses (table AI.3), respectively. The choice of ion energy and layer thicknesses ensured that the majority of
implanted oxygen ions (projected range $R_p=380$ nm) came to rest in the alloy layer for wafer #2. The kinetic energy of the ion beam was used to achieve beam heating of the wafers, which were clamped onto small silicon tips with thin stainless steel springs. Conduction losses from the wafer were small and an equilibrium temperature of about 500°C could be achieved by adjusting the beam current.

In this experiment the average total beam current incident upon the sample was 58 µA which heated the wafer to a temperature of about 500°C. Lateral uniformity of the implanted dose was achieved by electrostatic beam scanning at frequencies of 61 Hz and 380 Hz in the horizontal and vertical directions, respectively. The implanted area was defined by a silicon aperture with an area of $2.5 \times 2.5 \text{ cm}^2$ mounted in front of the wafer. When the O$^+$ dose reached $0.6 \times 10^{18}$ O$^+$/cm$^2$ the wafer was moved laterally ~1.25 cm and a further dose of $1.2 \times 10^{18}$ O$^+$/cm$^2$ was implanted. By this means an area of $3.7 \times 2.5 \text{ cm}^2$ with three different doses namely $0.6 \times 10^{18}$ O$^+$/cm$^2$, $1.8 \times 10^{18}$ O$^+$/cm$^2$, and $1.2 \times 10^{18}$ O$^+$/cm$^2$ was obtained at the centre of the 3 inch diameter wafer. During implantation secondary electron suppression was employed to prevent the secondary electrons adding to the beam current and giving a false reading. This was accomplished by biasing a suppresser electrode to -300V with respect to earth. Selected samples, as listed in table A1.3, were subsequently annealed at 800°C, 900°C and 1000°C for 1 hour in flowing nitrogen at atmospheric pressure (see section 4.2).

4.4 Rutherford backscattering spectrometry

All the samples were studied by RBS analysis to determine the layer thicknesses (hence oxide growth rates), the redistribution of Ge during thermal oxidation and the volume concentration of Si, Ge and O.

4.4.1 Rutherford backscattering spectrometry system set up

The 2 MV Van de Graaff accelerator in the D. R. Chick Accelerator Laboratory was used for the RBS analysis. The major components and layout of the RBS system are shown schematically in figure 4.1. Typically, the Van de Graaff accelerator provides a $^4$He$^+$ ion beam with an energy of 1.5 MeV (or 2 MeV), which is selected by a magnetic analyser.
Figure 4.1 Schematic diagram of the backscattering spectrometry system.
The $^4\text{He}^+$ beam is collimated using a pair of analysis slits and two apertures. Additionally the beam could be electrostatically steered in the horizontal and vertical directions. The He$^+$ ion beam current on the sample is typically 20-25 nA with a beam spot diameter of 1 mm. Energy analysis of the backscattered He$^+$ ion is achieved using an Ortec system consisting of a surface barrier detector, charge to voltage preamplifier and pulse shaping spectroscopy amplifier. The detector is at a scattering angle of $\theta=160^\circ$ ($\theta=180^\circ-\theta_s$ as shown in figure 4.1, where the direction of the He$^+$ ion beam is normal to the surface of the sample). The amplitude of the signal (pulse) from the amplifier is proportional to the energy of the backscattered particle. The pulse train due to the incident He$^+$ ions is converted into an energy spectrum using a multichannel analyser and the data is stored and handled by a computer. The system energy resolution is about 15 keV. The scattering chamber and beam line were maintained at a vacuum of the order of $\sim 10^{-6}$ Torr.

The samples to be analysed were mounted on a stainless steel target holder, which would accept about 7-10 specimens. The sample holder was mounted vertically on a motor driven goniometer with two axes of rotation providing tilt in two planes (theta and phi). The goniometer includes a translational movement to position the samples sequentially on the beam axis. To standardise the spectrum, the integrated charge Q is set to 10 $\mu$C, which is determined by integrating the current incident on the sample. Secondary electron suppression is achieved by biasing the sample plate to +250 V with respect to earth. During data collection the sample is rocked, between -6$^\circ$ and -8$^\circ$ to the normal direction, in the two tilt directions in order to restrict spectral distortions due to channelling of the He$^+$ ions and to achieve a good random spectrum.

4.4.2 Calibration of the Rutherford backscattering spectrometry system

The desired RBS spectrum is accumulated by recording the amplitude of each pulse (proportional to the kinetic energy of the back scattered $^4\text{He}^+$) and storing it in an appropriate channel width $\delta E$ at energy $E_i,0(M)$ (figure AII.2). The energy calibration of the spectrum must be established experimentally and this has been done using reference samples, namely 3 nm of Au on Si, bulk Ge and 320 nm of SiO$_2$ on Si. Figure 4.2 shows a
Figure 4.2 A series of RBS spectra from (a) SiO$_2$ on Si, (b) bulk Ge and (c) Au on Si.
series of RBS spectra of (a) SiO₂ on Si, (b) bulk Ge and (c) Au on Si. These spectra are displayed as a histogram showing the number of backscattered He⁺ ions (yield), which are recorded by the detector as a function of their channel number (energy). The surface positions of O, Si and Ge, where He⁺ ions backscattered from, are defined by the half yield positions of the leading edges of the O, Si and Ge signals. The gold position was defined by the peak position of the gold signal in the channel number (see figure 4.2). They are listed in table 4.2 column 4. The surface position of each element is related to the energy \( E_{0,M} = K_M E_0 \) (equation (AII.1)) of He⁺ ions which are scattered from element M located at the surface of the target. From the known kinetic recoil factor of \( K_M \) (equation (AII.2)) and the incident He⁺ ion energy \( E_0 \) (=1.5MeV in this experiment) the energy of the backscattered ions \( K_M E_0 \) can be calculated (equation (AII.1)), as listed in table 4.2. A plot of the energy of the backscattered ions (ordinate) against channel number (abscissa) is shown in figure 4.3.

Table 4.2 Backscattered energy and channel number of 1.5 MeV He⁺ ions scattered from O, Si, Ge and Au

<table>
<thead>
<tr>
<th>Element</th>
<th>( K_M ) (for ( \theta=160^\circ ))</th>
<th>( E_{0,M} ) (keV)</th>
<th>Channel number</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.3709</td>
<td>556</td>
<td>181</td>
</tr>
<tr>
<td>Si</td>
<td>0.5732</td>
<td>860</td>
<td>279</td>
</tr>
<tr>
<td>Ge</td>
<td>0.8073</td>
<td>1211</td>
<td>393</td>
</tr>
<tr>
<td>Au</td>
<td>0.9242</td>
<td>1386</td>
<td>448</td>
</tr>
</tbody>
</table>

The plot shows a linear dependence where the gradient represents the energy interval (\( \delta E \)) per channel, which has a value of 3.10 keV/channel determined using a least squares fitting routine. As discussed in Appendix II the abscissa of the spectrum can be converted into an energy scale and then to a mass scale using the experimental value of the channel width determined from figure 4.3.

4.4.3 Data reduction

From an exact analysis of the RBS spectra it is possible to obtain quantitative information regarding the concentration depth profile of each element. In order to determine the layer thicknesses and their compositions, it is necessary to define the position of the surface for
Figure 4.3 A plot of the backscattered energy versus channel number of 1.5 MeV He$^+$ ions at 160° backscattering angle.
each constituent element and the area under the spectrum. Figure 4.4 (a) shows an RBS spectrum from an oxide layer grown on SiGe alloy (w001, table A1.1 (i)). It is a complicated curve due to the overlap of the signals, associated with the finite thicknesses of the Si, O and Ge profiles. As pointed out in Appendix II and figure 4.3 the channel number scale can be converted to an energy scale which is shown in figure 4.4 (a) (upper abscissa). The experimental surface positions of Si, O and Ge in the channel number, which are indicated by the arrows, agree well with their expected positions on the energy scale. The channel number scale is able to be converted to a depth scale, via the energy scale, as individually illustrated in figure 4.4 (a) for each element.

The spectrum shown in figure 4.4 (a) contains six specific features identified as I to VI. Regions I, III and IV are Si signals from the Si substrate, Si in the SiGe alloy and Si in the oxide layer, respectively. The oxygen, which is accommodated in the oxide layer, is represented by region II, which overlaps the continuous spectrum of the Si substrate. The broad peak labelled region V corresponds to Ge in the SiGe alloy, whilst region VI is due to Ge in the oxide. From the depth scale it can be seen that region VI contains an enhanced Ge signal at the surface and at greater depth there is a decrease in Ge signal. This region is related to the Si signal in region IV at the same depth. The decreasing Ge signal (yield deficiency) in region VI corresponds to the increase in the Si signal in region IV. This is due to a decreasing Ge concentration and an increasing Si concentration with increasing depth. The increasing Ge signal in region V just beneath region VI and peak 'k', which is followed by a decrease at greater depths (between ~300nm to 400 nm), are mirrored in the Si signal which shows an initial decrease, dip 'e', and a further increase over the same range (300 nm to 400 nm). The changes in the RBS yield indicate that the region just beneath the oxide is rich in Ge. The oxygen signal (region II) is constant with depth indicating that the oxygen concentration is constant.

In order to determine the compositions and the layer thicknesses, it is necessary to define areas under the spectrum and the position of the surface for each constituent element. Figure 4.4 (b) illustrates the equivalent area of each part of the Si and Ge signals, which are obtained by integrating under the curve between channel numbers 213 to 240 for region III and 240 to 300 for region IV and channel numbers 300 to 361 for region V and 361 to 400 for region VI, respectively. Figure 4.5 shows the low energy part of the spectrum taken
Figure 4.4 Data reduction of RBS spectra. (a) RBS spectrum from an oxide grown on SiGe alloy during wet oxidation at 1000°C for 5 minutes. (b) Equivalent area of each part of the spectrum signal, which is obtained by integrating under the curve.
Figure 4.5 Subtraction of the oxygen signal from the continuous spectrum of the Si substrate.
from figure 4.4 which contains the O signal. In order to subtract the oxygen signal (region II) from the Si signal (region I), a spectrum from bulk Si (the solid line in figure 4.5) was used as a reference and was fitted to the Si substrate signal (region I) as shown in figure 4.5. The reason for using experimental data from bulk Si instead of a theoretical curve is to achieve a better fit to the experimental data. The yield $H_{0i}(E_i)$ from the $i$th layer can be approximately obtained by subtracting $H_{si}$ from $H_{s0}$. The area $A(O)$ under the oxygen signal can be obtained by integrating the yield $H_0(E_i)$ between channel numbers 146 to 186, thus $A(O) = \sum H_0(E_i)$. By using the method discussed in chapter 4b the RBS spectrum with three elements can then be fully described. The density of $\text{Si}_{1-x}\text{Ge}_x\text{O}_2$ has been taken to be $2.1 \times 10^{22}$ $\text{Si}_{1-x}\text{Ge}_x\text{O}_2$ molecules/cm$^3$ [37] which is close to the density of $\text{SiO}_2$ namely $2.2 \times 10^{22}$ $\text{SiO}_2$ molecules/cm$^3$ [37].

An alternative method of interpreting the data is to simulate the RBS spectrum using computer software. Figure 4.6 (lower section) includes a spectrum (open circle) from sample d411 (see table A1.2 (i)). The Si, Ge and O signals are difficult to separate due to the thick SiGe alloy layer. The computed curve from the RBS simulation is included in the figure as a solid line. The test sample (input data) was divided into 10 layers for this simulation and the concentration depth profiles for O, Si and Ge are shown in the upper section of figure 4.6.

4.5 Infrared transmission spectroscopy

Selected samples were analysed by IR transmission spectrometry to investigate the chemical bonding of O to Si and Ge in the oxidised samples formed both by thermal and internal oxidation. IR measurements were achieved using a Perkin-Elmer 577 Grating Spectroscopy in the Department of Chemistry, University of Surrey. Infrared radiation over the wavenumber range between 4000 cm$^{-1}$ to 200 cm$^{-1}$ was generated by a voltage-stabilised air cooled tungsten-halogen lamp with a quartz envelope. The detector was TriGlycine Sulfate (TGS). The transmission spectra were plotted by a chart recorder over the wave number range 4000 cm$^{-1}$ to 200 cm$^{-1}$. Reference samples were prepared from the same wafers before oxidation to obtain the background signal.
Figure 4.6 Lower, the RBS spectra from sample d411 (open circle) and an RBS simulate spectrum (solid curve). Upper, the concentration depth profile of the constituent elements used for the simulation.
Figure 4.7 shows an IR transmission spectrum from a 150 nm thick dry oxide grown on bulk Si (sample d006 in table A.II.2(i)). The spectrum contains three characteristic Si-O-Si absorption bands [81,82] at wavenumbers of 1075 cm\(^{-1}\) (stretching vibration), 800 cm\(^{-1}\) (bending vibration) and 460 cm\(^{-1}\) (rocking mode) as indicated in the figure. The position and the full width at half maximum (FWHM) of the peaks are the two important parameters which indicate the quality of the SiO\(_2\) films. For example, the 1075 cm\(^{-1}\) band is associated with the Si-O-Si bond angle, \(\theta\), which is the angle between adjacent SiO\(_4\) tetrahedra and is a measure of the Si-Si distance which relates directly to the separation of tetrahedra and hence the SiO\(_2\) density. The higher the wavenumber, the smaller \(\theta\) is and hence the shorter the Si-Si distance and the higher the film density. The peak position is easily determined from the position of the minima. In order to define the FWHM, it is necessary to define a straight line as a base from which the half height can be determined as shown in the figure. In this figure the FWHM of the stretching band is about 80 cm\(^{-1}\), which is an average value as reported in the literature [81,82].

4.6 X-ray photoelectron spectroscopy

The electronic states of Si and Ge in the oxide layers were determined using XPS. For the O\(^+\) implanted samples the XPS was carried out using a VG Scientific ESCALAB MkII system with an X-ray source of Al K\(\alpha\) radiation (1486.6 keV) in the Department of Material Science, University of Surrey. Depth profiles were achieved using Ar\(^+\) sputtering with a target current of 15 \(\mu\)A. Additional samples, which were thermal oxides, were analysed using a PHI 550 spectroscopy with a Mg K\(\alpha\) (1253.6 eV) X-ray source at the Institute of Semiconductors, Chinese Academy of Sciences, Beijing.

Figure 4.8 shows XPS spectra of the Si 2p core-level from sample d004 (table A.I.2 (ii)), which were recorded from different depths namely (i) within the SiO\(_2\), (ii) at the SiO\(_2\)/Si interface and (iii) in the Si substrate. It can be seen from the figure that the Si 2p peak shifts from 102.8 eV, which corresponds to Si\(^{4+}\), to 98.6eV, which corresponds to Si\(^0\) when the spectrum originates from the oxide layer and Si substrate, respectively. The signal from the SiO\(_2\)/Si interface contained both Si\(^{4+}\) and Si\(^0\) components as indicated by the dashed lines.
Figure 4.7 The three Si-O-Si absorption bands in the IR transmission spectrum from SiO₂.
Figure 4.8 The XPS spectra of the Si 2p core-level from SiO$_2$ grown on a Si substrate.
CHAPTER 4b
INTERPRETATION OF RBS DATA - TERNARY SYSTEM

The basic concept of RBS is described in Appendix II, which concerns the interpretation of spectra from samples containing two elements. In practice the spectra may be more complicated as samples often contain three or more different elemental species, for example, there are three elements, Si, Ge and O in samples generated in the present experiment. In order to achieve a direct and accurate interpretation of spectra from these latter samples the author has refined and generalised the method reported by Chu et al (1978) [83] to interpret spectra from samples containing three elemental species of widely different mass.

The procedure for interpreting the spectrum can be described by reference to figure 4.9 (a), which gives a schematic diagram of the backscattering geometry and notation, and figure 4.9 (b), a 2 MeV $^4$He$^+$ ion RBS energy spectrum from wafer #5 (Si$_{0.35}$Ge$_{0.47}$/Si) implanted with 200keV O$^+$ ions to a dose of $1.2 \times 10^{18}/\text{cm}^2$. Assuming the material consists of $A_mB_nC_p$ with a thickness $x$, where the labels A, B, and C are used to denote the constituent elements, for example, A for Si, B for Ge and C for O whilst $m$, $n$, and $p$ represent the composition for each element in figure 4.9(b), the spectrum can be recorded with the $^4$He$^+$ particles of incident energy $E_0$ at an angle of $\theta_1$ (usually in the experiment $\theta_1=0$) and scattered from the surface at a backscattering angle of $\theta$. The incident particles, the back scattered particles and the normal to the sample are all contained on one plane, so that the scattering angle in the laboratory frame of reference is given by $\theta=180^\circ-\theta_1-\theta_2$, where $\theta_1$ and $\theta_2$ are the angles between the sample normal and the direction of the incident beam and of the scattered particle, respectively (figure 4.9 (a)).

From equation AII.1 and as shown schematically in figure 4.9 (a) it can be seen that the incident particles scattered from the surface have energies $E_{q_0}(A)=K_AE_0$, $E_{q_0}(B)=K_BE_0$ and $E_{q_0}(C)=K_CE_0$. As the particles penetrate the target, there is an energy loss $dE/dx$. 

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Figure 4.9 (a) Schematic diagram of the backscattering geometry and notation.
(b) 2 MeV $^4$He$^+$ ion RBS energy spectrum from a SiGe alloy (wafer #5) implanted with 200keV O$^+$ to a dose of $1.2 \times 10^{18}$/cm$^2$. 
Figure 4.9 (a) illustrates that the energy immediately before scattering at a depth $x_i$ is $E_i$, where the energy loss along the incoming path is $\Delta E_i = E_0 - E_i$ and the energy after backscattering becomes $K_A E_i$, $K_B E_i$ and $K_C E_i$.

Additionally, the particles lose energies $\Delta E_{i0}(A)$, $\Delta E_{i0}(B)$ and $\Delta E_{i0}(C)$ along the outward path and emerge from the target with the energies $E_{i0}(A)$, $E_{i0}(B)$ and $E_{i0}(C)$, respectively. The essence of concentration depth profiling is to relate a spectrum yield (height) $H(E_i)$ to a slab of material of thickness $\delta x_i$ at a depth $x_i$ as illustrated in figure 4.9 (a). For an integrated charge, $Q$, of He$^+$ particles and detector solid angle, $\Omega$, the spectrum height, $H$, at energy $E_i$, which corresponds to a certain depth $x_i$, is given in equation (4.19) as:

$$H_A(E_i) = \frac{\Omega Q(m_i)\sigma_A(E_i)\delta(K_A E_i)}{[K_A e^{\text{mat}}(E_i)/\cos\theta_1 + e^{\text{mat}}(K_A E_i)/\cos\theta_2] \cos\theta_1}$$ (4.1)

$$H_B(E_i) = \frac{\Omega Q(n_i)\sigma_B(E_i)\delta(K_B E_i)}{[K_B e^{\text{mat}}(E_i)/\cos\theta_1 + e^{\text{mat}}(K_B E_i)/\cos\theta_2] \cos\theta_1}$$ (4.2)

$$H_C(E_i) = \frac{\Omega Q(p_i)\sigma_C(E_i)\delta(K_C E_i)}{[K_C e^{\text{mat}}(E_i)/\cos\theta_1 + e^{\text{mat}}(K_C E_i)/\cos\theta_2] \cos\theta_1}$$ (4.3)

The composition at depth $x_i$ is

$$A_{m_i} B_{n_i} C_{p_i}$$

where by definition the total composition of the species is 100%,

$$m_i + n_i + p_i = 1$$ (4.4)

From equation (4.1) we have

$$\Omega Q = \frac{H_A(E_i) [K_A e^{\text{mat}}(E_i)/\cos\theta_1 + e^{\text{mat}}(K_A E_i)/\cos\theta_2] \cos\theta_1}{\sigma_A(E_i)(m_i)\delta(K_A E_i)}$$ (4.5)

By substitution of equation (4.5) into equations (4.2) and (4.3) we obtain
\[ H_b(E_i) / H_A(E_i) = [\sigma_b(E_i) / \sigma_A(E_i)][n/m]F_1 \]  
(4.6)

\[ H_c(E_i) / H_A(E_i) = [\sigma_c(E_i) / \sigma_A(E_i)][p/m]F_2 \]  
(4.7)

where

\[ F_1 = \frac{\left\{ [K_a e^{\text{mat}}(E_i) / \cos \theta_1 + e^{\text{mat}}(K_a E_i) / \cos \theta_2] \delta (K_b E_i) \right\} }{\left\{ [K_b e^{\text{mat}}(E_i) / \cos \theta_1 + e^{\text{mat}}(K_b E_i) / \cos \theta_2] \delta (K_a E_i) \right\} } \]  
(4.8)

\[ F_2 = \frac{\left\{ [K_c e^{\text{mat}}(E_i) / \cos \theta_1 + e^{\text{mat}}(K_c E_i) / \cos \theta_2] \delta (K_b E_i) \right\} }{\left\{ [K_b e^{\text{mat}}(E_i) / \cos \theta_1 + e^{\text{mat}}(K_b E_i) / \cos \theta_2] \delta (K_c E_i) \right\} } \]  
(4.9)

The values of \( F_1 \) and \( F_2 \) are generally very insensitive to the composition of the target and the collision energy \( E_0 \). To illustrate this point, the values of \( F_1 \) and \( F_2 \) were calculated for the matrix values \( m:n:p \), which varied from 1:1:0-4:1:8 over the typical range of collisional energies \( E_0 \) of 1000 keV to 2000 keV. Figure 4.10 (a) and (b) shows plots of the \( F \) values as a function of the energy: (a) \( F_1 \) and \( F_2 \) from 1000 keV to 1600 keV, whilst (b) from 1400 keV to 2000 keV. In general, the collisional energies span the range from 2000 keV to about 1700 keV for \( E_0 = 2000 \) keV and 1500 keV to 1200 keV for \( E_0 = 1500 \) keV. From figure 4.10 average values have been taken and within an error of less than 2% are \( F_1 = 0.93 \) and \( F_2 = 1.08 \) for \( E_0 = 2000 \) keV and \( F_1 = 0.90 \) and \( F_2 = 1.14 \) for \( E_0 = 1500 \) keV, respectively. For simplification these values have been substituted into equations (4.6) and (4.7). By using equations (4.4), (4.6) and (4.7) the composition of each element at depth \( x_i \) can be obtained by

\[ m_i = 1/[R_1/G_1 + R_2/G_2 + 1] \]  
(4.10)

\[ n_i = [R_1/G_1] / [R_1/G_1 + R_2/G_2 + 1] \]  
(4.11)

\[ p_i = [R_2/G_2] / [R_1/G_1 + R_2/G_2 + 1] \]  
(4.12)

where

\[ R_1 = H_b(E_i) / H_A(E_i) \]  
(4.13)

\[ R_2 = H_c(E_i) / H_A(E_i) \]  
(4.14)

and

\[ G_1 = [\sigma_b(E_i) / \sigma_A(E_i)]F_1 \]  
(4.15)

\[ G_2 = [\sigma_c(E_i) / \sigma_A(E_i)]F_2 \]  
(4.16)
Figure 4.10 A plot of the values of $F_1$ and $F_2$ as a function of energy:
(a) for a $1500\text{keV}$ analysing $^4\text{He}$ beam and
(b) for a $2000\text{keV}$ analysing $^4\text{He}$ beam.
It is known \cite{83, 97} that \( \sigma_n(E_i)/\sigma_a(E_i) \approx [Z_p/Z_A]^2 \), \( \sigma_n(E_i)/\sigma_a(E_i) \approx [Z_p/Z_A]^2 \) and \( F_i \) and \( F_j \) have the values calculated above. In order to determine the composition of the target (\( m_i \), \( n_o \), and \( p_j \)), it is necessary to compare the yield height \( H_{\alpha}(E_i) \), \( H_{\beta}(E_j) \) and \( H_{\gamma}(E_\epsilon) \) at the same incident energy \( E_{\text{in}} \), namely at the same depth \( x_i \) (equations (4.10) to (4.16)). A simple but very helpful procedure is to obtain \( E_i \) as a function of \( E_{\text{in}} \) and \( E_\text{0} \) as described by Lever (1976) \cite{84}. He assumes that the ratio, \( \alpha \), of the energy lost along the outgoing path, \( \Delta E_{\text{out}} \), to that lost along the incoming path, \( \Delta E_{\text{in}} \), is independent of depth, so that \( \alpha=\Delta E_{\text{out}}/\Delta E_{\text{in}}=\text{constant} \) \cite{83, 84}. This simplification has been adopted in this analysis. From figure 4.9 (a) it is clear that \( \Delta E_{\text{out}}=K_mE_i-E_{\text{in}} \) and \( \Delta E_{\text{in}}=E_\text{0}-E_i \) and the ratio is \( \alpha=[K_mE_i-E_{\text{in}}]/[E_\text{0}-E_i] \) when the value of \( E_i \) is given by

\[ E_i=[E_{\text{in}}+\alpha E_\text{0}]/[K_m+\alpha] \]  

(4.17)

An approximate value for \( \alpha \) can be determined from the surface energy approximation

\[ [E_\text{0}-E_i]/[\sigma(E_\text{0})]=x/\cos\theta, \text{ and } [K_mE_i-E_\text{0}]/[\sigma(K_mE_\text{0})]=x/\cos\theta _2 \] \cite{83, 84}

\[ \alpha\approx[\sigma(K_mE_\text{0})/\sigma(E_\text{0})]\beta \]  

(4.18)

and  

\[ \beta = \cos\theta_1/\cos\theta_2 \]  

(4.19)

In the present case, the scattering from atoms of Si, Ge and O at a depth \( x_i \) is illustrated in figure 4.9 (a). Particles scattered from different elements have a different energy loss and the ratio \( \alpha \) is different

\[ \alpha\approx[\sigma(K_mE_\text{0})/\sigma(E_\text{0})]\beta \]  

(4.18a)

\[ \alpha\approx[\sigma(K_mE_\text{0})/\sigma(E_\text{0})]\beta \]  

(4.18b)

and  

\[ \alpha\approx[\sigma(K_mE_\text{0})/\sigma(E_\text{0})]\beta \]  

(4.18c)

The energy \( E_i \) at a depth \( x_i \) is

\[ E_i = [E_{\text{in}A}(A)+\alpha\alpha_0 E_\text{0}]/[K_\alpha+\alpha_\alpha] \]  

(4.20)

\[ E_i = [E_{\text{in}B}(B)+\alpha_\beta E_\text{0}]/[K_\beta+\alpha_\beta] \]  

(4.21)

\[ E_i = [E_{\text{in}C}(C)+\alpha_\gamma E_\text{0}]/[K_\gamma+\alpha_\gamma] \]  

(4.22)
In the present experiment, the values of $\alpha$ are 1.28, 1.30 and 1.09 for $\alpha_{Si}$, $\alpha_{O}$ and $\alpha_{Ge}$, respectively.

In order to construct the composition profiles of elements A, B and C, it is necessary to define a yield $H_{ij}(E_j)$ for element B (figure 4.9 (b)) at a depth $x_i$ where the backscattering ions have the energy $E_{i0}(B)$. The composition of the sample then depends upon the determination of the yield $H_{iA}(E_j)$ and yield $H_{iC}(E_j)$ for elements A and C at the same depth, where the backscattering ions have energy $E_{i0}(A)$ and $E_{i0}(C)$. From equations (4.20) to (4.22) which can be calculated as

\[
E_{i0}(A) = \left[ E_{i0}(B) + \alpha_B E_{i0} \right] \left[ K_A + \alpha_A \right] / \left[ K_B + \alpha_B \right] - \alpha_A E_{i0}
\]

(4.23)

\[
E_{i0}(C) = \left[ E_{i0}(B) + \alpha_B E_{i0} \right] \left[ K_C + \alpha_C \right] / \left[ K_B + \alpha_B \right] - \alpha_C E_{i0}
\]

(4.24)

The energy scale for the RBS spectrum can be converted to the collision energy $E_i$ as indicated in figure 4.9 (b). From equations (4.1)-(4.3) and (4.10)-(4.16) the composition in each layer can be determined, whilst the thickness $\delta x_i$ of the layer can be calculated using the RBS formula presented in equation AII.11 or AII.12. Thus,

\[
\delta x_i = \left[ E_{i0}(B) - E_{i+1,0}(B) \right] / \left\{ N_{m}e^{\text{max}(E_i)/\cos \theta_1} + e^{\text{max}(K_B E_i)/\cos \theta_2} \right\}
\]

(4.25)

By using this analytical method the Si, Ge and O composition depth profiles can be calculated. As an example, figure 4.11 (a) shows a series of RBS spectra from samples (i14a, i14c and i14b in table A1.3) implanted with 200 keV O$^+$ to doses of $0.6 \times 10^{18}$ O$^+$ cm$^2$ (curve i), $1.2 \times 10^{18}$ O$^+$ cm$^2$ (curve ii) and $1.8 \times 10^{18}$ O$^+$ cm$^2$ (curve iii), respectively. Figure 4.11 (b) shows the composition profiles of O, Si and Ge in the samples calculated using the computer programme DEPTH based upon the above discussion, which was written by the author. The results, labelled (i), (ii) and (iii) in figure 4.11 (b) show the evolution of the oxygen profile and redistribution of Si and Ge with increasing dose. The mean projected range ($R_p$) of around 390 nm was determined from the data shown in figure 4.11 (b) and is in good agreement with the value of 380 nm calculated using TRIM [98].
Figure 4.11 (a) 2000keV He\(^+\) ion RBS spectra from Si\(_{0.57}\)Ge\(_{0.43}\) alloy (wafer #5) implanted with 200keV O\(^+\) to doses of (i) 0.6x10\(^{18}\)/cm\(^2\), (ii) 1.2x10\(^{18}\)/cm\(^2\) and (iii) 1.8x10\(^{18}\)/cm\(^2\). (b) The composition profiles calculated from the RBS spectra in (a).
CHAPTER 5

EXPERIMENTAL RESULTS - I
THERMAL OXIDATION - WET

The purpose here is to report experimental studies of the wet oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy and to compare the grown layers with a thermal oxide grown on bulk Si in terms of the oxidation rate and composition. In addition, the thickness and composition of oxides grown on Si$_{0.5}$Ge$_{0.5}$ alloy with and without preheating are also included in this chapter. The redistribution of Ge, composition and the thickness of the oxides have been characterised by using Rutherford backscattering spectroscopy (RBS). The formation of an oxide has been confirmed by X-ray photoelectron spectroscopy (XPS) and Infrared transmission spectroscopy (IR).

5.1. Experimental data - Rutherford backscattering spectrometry

The samples used to study wet oxidation are listed in table AI.1 (i) and in this section the experimental RBS spectra from wafer #1 (Si$_{0.5}$Ge$_{0.5}$/Si), wafer #2 (Si/Si$_{0.5}$Ge$_{0.5}$/Si) and wafer #4 (bulk Si) after wet oxidation are presented.

Figure 5.1 (a) and (b) shows RBS spectra from wafer #4 oxidised at 1000°C for 20 minutes and 45 minutes (w009 and w015 in table AI.1 (i)), respectively. For reference and to facilitate data reduction, the spectrum from bulk Si before oxidation is plotted, as a solid line, in the figure.

The open diamond curves in figure 5.2 (a), (b), (c) and (d) show typical RBS spectra from samples: w008, w011, w014, and w017, all from wafer #2, after oxidation at 1000°C for various times, respectively. The surface positions (see table 4.4) of O, Si and Ge are indicated in the figure. Also shown as a reference is the spectrum (solid line) from a sample before oxidation. In this spectrum the signals from Si and Ge within the Si$_{0.5}$Ge$_{0.5}$ matrix lie between channel numbers 138-267 and 226-380, respectively and as a consequence of the thickness of the SiGe layer the Si signal partially overlaps the Ge signal between channel numbers 226 and 267. The peak 'S', superposed upon the Ge signal between channel numbers 267-279, is due to the Si capping layer. A comparison of the curves in figure 5.2
Figure 5.1 RBS spectra from bulk Si (wafer #4) after wet oxidation at 1000°C for (a) 20 minutes (b) 45 minutes (solid line - before oxidation).
Figure 5.2 RBS spectra from Si capped wafer #2, Si/Si$_x$Ge$_{1-x}$/Si$_{sub}$, after oxidation at 1000°C for (a) 20 minutes, (b) 35 minutes, (c) 45 minutes and (d) 1 hour, (solid line - before oxidation).
before and after oxidation shows that the peak 'S' vanishes whilst the oxygen signals, labelled 'o' which overlap the silicon signals, grow. The width of the oxygen signal 'o' increases and the front edge of the Ge signal shifts to lower energy from channel numbers ~380 to ~315 with increasing oxidation time.

Figure 5.3 shows the spectra from samples w001, w004 and w013, which were oxidised at 1000°C for 5 (open circle), 10 (full circle), and 45 (open diamond) minutes. Figure 5.4 (a), (b), (c) and (d) shows a series of RBS spectra from samples: w007, and w010, w013 and w017, (table A1.1 (i)). For reference the spectrum from a sample before oxidation is also presented as a solid line in these two figures (figures 5.3 and 5.4). As an example the spectrum from the sample oxidised for 5 minutes (open circle curve in figure 5.3) has been interpreted in section 4.4.3. Spectra from samples oxidised for 10 minutes to 1 hour are shown in figures 5.3 and 5.4 and it is evident that the area of peak 'p', which constitutes part of the Ge signal is almost constant. This peak 'p' in figure 5.4 is located in region I. The absence of the Ge signal in region II (figure 5.4) between peaks 'p' and 'g' is due to the rejection of Ge from the oxide. The width of region II increases with increasing oxidation time. The accumulation of Ge (peak 'g' in figure 5.3) below the oxide/alloy interface is evident after 5 minutes oxidation and the accumulation increases with increasing oxidation time (>10 minutes) as shown by the increase in height of peak 'g' in figure 5.3. However, after oxidation for 20 minutes the area under this peak is unchanged as the area of peak "g" is constant (figure 5.4).

From the channel width for the O signal it is possible to determine the thickness of the oxide layer. By measuring the appropriate yields or integrating the yield under the signals, the composition of the oxide, alloy and areal density of Ge, which is trapped just beneath the surface, can be calculated using the method described in chapter 4b and Appendix II. The results are listed in tables 5.1, 5.2 and 5.3 for samples #4, #2, and #1, respectively.

5.2. Growth rate of the oxides

The thicknesses of the wet oxide layers grown at 1000°C versus time for the three wafers #1, #2 and #4 are shown in figure 5.5. For all wafers the thickness of the oxides increases with increasing oxidation time. Compared to bulk Si (#4) the thickness of the oxide layer

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Figure 5.3 RBS spectra from wafer #1 Si$_{0.5}$Ge$_{0.5}$/Si$_{um}$ after wet oxidation at 1000°C for 5 (open circle), 10 (full circle), and 45 (open diamond) minutes and, also, before oxidation (solid line).
Figure 5.4 RBS spectra from uncapped wafer #1 Si$_{0.3}$Ge$_{0.7}$/Si$_{hub}$ after wet oxidation at 1000°C for (a) 20 minutes, (b) 35 minutes, (c) 45 minutes and (d) 1 hour, (solid line-before oxidation).
Table 5.1 Thicknesses and composition of thermal oxide grown on wafer #4 (bulk Si)

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Oxidation time (minutes)</th>
<th>Thickness of oxide (nm)</th>
<th>Composition of the oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>w003</td>
<td>5</td>
<td>53</td>
<td>SiO₂</td>
</tr>
<tr>
<td>w006</td>
<td>10</td>
<td>80</td>
<td>SiO₂</td>
</tr>
<tr>
<td>w009</td>
<td>20</td>
<td>153</td>
<td>SiO₂</td>
</tr>
<tr>
<td>w012</td>
<td>35</td>
<td>239</td>
<td>SiO₂</td>
</tr>
<tr>
<td>w015</td>
<td>45</td>
<td>292</td>
<td>SiO₂</td>
</tr>
<tr>
<td>w018</td>
<td>60</td>
<td>352</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

* The values of thickness and composition of the oxides have an average error of ~±4% due to uncertainty in the values of the stopping cross sections.
<table>
<thead>
<tr>
<th>Sample number</th>
<th>Oxidation time (minutes)</th>
<th>Surface mixture oxide</th>
<th>Areal density of Ge (x10(^{17}) atoms/cm(^2))</th>
<th>Thickness of SiO(_2) (nm)</th>
<th>Composition of SiGe alloy at the interface of oxide/alloy</th>
<th>Composition of SiGe alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w002</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>53</td>
<td>0</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w005</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>0</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w008</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>159</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w011</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>226</td>
<td>Si(<em>{0.37})Ge(</em>{0.63})</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w014</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>286</td>
<td>Si(<em>{0.34})Ge(</em>{0.66})</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
<tr>
<td>w017</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>352</td>
<td>Si(<em>{0.27})Ge(</em>{0.73})</td>
<td>Si(<em>{0.5})Ge(</em>{0.5})</td>
</tr>
</tbody>
</table>

* The values of thickness and composition of oxide and composition of SiGe have an average error of \(\pm 4\%\) due to uncertainty in the values of the stopping cross sections.
Table 5.3 Details of oxides and Ge redistribution in wafer #1 (Si_{0.5}Ge_{0.5}/Si)

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Oxidation time (minutes)</th>
<th>Thickness of SiO$_2$ (nm)</th>
<th>Composition of SiGe at the interface of oxide/alloy</th>
<th>Composition of SiGe alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Si$<em>{0.5}$Ge$</em>{0.5}$</td>
</tr>
<tr>
<td>w001</td>
<td>5</td>
<td>142</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.49</td>
<td>Si$<em>{0.37}$Ge$</em>{0.63}$</td>
</tr>
<tr>
<td>w004</td>
<td>10</td>
<td>145</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.50</td>
<td>Si$<em>{0.37}$Ge$</em>{0.63}$</td>
</tr>
<tr>
<td>w007</td>
<td>20</td>
<td>148</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.52</td>
<td>Si$<em>{0.23}$Ge$</em>{0.75}$</td>
</tr>
<tr>
<td>w010</td>
<td>35</td>
<td>145</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.51</td>
<td>Si$<em>{0.23}$Ge$</em>{0.75}$</td>
</tr>
<tr>
<td>w013</td>
<td>45</td>
<td>145</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.49</td>
<td>Si$<em>{0.23}$Ge$</em>{0.75}$</td>
</tr>
<tr>
<td>w016</td>
<td>60</td>
<td>142</td>
<td>Si$<em>{0.3}$Ge$</em>{0.7}$ O$_2$ 1.48</td>
<td>Si$<em>{0.23}$Ge$</em>{0.75}$</td>
</tr>
</tbody>
</table>

* The values of thickness and composition of oxide, areal density of Ge and composition of SiGe have an average error of $\pm 4\%$ due to uncertainty in the values of the stopping cross sections.
Figure 5.5 Thickness of wet oxide layers versus oxidation time at 1000°C for wafers #1, #2 and #4.
grown on $\text{Si}_{0.5}\text{Ge}_{0.5}/\text{Si}_{\text{sub}}$ (#1) initially (for 5 minutes) increases faster than that of the bulk Si but after 20 minutes the rate ($dx/dt$) of oxide growth slows down to the same value for all three wafers.

The thickness of the oxide ($x$) versus oxidation time / oxide thickness ($t/x$), calculated from figure 5.5, is shown in figure 5.6. This manner of plotting allows the growth parameters, $A$ and $B$, as defined in chapter 2 equation 2.3, to be determined graphically. As the time for the oxidation furnace to reach the equilibrium temperature is about 7–8 minutes, this figure does not include data for oxidation times of 5 and 10 minutes. The parabolic rate constant $B$ is given by the gradient of the lines, and the intercept of the line with the ordinate gives the value of $(-A)$, from which the linear rate constant $B/A$ can be obtained. Values of the constants $A$ and $B$ determined from this plot for the three wafers are listed in table 5.4. For a reference a curve for bulk Si (dashed line) has been calculated using values of $A$ and $B$ taken from Deal-Grove [44]. All of these theoretical values are for wet oxidation of bulk Si at 1000°C and at a pressure of 640 torr. For both theoretical and experimental calculations the value of $t_0$ was taken to be $t_0=0$ as Deal-Grove [44] suggested. It is noted in the table that the values of the oxidation rate constant $B$ and $B/A$ for bulk Si (wafer #4) and the capped SiGe (wafer #2) are identical even when the cap itself has been oxidised. In contrast, the linear rate constant $B/A$ is much larger for the uncapped SiGe (wafer #1) than that for bulk Si (wafer #4), which implies a fast initial oxidation rate though the parabolic constant is the same in these two cases.

Table 5.4 Rate constants for wet oxidation of Si and SiGe alloy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$</th>
<th>$B$</th>
<th>$B/A$</th>
<th>$t_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μm)</td>
<td>(μm²/hr)</td>
<td>(μm/hr)</td>
<td>(hr)</td>
</tr>
<tr>
<td>#1 Si$<em>{0.5}$Ge$</em>{0.5}$/Si</td>
<td>0.02</td>
<td>0.24</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>#2 Si/Si$<em>{0.5}$Ge$</em>{0.5}$/Si</td>
<td>0.42</td>
<td>0.24</td>
<td>0.71</td>
<td>0</td>
</tr>
<tr>
<td>#4 bulk Si</td>
<td>0.42</td>
<td>0.24</td>
<td>0.71</td>
<td>0</td>
</tr>
<tr>
<td>Theoretical [44]</td>
<td>0.226</td>
<td>0.287</td>
<td>1.27</td>
<td>0</td>
</tr>
</tbody>
</table>

56
Figure 5.6 Thickness of oxide grown at 1000°C versus time/thickness for wafer #1, #2 and #4 and a theoretical curve for bulk Si.
5.3 Composition of the oxides

From the RBS spectra shown in figures 5.1 and 5.2 and data presented in tables 5.1 and 5.2, it is clear that the composition of the oxides grown on the bulk Si (#4) and SiGe alloy without a cap (#2) is SiO$_2$. The absence of a measurable signal in figure 5.2 in channel numbers between ~330 and ~380 confirms that the oxide grown on the capped samples (#2) contains no germanium. Figure 5.2 (a) shows that the signals from Si and Ge in the alloy layer remain the same shape as that before oxidation. This means that the whole Si cap is consumed to form a SiO$_2$ layer on top of the material after oxidation for 20 minutes and that Si and Ge in the alloy are not involved in the initial oxidation process. After further oxidations of 35 minutes to 1 hour the peak labelled 'g' in figure 5.2 (b), (c) and (d) appears and the area increases with increasing oxidation time.

For the oxidation of the uncapped sample (#1) about $2.1 \times 10^{17}$ Ge/cm$^2$ are involved in oxidation with $1.5 \times 10^{17}$ Ge/cm$^2$ being trapped at the surface (peak 'p') whilst about $0.6 \times 10^{17}$ Ge/cm$^2$ is pushed away from the oxide front, and accumulates at the oxide/alloy interface during the first 5 minutes of oxidation (figure 5.3 open circle). The oxide near the surface is a mixed Si$_{0.5}$Ge$_{0.5}$O$_2$ layer which is confirmed by IR (not shown) and XPS analysis (to be shown later in this section). When prolonging the oxidation time to 10 minutes no further increase in the areal density of trapped Ge can be observed within the sensitivity of the RBS analysis. The Ge distribution in this layer (region I in figure 5.4) is thermally stable and is not significantly changed upon increasing the oxidation time from 20 minutes to 1 hour (figure 5.4 (a)-(d)). The absence of a signal in region II in any of the spectra in figure 5.4 confirms that no Ge is trapped at depths greater than about 145 nm within the thermal oxide. The composition of this region is essentially pure SiO$_2$. The peak labelled 'g' (region III in figure 5.4) is associated with the unoxidised Ge beneath the thermal oxide. Integration under this peak, plus corrections for the $1/E^2$ dependence of the Rutherford cross section, shows that a constant areal density of $5.5 \times 10^{17}$ Ge/cm$^2$ (table 5.3), which corresponds to an alloy of composition Si$_{0.25}$Ge$_{0.75}$ (table 5.3) and a thickness of 160 nm, is pushed ahead of the advancing SiO$_2$/alloy interface when the oxidation time is longer than 20 minutes. It confirms that Ge is ejected from the oxide and forms a Ge rich layer just beneath the interface of the oxide/alloy. It is concluded that the Si$_{0.5}$Ge$_{0.5}$O$_2$ mixed oxide
layer is formed during the first minutes of oxidation.

Selected samples were analysed using XPS to determine the oxidation states of the constituents (Si and Ge). Figure 5.7 (a) and (b) shows the Si 2p and Ge 3d spectra from sample w007 after wet oxidation at 1000°C for 20 minutes. The photoelectron spectra were collected from different depths using Ar⁺ sputtering to achieve layer removal. The spectrum was recorded from (i) the surface layer, (ii) the middle layer, and (iii) the SiGe alloy. The peak positions of Si 2p are located at 104.0 eV and 98.4 eV and that of Ge 3d are at 33.2eV and 28.8 eV, respectively. It is clear from figure 5.7 that the Si 2p peak shifts from 104.0 eV, which corresponds to Si⁴⁺, to 98.6 eV corresponding to Si⁰ in the underlying alloy. Similarly to Si, the peak of the photoelectron emission Ge 3d changes from 33.4eV, which corresponds to Ge⁴⁺, to 28.6 eV corresponding to Ge⁰. It is noted that by comparison with figure 4.8, the position of Si 2p (104.2 eV) in this figure is 1.2 eV greater than the position of Si 2p (102.8 eV) from SiO₂ grown on bulk Si. This difference can be attributed to the Ge which changes the environment of SiO₂. In addition, figure 5.7 (a) curve (iii) also shows two intensive peaks located at 107.5 eV and 103.6 eV, respectively, in the spectrum of Si 2p from the SiGe alloy layer. These two peaks do not come from the Si 2p core level but from the Ge, L₃Mₑ₅₅Mₑ₅₅, Auger electron emission. In the mixed Si₀₅Ge₀₅O₂ layer these Ge Auger peaks shift to higher energy with a broad profile because of the oxide environment.

5.4 Wet oxidation with sample preheating

The effect of preheating samples (table A1.1.(ii)) in dry N₂ prior to oxidation (see section 4.2 for details of the preheating process) has been investigated. Figure 5.8 shows RBS spectra from wafer #1 (Si₀₅Ge₀₅/Siₙb) before (solid line) and after (open diamond) preheating in flowing nitrogen at 1000°C for 15 minutes. The similarity of the spectra, especially the near coincidence of the back edge of the Ge and Si signals, confirms that the Ge has not redistributed during the period of preheating and that no significant oxidation occurs. It is estimated that the maximum oxide thickness is < 6 nm in the sensitivity of RBS analysis. Figure 5.9 shows a series of spectra from wafer #1 oxidised for 15 minutes at (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C without (solid line) and with (open diamond)
Figure 5.7 XPS spectra of (a) Si 2p and (b) Ge 3d from wafer #1 after wet oxidation at 1000°C for 20 minutes and from (i) the surface layer, (ii) the middle layer and (iii) from the SiGe alloy.
Figure 5.8 RBS spectra from wafer #1 Si$_{0.5}$Ge$_{0.5}$/Si$_{sub}$ before (solid line) and after preheating at 1000°C for 15 minutes in dry N$_2$ (open diamond).
Figure 5.9  RBS spectra from wafer #1 $\text{Si}_{0.3}\text{Ge}_{0.7}/\text{Si}_{\text{sub}}$ oxidised at (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C with (open diamond) and without (solid line) preheating.
preheating, respectively. A clear trend is evident in the oxidation temperature dependence of the Ge redistribution, however, with reducing temperature there is less redistribution of Ge during oxidation such that the oxides grown at 700°C, 800°C and 900°C contain a uniform concentration of this constituent in the case without preheating (figure 5.9 (a), (b) and (c) open diamond curves). The oxides grown at 700°C (figure 5.9 (a)) in both samples with and without preheating have the same composition Si$_{0.5}$Ge$_{0.5}$O$_2$ although the oxide is thinner in the sample without preheating. In the preheated samples, in which oxidation only occurs at the prescribed temperature, there is no trapped Ge in the oxide grown at 1000°C (figure 5.9 (d) open diamond) whilst there is a uniform oxide layer formed at 700°C and 800°C (figure 5.9 (a) and (b) open diamond). The thickness of the oxide layer is greater in the sample without preheating than that with preheating for the oxidations at 800°C, 900°C and 1000°C (figure 5.9 (b)-(d)).

Figure 5.10 shows the dependence of the oxide thickness upon the oxidation temperature over the range 700°C to 1000°C both without (dotted line) and with (solid line) preheating. As a reference the measured thickness of the oxide grown on bulk Si at 1000°C is indicated. The oxidation time for all samples was 15 minutes, however, the preheated samples experienced a longer time at high temperature as they were pushed into the furnace tube (in a nitrogen ambient) 15 minutes before commencing oxidation. A plot of the areal density (Nx) of the oxide components versus temperature is shown in figure 5.11 (a) for the samples without preheating and 5.11 (b) with preheating, respectively. It is evident that the amount of Si$_{0.5}$Ge$_{0.5}$O$_2$ is nearly the same, namely $\sim7\times10^{17}$ cm$^{-2}$, after oxidations at 800°C in both cases with and without preheating. However, the amount of GeO$_2$ increases with increasing temperature from 700°C to 900°C but reduces at 1000°C, whilst the areal density of SiO$_2$ reaches a maximum value between 900°C and 1000°C in the case without preheating. For the sample with preheating the areal density of GeO$_2$ decreases at 900°C and drops to zero at 1000°C. This behaviour is similar to that seen in figure 5.10 for the variation of oxide thickness with temperature.

5.5 **Summary**

The behaviour of SiGe alloy layers (wafer #1, #2 and #4) during wet oxidation has been
Figure 5.10 Variation of the oxide thickness grown on Si$_{0.5}$Ge$_{0.5}$ alloy during wet oxidation for 15 minutes against temperature with preheating in N$_2$ for 15 minutes and without preheating.
Figure 5.11 Areal density of oxides grown on wafer #1 Si_{0.5}Ge_{0.5}/Si versus temperature without (a) and with (b) preheating.
studied using RBS, infrared transmission spectroscopy and XPS analysis. The results can be summarised as follows: (i) the thickness of the oxide layer is greater for the uncapped Si$_{0.5}$Ge$_{0.5}$ alloy (wafer #1) than for both bulk Si (wafer #4) and capped Si$_{0.5}$Ge$_{0.5}$ alloy (wafer #2); (ii) germanium is snow-ploughed by the advancing oxidation front in both capped and uncapped layers during prolonged oxidation times; (iii) after warm up, when the sample is at a constant temperature, the major constituent of the growing oxide at a temperature between 700°C to 900°C is Si$_{0.5}$Ge$_{0.5}$O$_2$ whilst it is SiO$_2$ at 1000°C; and (iv) in contrast to bulk Si, the oxidation rate of Si$_{0.5}$Ge$_{0.5}$ alloy decreases at 1000°C for both preheating and non preheating samples due to the formation of GeO$_2$ at lower temperatures in the range 800°C to 900°C. The presence of GeO$_2$ inhibits oxide growth.
CHAPTER 6

EXPERIMENTAL RESULTS - II
THERMAL OXIDATION - DRY

The aim in this chapter is to report the experimental results of dry oxidation. The behaviour of dry oxide grown on Si$_{x}$Ge$_{1-x}$ alloy (wafer #3) at 1000°C (section 6.1) and 900°C (section 6.2) is compared with bulk Si (wafer #4) and also a comparison is made of oxidation with and without preheating.

6.1 Oxidation of SiGe alloy at 1000°C

6.1.1 Thickness of the oxide layer

Dry oxidation of Si$_{x}$Ge$_{1-x}$ alloy (wafer #3) and bulk Si (wafer #4) was performed at 1000°C for various times with and without preheating (section 4.2). Figure 6.1 (a) and (b) show RBS spectra from bulk Si samples (d002 and d010 in table A.I.2(i)) oxidised at 1000°C for (a) 1 hour and (b) 24 hours, respectively. By comparison of the width of the O signal $\Delta E$(O) in these two spectra, it is evident that the thickness of the oxide layer increases about 5 times upon increasing the oxidation time from 1 hour to 24 hours. The oxide thickness ($x$) grown on bulk silicon determined from the channel width, as described in Appendix II, is plotted against oxidation time ($t$) in figure 6.2 (empty squares). For comparison, theoretical values (dashed line) are also included where these have been calculated using the Deal-Grove linear parabolic equation $x^2 + Ax = B(t + t_o)$, where $A=0.165\mu$m, $B=0.0117\mu$m$^2$/hr and $t_o=0.37$hr [44]. The experimental points show good agreement with the theoretical curve only deviating by less than 8%, which may be due to the actual experimental conditions being different to the conditions assumed in calculating the theoretical thickness. Additionally, the error in the RBS analysis is about 5% due to uncertainty in the absolute value of the stopping cross section.

Figure 6.3 (a) and (b) shows RBS spectra from bulk Si oxidised at 1000°C for 4 hours.
Figure 6.1. Non-channelled 1.5 MeV "He" RBS spectra from dry oxides grown on bulk Si (wafer #4) at 1000°C (a) for 1 hour and (b) for 24 hours.
Figure 6.2 Dependence of dry oxide thickness against oxidation time at 1000°C.
Figure 6.3 Non-channelled 1.5 MeV 'He' RBS spectra from dry oxides grown on bulk Si (wafer #4) at 1000°C (a) without and (b) with preheating.
(a) without (sample d408) and (b) with preheating (d406), respectively. The figure shows that the widths of the O signal \( \Delta E(O) \) and Si signal \( \Delta E(Si) \) in these two spectra are essentially the same for the samples with and without preheating. The experimental values of the \( \Delta E(O) \) is 68 keV, which is equivalent to 145 ±10nm in both cases with and without preheating. It indicates that the oxidation behaviour of bulk Si is not affected by preheating.

Figure 6.4 (a), (b) and (c) shows RBS spectra from samples (a) d403, (b) d407, and (c) d411 without preheating (full circle), whilst the open circle spectra are from samples (a) d401, (b) d405 and (c) d409 with preheating, respectively. As a reference, a spectrum from a sample before oxidation (t=0) is shown as a solid line. The thickness of the oxide layers, calculated as before, has been included in figure 6.2 for the sample with no preheating (asterisks) and for the sample with preheating (full squares). It can be seen from figure 6.2, that for the short oxidation time (1 hour) the oxide grown on the alloy without preheating is about twice as thick as the oxide grown on bulk Si. In contrast, when the samples are preheated the thickness of the oxide on the alloy is almost the same as for bulk Si. The thickness of the oxide layers increases monotonically with increasing oxidation time (figure 6.2), however, the incremental thickness is significantly smaller than recorded for the oxide grown on bulk Si (figure 6.2). After an 18 hour oxidation the oxide thickness is about 1.5 times thicker on bulk Si than on the alloy without preheating whilst it is three times thicker than with preheating. These results clearly show that the growth rate \( (dx/dt) \) of the oxide on the Si\(_{0.45}\)Ge\(_{0.55}\) alloy is significantly retarded with respect to bulk Si when the oxidation time is longer than 1 hour. A similar experiment has been performed using wafers #1, Si\(_{0.5}\)Ge\(_{0.5}\)/Si alloy, and #4, bulk Si, (d001-d010) and a retarded oxidation rate of the alloy was similarly observed. These results were published by the author in reference 38.

6.1.2 Composition of the oxides

The composition of the oxides can also be determined from the RBS data, which are shown in figure 6.4. The features relevant to the growth of the oxide are the peaks 'p' which are due to a build up of Ge near the surface and which are unchanged during extended oxidation times, in this case from 2 hours to 18 hours, having an areal density of 8.4x10\(^{16}\) Ge/cm\(^2\) (table 6.2) and a composition of Si\(_{0.3}\)Ge\(_{0.7}\)O\(_2\). It is clear from figure 6.4 that there is
Figure 6.4. Non-channelled 1.5 MeV \(^{4}\text{He}\) RBS spectra from dry oxides grown on wafer \#3 \(\text{Si}_{0.45}\text{Ge}_{0.55}\) alloy at 1000°C without (full circles) and with preheating (open circles) and before oxidation (solid line).
no peak 'p' in the RBS spectra when the samples are preheated (open circle). This indicates that no Ge is trapped in the oxide layer during oxidation. The oxide formed on the alloy is essentially SiO₂ when preheating is employed.

In comparison with the sample before oxidation, it is noticed in figure 6.4 that the slope of the back edge of the Ge signal is increased and the height of the Ge signal is decreased for the alloy samples both with and without preheating. This indicates that Ge in the alloy layer redistributes and diffuses into the Si substrate during long oxidation times.

The chemical bonding of the constituents was determined using IR transmission spectroscopy and a typical spectrum from an oxide layer grown on wafer #1 during dry oxidation at 1000°C for 24 hours (d009) is shown in figure 6.5. As a reference, the spectrum from a thermal oxide on bulk Si (d010) grown under the same conditions is also included in the figure. Three strong absorption bands at wavenumbers 1075cm⁻¹, 800cm⁻¹, and 450cm⁻¹, which correspond to the vibrational modes of the Si-O-Si structure (section 4.6), are contained in the IR spectra for both samples. However, the intensity of the peaks is stronger for the oxide grown on the bulk Si than that grown on the SiGe alloy due to the different thicknesses (section 4.6). The position and the FWHM of the IR peaks from oxides grown on Si and SiGe are listed in table 6.1. It is concluded, therefore, that the oxide layers consist primarily of SiO₂. The formation of GeO₂ has been confirmed by XPS analysis for a few selected samples (not shown).

Table 6.1 The position and the FWHM of the IR peaks of the oxides grown on 
Si₀.₅Ge₀.₅/Si alloy (d009) and bulk Si (d010) at 1000°C for 24 hours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stretching bond position (cm⁻¹)</th>
<th>FWHM</th>
<th>Bending bond position (cm⁻¹)</th>
<th>Rocking bond position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d009</td>
<td>1070</td>
<td>100</td>
<td>800</td>
<td>460</td>
</tr>
<tr>
<td>d010</td>
<td>1075</td>
<td>90</td>
<td>800</td>
<td>460</td>
</tr>
</tbody>
</table>
Figure 6.5 IR transmission spectra from samples: (i) bulk Si-d010 and (ii) Si$_{0.45}$Ge$_{0.55}$ alloy - d009 oxidised at 1000°C for 24 hours.
6.2 Oxidation of SiGe alloy at 900°C

Dry oxidation at 900°C for various times has been carried out on samples prepared from the Si$_{0.45}$Ge$_{0.55}$ alloy (wafer #3) and bulk Si (wafer #4) with and without preheating (table AII. 2 (ii)).

6.2.1 Thickness of the oxide layer

A series of RBS spectra of wafer #3 which were oxidised at 900°C for various times are presented in figure 6.6 (a), (b), (c) and (d). The full circle curves in figure 6.6 are the spectra of the samples without preheating, (a) d415, (b) d419, (c) d423 and (d) d427, whilst the open circle curves are spectra from the samples with preheating: (a) d413, (b) d417, (c) d421 and (d) d425, respectively. As a reference, the spectrum from a sample before oxidation (t=0) is shown as a solid line. By comparing both the width of the oxygen signal around channel numbers 150 to 180 and the shift of the front edge of the Ge signal around channel numbers 360 to 400, the thickness of the oxide layer can be calculated as before. It is evident that the thickness of the oxide layer is smaller when the samples are preheated. The thickness of the oxide layer versus oxidation time is plotted in figure 6.7 with (full squares) and without (asterisks) preheating for SiGe alloy and bulk Si (empty squares). The theoretical curve (dashed line) was taken from Berger et al [89]. It seems that the experimental data from bulk Si does not agree well with the theoretical curve. This may be due to the difference between the theoretical calculation and experimental condition or due to the experimental error in the temperature measurement. The thickness dependence of time is qualitatively similar to figure 6.2 although the thickness of the oxide on bulk Si at this temperature is smaller compared with the oxidation at 1000°C (figure 6.2). For the preheated samples the thickness of the oxide on the alloy is about the same as on bulk silicon during the first hour of oxidation, whilst the oxide thickness in the alloy without preheating is about twice as thick as the oxide grown on bulk Si. The thickness of the oxide layers increases monotonically with increasing oxidation time (figure 6.7), however, the incremental thickness is significantly smaller than recorded for the oxide grown on bulk Si (figure 6.7). After 24 hours the oxide thickness is about 1.2 times thicker for bulk Si than for the alloy without preheating whilst it is about 2.3 times thicker than
Figure 6.6 Non-channelled 1.5 MeV "He" RBS from dry oxides grown on wafer #3 
(Si_{0.45}Ge_{0.55} alloy) at 900°C (open circle) with and (full circle) without 
preheating and (solid line) before oxidation.
Figure 6.7. Dependence of dry oxide thickness against oxidation time at 900°C.
that for the alloy with preheating. These results clearly show that the growth rate of the oxide on alloy is significantly retarded with respect to bulk Si for oxidation times longer than 1 hour.

6.2.2 Composition of the oxides

It is found that there is a specific difference displayed by the samples with and without preheating. The Ge peak 'p' only appears in spectra from samples which were not preheated. The presence of this peak again indicates that Ge is trapped in the region near the surface and, also, that the areal density is independent of the oxidation time for \( t > 4 \) hours and has a value of \( 8.7 \times 10^{16} \text{Ge/cm}^2 \) (table 6.2) and a composition of \( \text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_2 \).

A pile up of Ge at the oxide/alloy interface was not observed. However, changes in the Ge yield and in the slope of the back edge of the Ge signal occur during the oxidation of both sets of samples (with and without preheating). It is concluded that diffusion and redistribution of Ge has occurred. Due to this redistribution the composition of the alloy layer changes from \( \text{Si}_{0.45}\text{Ge}_{0.55} \) to \( \text{Si}_{0.47}\text{Ge}_{0.53} \) during dry oxidation at 900°C for 24 hours (table 6.2).

Table 6.2. The areal density of trapped Ge and composition of the alloys after a long oxidation time (\( t > 4 \) hours)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidation temperature (°C)</th>
<th>Areal density of trapped Ge ( \times 10^{16}/\text{cm}^2 )</th>
<th>Final composition of the alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>#3 ( \text{Si}<em>{0.45}\text{Ge}</em>{0.55} )</td>
<td>1000</td>
<td>8.4</td>
<td>( \text{Si}<em>{0.5}\text{Ge}</em>{0.5} )</td>
</tr>
<tr>
<td>#3 ( \text{Si}<em>{0.45}\text{Ge}</em>{0.55} )</td>
<td>900</td>
<td>8.7</td>
<td>( \text{Si}<em>{0.47}\text{Ge}</em>{0.53} )</td>
</tr>
</tbody>
</table>

6.3 Summary

The growth of dry oxides at 1000°C and 900°C on samples prepared from wafers #1, #3 and #4 has been studied using RBS and IR analysis. From the results above we can
conclude that: (i) the thickness of oxides grown on the alloy and bulk Si is very much dependent upon the oxidation time and the oxidation method (with or without preheating), however, the oxides are much thinner for Si$_{0.45}$Ge$_{0.55}$ alloy than for bulk Si when the oxidation time is longer than 20 hours; (ii) the oxide layer consists of SiO$_2$ with a mixed Si$_{0.5}$Ge$_{0.5}$O$_2$ layer in the near surface region during dry oxidation at 1000°C and 900°C without preheating whilst only a pure SiO$_2$ layer is formed when the sample is preheated; (iii) during prolonged oxidation times (>4 hours) Ge diffuses from the oxide/alloy interface into the alloy material below.
In this experiment 200 keV O\(^+\) ions were implanted into a Si capped Si\(_{0.5}\)Ge\(_{0.5}\) alloy layer of 900nm thickness (wafer #2) to form a buried oxide layer. Thus, the implanted samples contained three distinct layers, namely (i) a crystalline overlayer, (ii) the amorphous, buried oxide and (iii) the crystalline alloy substrate. The buried oxide was spatially defined by two broad interfaces between layers (i) and (ii) (upper interface) and (ii) and (iii) (lower interface). In contrast to the thermal oxidation studies (chapter 5 and 6), the oxygen source was finite being defined by the implanted dose of oxygen.

7.1. As-implanted samples

7.1.1 Oxygen implantation

This study of internal oxidation has been accomplished by synthesising an oxide in a thick capped Si\(_{0.5}\)Ge\(_{0.5}\) alloy layer (wafer #2) and by oxygen implantation as described in section 4.3. Details of the samples are listed in table A1.3. Figure 7.1 shows a series of non-channelled RBS spectra from the samples before and after implantation. The positions of the signals from the surface atoms of O, Si and Ge are marked on the figure. Curve (i) is a spectrum from a sample before O\(^+\) ion implantation, which was interpreted in section 5.1. Curves (ii), (iii) and (iv) are non-channelling spectra from the low, medium and high dose samples, respectively. By comparing these spectra with curve (i), a reduction in area of peak 'S' and a movement of the high energy edge of the Ge signal to higher channel numbers are observed. This is due to the sputter erosion of the Si cap which depends on the implanted O\(^+\) dose. For the low dose sample (curve (ii)), it is found that about 40 percent of the Si top layer, originally of thickness 75 nm, has been sputtered whilst for the medium dose sample less then 10 nm of the Si film remains. These measured losses of Si enable an experimental value of the sputtering rate of about 0.26 Si atom/O ion to be determined,
Figure 7.1 RBS spectra from Si capped wafer #2 (Si$_{0.5}$Ge$_{0.5}$/Si$_{sub}$ alloy) implanted at 200keV (i) before implantation, and after implantation with a dose of (ii) 0.6x10$^{18}$ O/cm$^2$ (low dose), (iii) 1.2x10$^{18}$ O/cm$^2$ (medium dose) and (iv) 1.8x10$^{18}$ O/cm$^2$ (high dose).
which was published by the author in reference 32. For the high dose sample the edge of the Ge signal is at channel number 395 indicating that the Ge atoms are at the surface, thus confirming that all of the top silicon layer has been removed by sputtering.

7.1.2 Profiles of O, Si and Ge

The yield deficiency of Ge between channel numbers 280 to 380, which develops with increasing dose, is due to the lower volume concentration of Ge atoms within the buried oxide layer. The presence of the dips enables a quantitative calculation of the oxygen concentration depth distributions to be carried out. Using the methods described in section 4.3 and chapter 4b the depth profiles of the implanted O and redistributed Si and Ge have been calculated and are plotted in figure 7.2 for the high dose sample. Figure 7.3 shows the oxygen depth profiles with different doses, which exhibit a similar dose dependence to the distributions reported previously [86] for O⁺ implantation into bulk Si. For the high dose sample the distribution of oxygen is broader than a Gaussian profile, which is typical of a high dose implanted profile in SIMOX [29,30] material and also shows saturation in the oxygen concentration. These characteristics are similar to oxygen profiles in SIMOX material [29,30] which result from the diffusion of excess oxygen to the upper wing of the distribution and by the processes of sputtering and swelling [61]. Saturation of the oxygen concentration is achieved only within the central region of the buried layer, of thickness 200 nm, which is centred at a depth of around 380 nm beneath the surface.

7.1.3 The composition of the O⁺ implanted layers

Figure 7.4 shows IR transmission spectra from implanted samples i7a, i7b and i7c. Three absorption bands are evident which are due to the vibrational modes of the Si-O-Si local bonding unit at 1000 cm⁻¹ to 1100 cm⁻¹, about 800 cm⁻¹, and 450 cm⁻¹ [81,82]. The position of each of the three bands shifts to larger wavenumbers with increasing dose of implanted oxygen. This data is qualitatively similar to earlier studies [76] of bulk Si implanted with oxygen at doses greater than 1x10¹⁸ cm⁻². To have a more detailed analysis of these effects the dominant band in the 1000 cm⁻¹ to 1100 cm⁻¹ region, which is due to the asymmetric stretching vibration, has been examined. For reference, the dashed curves shown in the

82
Figure 7.2 Experimental depth profiles of O, Si and Ge in capped Si$_{0.5}$Ge$_{0.5}$ alloy (wafer #2) after implantation of O$^+$ at 200 keV with a dose of 1.8x10$^{16}$cm$^{-2}$. 
Figure 7.3 Oxygen depth profiles of capped Si$_{0.5}$Ge$_{0.5}$ alloy (wafer #2) implanted with O$^+$ at 200keV to different doses.
Figure 7.4 Normalised IR transmission spectra from wafer #2 Si/Si$_{0.5}$Ge$_{0.5}$/Si implanted with different doses.
figure are the stretching bending vibration (lower) from SiO$_2$, with a thickness of 400 nm grown on bulk Si by dry oxidation at 1000°C, and (upper) from GeO$_2$, which is formed by implanting 200 keV O$^+$ ion to a dose of 1.8x10$^{18}$ cm$^2$. The implanted SiGe samples all exhibit absorption at a lower wavenumber which is indicative of the existence of sub-oxides (SiO$_y$ with y<2) or of compressive stress as found in low temperature thermal oxides [32]. Within our experimental sensitivity we observed no evidence for Ge-O bonding (850 cm$^{-1}$) using this IR technique.

The chemical-state depth profiles of as-implanted samples (i7a, i7b and i7c, see table AI.3), which were prepared by the author, have been reported by Liu in his thesis [90] in 1993 using XPS analysis. Figure 7.5 (a) [90,91] shows chemical-state depth profiles of Si, Ge and O from the sample (i7b) implanted with the high dose of O$^+$. These data [90] qualitatively indicate that most of the oxygen atoms are bonded to Si to form SiO$_2$ (Si$^{4+}$) and SiO$_y$ (Si$^{y+}$) and a minority of the oxygen atoms are bonded to Ge to form GeO$_y$ (Ge$^{y+}$), but not GeO$_2$ (Ge$^{4+}$), following the low dose implantation. In this case, elemental Si and Ge are found in the implanted layer. It is evident that O preferentially reacts with Si rather than Ge. Upon increasing the dose, the concentration of elemental Si and Ge decreases and that of SiO$_y$ decreases. The amounts of SiO$_2$ and GeO$_2$ increase with increasing oxygen dose and only SiO$_2$ and GeO$_2$ can be found in the saturated region following the high dose implantation (figure 7.5). Figure 7.6, which is based upon the chemical-state profiles shown by Liu in his thesis [90], quantitatively shows the dose dependence of the relative concentration of (a) Si, SiO$_y$ (here 2 > y > 0) and SiO$_2$ in the saturated region at a depth of 380nm, which corresponds to the oxygen projected range, and of (b) Ge, GeO$_y$ (2>y>0) and GeO$_2$. The total concentration of Si plus Ge is considered to be 100% with 50% Si and 50% Ge before O$^+$ implantation. From figure 7.6 (a) and (b) it can be seen that after the low dose implantation about 22% of the Si atoms are bonded to O to form sub-oxide SiO$_y$, 14% of the Si atoms are bonded to O to form stoichiometric SiO$_2$ and 14% of the Si remains as elemental Si whilst 3.5% of the Ge atoms are bonded to O to form sub-oxide GeO$_y$ and 46.5% of the Ge remains as elemental. No stoichiometric GeO$_2$ was observed in this case. Upon increasing the O$^+$ ion dose to 1.2x10$^{18}$ cm$^2$ more Si and Ge atoms have an opportunity to bond to O and it is clear in figure 7.6 that the amount of stoichiometric SiO$_2$ has increased to 60% (we noted that this value is higher than 50%, which corresponds to
Figure 7.5 XPS depth profiles of the chemical-states of Si, Ge and O from wafer #2 implanted with 200 keV $1.8 \times 10^{18} \text{ O}^+ \text{ cm}^{-2}$, (a) as implanted and annealed at (b) 800°C and (c) 1000°C [90,91].
Figure 7.6 The dose dependence of the relative concentration of SiO$_y$, and GeO$_y$ ($y = 0$, $2 > y > 0$ and 2) at the depth of 380nm.
the original composition of Si₅₄Ge₀₅ alloy) whilst the amount of sub-oxide SiOₓ decreases to about 5.5%. No elemental Si is observed. Meanwhile the atomic concentration of GeOₓ and GeO₂ is enhanced to 8.1% and 2.6%, respectively. In this case, all of the Si bonds to O, mainly to form SiO₂ but still 24% of the Ge remains as elemental Ge. When increasing the dose to 1.8x10¹⁹/cm², a stoichiometric oxide consisting of 62% SiO₂ and 38% GeO₂ is formed at the projected range. It is concluded that for the sample implanted with the low dose of oxygen the dominant oxide is the sub-oxide SiOₓ, but with SiO₂ being formed around the projected range. Upon increasing the dose SiO₂ becomes the most abundant oxide. When the oxygen dose is high enough a mixed dioxide layer SiₓGeₓO₂, which is Siₜ₆₂Geₜ₃₈O₂ at the projected range, is formed.

7.2 Annealing effects

Figures 7.7, 7.8 and 7.9 show a series of RBS spectra from low, medium and high dose samples after annealing for 1 hour at (b) 800°C, (c) 900°C and (d) 1000°C, respectively. As a reference, the spectrum from an as-implanted sample is shown in curve (a) in each figure. The similar shapes of the Ge signal spectra in figure 7.7 indicate that for the low dose implantation very little mass transport of Si, Ge or O has occurred during the anneal. The results from XPS analysis [90] also confirm that for the low dose implantation no detectable mass transport occurs during the anneal. The yield deficiency of Ge is greater in the sample with medium dose annealed at 1000°C (figure 7.8 (d) between channel numbers 250 to 350) and also, there are more pronounced wings in the buried oxide which can be inferred from the spectrum. Inspection of the RBS spectra from samples annealed at 1000°C for 1 hour (curves (d) in figures 7.8-7.9) shows that the samples implanted with a dose higher than 1x10¹⁹/cm² undergo significant reordering at this temperature, with the formation of relatively abrupt SiGe/oxide interfaces and strong segregation of Ge atoms to the SiGe alloy at both the upper and lower interfaces. It is clearly shown in figure 7.9 (d) that the local volume concentration of Ge rises above the original atomic 50% to the higher value of >60% atoms at the upper and lower interfaces. The chemical-state depth profiles of O, Si and Ge in a normalised format from the samples implanted with a high dose (7b in table A1.3) and annealed at 800°C (7b8), 900°C (7b9) and 1000°C (7b10) were reported in the thesis of Liu [90]. The XPS analyses from these annealed samples confirm the
Figure 7.7 RBS spectra from wafer #2 capped Si$_{0.5}$Ge$_{0.5}$ implanted at 200keV with a dose of $0.6 \times 10^{18}$ O$^+$ cm$^{-2}$ (low dose) (a) before annealing and annealed at (b) 800$^\circ$C, (c) 900$^\circ$C and (d) 1000$^\circ$C.
Figure 7.8 RBS spectra from wafer #2 capped Si$_{0.3}$Ge$_{0.7}$ implanted at 200keV with a dose of 1.2x10$^{18}$ O$^+$ cm$^{-2}$ (medium dose) (a) before annealing and annealed at (b) 800°C, (c) 900°C and (d) 1000°C.
Figure 7.9 RBS spectra from wafer #2 capped Si$_5$Ge$_{93}$ implanted at 200keV with a dose of $1.8 \times 10^{18}$ O$^+$ cm$^{-2}$ (high dose) (a) before annealing and annealed at (b) 800°C, (c) 900°C and (d) 1000°C.
conclusions drawn from the RBS data, namely that redistribution of Ge occurs during the 1000°C anneal leaving the implanted layer deficient in Ge and with more abrupt interfaces with the SiGe alloy. There is no significant chemical change at lower temperatures (800°C and 900°C) and lower oxygen doses (0.6x10^{18}/cm^2 and 1.2x10^{18}/cm^2). Figure 7.5 (b) and (c) [91] shows chemical-state depth profiles from the samples implanted with the high dose and annealed at (b) 800°C and (c) 1000°C. By comparing figure 7.5 (a) and (b) it is concluded that no significant difference exists between samples i7b (as implanted) and i7b8 (annealed at 800°C for 1 hour). Interestingly, a small increase in the concentration of Ge^{4+} corresponding to the decrease of Ge^{6+} is evident at the implanted region, whilst there is an increase in Si^{4+} and a reduction of Si^{5+} in both wings. A significant change has been observed for the sample implanted with the high dose after annealing at 1000°C (figure 7.5 (c)). The main feature is that the increase in the concentration of Si^{4+} is accompanied by a decrease of Ge^{4+} and also Ge^{0} and Ge^{2+} in the implanted region. Figure 7.10 shows the temperature dependence of the relative concentration of SiO$_2$, GeO$_2$ and GeO$_y$ from the higher dose sample (i7b10) determined at the peak of the oxygen concentration profile. The data in the figure is normalised so that the sum of the oxide concentrations is 100%, namely SiO$_2$+GeO$_y$+GeO$_2$ =100%. From figure 7.10 it is evident that the concentration of SiO$_2$ has not changed from a value of 60% after the anneals at 800°C and 900°C. However, upon increasing the annealing temperature to 1000°C the concentration of Ge oxides is reduced with a commensurate increase in the SiO$_2$ concentration to 90%. For the sample implanted with the high dose after annealing at 1000°C, the most abundant oxide in the region near the projected range is SiO$_2$ and the total Ge oxide concentration reduces with increasing temperature, in other words, Ge is ejected from the oxide layer.

Figure 7.11 (a) and (b) shows the temperature dependence of (a) the peak position and (b) FWHM of the IR absorption due to the Si-O asymmetry stretching vibrations. For all samples these parameters show a shift of peak position from lower than 1050 cm$^{-1}$ to higher than 1065 cm$^{-1}$ and of FWHM from larger than 140 cm$^{-1}$ to smaller than 120 cm$^{-1}$ with increasing anneal temperature which is indicative that an increasing proportion of the oxide has converted into stoichiometric SiO$_2$ with a commensurate reduction in stress. In all cases, the signals shift towards the values appropriate to a thermal oxide on bulk Si.
Figure 7.10 The relative concentration of SiO$_2$, GeO$_2$ and GeO$_x$ in high dose samples versus annealing temperature.
Figure 7.11 The anneal temperature dependence of (a) the position and (b) FWHM of the principle absorption bond in IR spectra.
7.3 Summary

The composition of a Si/Si$_{0.5}$Ge$_{0.5}$/Si$_{sub}$ layered structure (wafer #2) implanted with high doses of O$^+$ ions before and after annealing at 800°C, 900°C and 1000°C is reported. In common with bulk Si, the formation of the buried oxide layer in SiGe alloy during O$^+$ implantation is found to be controlled by sputtering, swelling and diffusion. The dominant component of the buried oxide layer is stoichiometric silicon dioxide, SiO$_2$. During annealing at 800°C, 900°C and 1000°C Si, O and Ge atoms are redistributed. Decomposition of GeO$_2$ and segregation of Ge occurs at an anneal temperature of 1000°C for the samples implanted with medium and high doses.
CHAPTER 8

DISCUSSION

The thermal oxidation (wet and dry) of Si$_{1-y}$Ge$_{y}$ ($y=0.5$) alloy at high temperatures (900°C and 1000°C) has been studied in this project (chapters 5 and 6). In addition, supporting experiments have been performed including wet oxidation at 700°C and 800°C (section 5.4 in chapter 5) and internal oxidation (chapter 7). All these experimental results are critically discussed in this chapter. In section 8.1 the results of thermal oxidation are summarised in general. The structures after oxidation (thermal and internal) are discussed in section 8.2 whilst the behaviour of the Si$_{1-y}$Ge$_{y}$ ($y=0.5$) alloy during oxidation is explained in terms of thermodynamic and kinetic mechanisms in sections 8.3 and 8.4, respectively.

8.1 General

It is evident that the oxidation behaviour of wafer #1 uncapped Si$_{1-y}$Ge$_{y}$ ($y=0.5$) alloy is very complicated and depends upon the oxidation temperature, time and method (wet or dry and with or without preheating). From a consideration of the kinetics and thermodynamics of the reactions we propose that the thermal oxidation of Si$_{1-y}$Ge$_{y}$ ($y=0.5$) alloy at 900°C and 1000°C can be considered to be a two stage process. As summarised qualitatively in table 8.1 during stage one (times less than 2 hours for dry oxidation and less than 20 minutes for wet oxidation) Ge is incorporated into the oxide when the sample is not preheated whilst only pure SiO$_2$ is formed when the sample is preheated. By comparison with bulk Si, the oxidation rate (both dry and wet) is higher for the alloy when preheating is not used whilst it is the same for dry oxidation, and is faster for wet oxidation when the sample is preheated. In contrast, during stage two (from 2 hours to 24 hours and from 20 minutes to 1 hour for dry and wet oxidation, respectively) only a SiO$_2$ layer is formed in all cases. Oxidation is characterised by a similar growth rate for the alloy and bulk Si during wet oxidation, but a significantly lower rate for the alloy during dry oxidation. All discussions in the following sections will be based upon this two stage process.
Table 8.1 Summary of the oxidation behaviour of wafer #1 Si$_{0.5}$Ge$_{0.5}$/Si alloy and wafer #3 Si$_{0.5}$Ge$_{0.5}$/Si alloy for thermal oxidation at 900°C (dry) and 1000°C (wet and dry)

<table>
<thead>
<tr>
<th>Region</th>
<th>Stage one</th>
<th>Stage two</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet (&lt;20 mins.)</td>
<td>Dry (&lt;2 hrs.)</td>
</tr>
<tr>
<td></td>
<td>no preheating</td>
<td>with preheating</td>
</tr>
<tr>
<td>Region I</td>
<td>Si$<em>{0.5}$Ge$</em>{0.5}$O$_{2}$</td>
<td>See Fig. 8.1</td>
</tr>
<tr>
<td>Region II</td>
<td>SiO$_{2}$</td>
<td>SiO$_{2}$</td>
</tr>
<tr>
<td>Region III</td>
<td>Si$<em>{y}$Ge$</em>{1-y}$</td>
<td>y&gt;0.5</td>
</tr>
<tr>
<td>Oxidation rate</td>
<td>&gt; Si</td>
<td>&gt; Si</td>
</tr>
</tbody>
</table>

* No data

8.2 Final structures after oxidation

8.2.1 Thermal oxidation - wet and dry

——— without preheating ———

From experimental data presented in chapters 5 and 6 it is evident that qualitatively similar structures were formed in both cases of wet and dry oxidation at high temperatures (≥900°C). In general, for wet and dry oxidation without preheating Ge atoms are trapped in the region near the surface (region I, table 8.1 and figure 8.1) and, subsequently, are ejected from the oxide (region II, table 8.1 and figure 8.1) as shown in figures 5.3 and 5.4 for wet oxidation and in figures 6.4 and 6.6 for dry oxidation. However, the areal density of trapped Ge is smaller for dry oxidation (~8.4x10$^{16}$/cm$^2$, table 6.2) than for wet oxidation (1.5 x10$^{17}$/cm$^2$ table 5.3). Taken together, the results from RBS, XPS and IR confirm that different structures are formed depending upon the temperature and method of oxidation.

The evolution of these structures is shown schematically in figure 8.1 (a), (b) and (c) where the horizontal axis is the oxidation time. In all cases, the alloy layers consist of three distinct regions of different composition (figure 8.1(a)).
Figure 8.1 A schematic diagram of the oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy region I - Si$_{0.5}$Ge$_{0.5}$O$_2$, region II - only SiO$_2$ and region III - Si$_{1-y}$Ge$_{y}$ alloy.
(I) Region I - near surface: a mixed oxide, Si_{0.5}Ge_{0.5}O_2 for both wet and dry oxidation,

(II) Region II - middle region: a pure SiO_2 layer,

and (III) Region III - lower region: the composition of the alloy layer below the oxide is modified to be Si_{1-y}Ge_y where y<0.5 during dry oxidation and y >0.5 during wet oxidation.

These layers are labelled in the figure 8.1.

________ with preheating ________

It has been found that the composition of the oxide layer depends critically upon the temperature-time profile for the complete oxidation cycle. This aspect is illustrated in figure 8.1 (b), which shows that when the samples were preheated to bring them up to the oxidation temperature of 900°C or 1000°C in a non oxidising atmosphere (N_2), only region II and region III formed. No trapped Ge was observed, within the sensitivity of the RBS analysis, as shown in figure 5.9 (d) open diamond curve for wet oxidation and in figures 6.4 and 6.6 open circle curves for dry oxidation. Similar structures were also obtained after wet oxidation of samples with a 75 nm Si capping layer (figure 5.2). During the warm up in flowing oxygen, only the Si cap is oxidised and the sample will have reached the required oxidation temperature before the Si cap is completely oxidised. Consequently, oxidation of the SiGe alloy only occurs once an equilibrium temperature has been reached, when the Ge is able to escape from the oxide.

In contrast, in the case of wet oxidation at lower temperatures (700°C and 800°C) for 15 minutes (figure 5.9 (a) and (b)), a uniform mixed oxide Si_{0.5}Ge_{0.5}O_2 layer is formed in all samples oxidised with or without preheating. Additionally, the unoxidised alloy just beneath the oxide layer is unchanged and retains the original composition of Si_{0.5}Ge_{0.5} as shown in figure 8.1 (c).

From the experimental data in figures 5.3, 5.4, 6.4 and 6.6 it is evident that the constant area under the Ge peaks 'p' indicates that the position, and the amount of Ge trapped during stage two are the same during both wet and dry oxidation, although the thickness of the oxide layer does increase. In addition, the oxide which is formed during stage two is SiO_2.
It is assumed that this new oxide is formed by long range migration of oxygen from the surface to the reaction front in a similar manner as that found in bulk Si. Thus, the moving species during oxidation of the SiGe alloy is oxygen and thermal oxidation of the SiGe alloy qualitatively follows the same steps as the oxidation of Si, as described by the Deal-Grove model (1964) [46]. Namely, oxygen is transported from the gas to the gas-oxide interface and then diffuses across the oxide layer, which is already present, to react with the Si just below the SiO$_2$/alloy interface.

8.2.2 Internal oxidation

It is clear from figures 7.1 and 7.6 that a Si-Ge mixed oxide layer whose composition is strongly dependent upon the dose of implanted O$^+$ ions, is formed during internal oxidation. For the lower doses the oxide layer contains sub-oxides SiO$_y$ (y<2) and stoichiometric oxide SiO$_2$ (figure 7.6 (a)) together with unoxidised Si and Ge. Upon increasing the O$^+$ dose the proportion of SiO$_2$ increases whilst the percentage of SiO$_y$ decreases as is evident in figure 7.6 (a). A mixed oxide layer consisting of Si$_{1-y}$Ge$_y$O$_2$ is formed when the O$^+$ dose is sufficiently high to exceed the solid solubility ($\approx$1x10$^{18}$/cm$^2$ at 1300°C) (figure 7.6 (a) and (b)). This result indicates that GeO$_2$ is only formed when the O$^+$ ion dose is high enough to fully oxidise all of the Si atoms. When a mixed oxide (Si$_{1-y}$Ge$_y$O$_2$) is formed, it is thermally stable during anneals at 800°C and 900°C. A significant redistribution of Si, O and Ge is only found after annealing at 1000°C for 1 hour for the samples implanted with the high and medium oxygen doses (figures 7.8(d) and 7.9 (d)). The most abundant oxide in this mixed layer is SiO$_2$ as the GeO$_2$ decomposes with the elemental Ge being rejected from the oxide.

8.3 Oxidation process

8.3.1 Thermodynamic considerations

8.3.1.1 Formation of pure SiO$_2$ during wet and dry thermal oxidation

A feature of these experiments is that during stage one a particular areal density of Ge is trapped in the oxide layer near the surface and then during further oxidation no further Ge is trapped, indeed Ge is rejected from the growing oxide. We have noted that during both
wet and dry oxidation, when the sample is not preheated, a mixed oxide (Si$_{1-x}$Ge$_x$O$_2$) is formed, but when the sample is preheated, only SiO$_2$, containing no Ge, is observed. Additionally, it is evident that the dominant phase that forms during both wet and dry oxidation at temperatures greater than 900°C, is SiO$_2$. These results indicate that oxygen preferentially reacts with Si. In order to describe these processes in terms of the thermodynamics of the Si-Ge-O system, it is necessary to invoke the free energy of reaction for the relevant mass-balance equations over the temperature range 1000 K to 1300 K (~700°C to 1000°C). The resulting data is shown in table 8.2. The calculation is based on the standard free energy of formation taken from Barin's data [85], which is listed in table 8.3. The oxidation reactions fall into two categories (i) and (ii) which characterise wet and dry oxidation:

(i) wet
\[ 2\text{H}_2\text{O} + \text{Si} = \text{SiO}_2 + 2\text{H}_2 \]  
\[ 2\text{H}_2\text{O} + \text{Ge} = \text{GeO}_2 + 2\text{H}_2 \]  
and (ii) dry
\[ \text{O}_2 + \text{Si} = \text{SiO}_2 \]  
\[ \text{O}_2 + \text{Ge} = \text{GeO}_2 \]

By comparing these two sets of equations it is evident that the free energy of the reaction (tables 8.2 and 8.3) is lower for the Si-O system (equations 8.1 and 8.3) than for the Ge-O system (equations 8.2 and 8.4). In other words, it is energetically favourable for O to react with Si rather than Ge. This conclusion can be used to explain why oxygen preferentially reacts with Si to form SiO$_2$ during both wet and dry oxidation.

8.3.1.2 Internal oxidation

The main characteristic of internal oxidation, which involves O$^+$ ion implantation, is that the quantity of available oxygen is defined by the oxygen dose. In common with SIMOX material (Kilner 1985) [86] the synthesis of a buried oxide layer in the Si$_{1-x}$Ge$_x$ alloy is controlled by the processes of sputtering, swelling and diffusion, which was reported by the author in 1991 and 1992 [29,32]. As discussed by Van Ommen (1989) [87] the presence of point defects, resulting from oxygen ion damage (generation of Frenkel pairs) and the reaction of the implanted oxygen with the matrix atoms, will control the evolution of the buried oxide. In the case of SiGe alloys, the situation is more complicated as it is necessary
Table 8.2  Free energy of reaction (kJ / mol) (Calculated from reference 85)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + \text{Si} = \text{SiO}_2 + 2\text{H}_2$</td>
<td>-344.829</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + \text{Ge} = \text{GeO}_2 + 2\text{H}_2$</td>
<td>-1.641</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{Si} = \text{SiO}_2$</td>
<td>-730.256</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{Ge} = \text{GeO}_2$</td>
<td>-387.068</td>
</tr>
<tr>
<td>$\text{GeO}_2 + \text{Si} = \text{SiO}_2 + \text{Ge}$</td>
<td>-343.188</td>
</tr>
</tbody>
</table>
Table 8.3  Standard free energy of formation (kJ/mol) [85]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>SiO$_2$ (s)</td>
<td>-981.521</td>
</tr>
<tr>
<td>Si (s)</td>
<td>-30.390</td>
</tr>
<tr>
<td>Ge (s)</td>
<td>-43.636</td>
</tr>
<tr>
<td>GeO$_2$ (s)</td>
<td>-651.579</td>
</tr>
<tr>
<td>O$_2$ (g)</td>
<td>-220.875</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-448.687</td>
</tr>
<tr>
<td>H$_2$ (g)</td>
<td>-145.536</td>
</tr>
</tbody>
</table>
to consider the reactions:

\[
2\text{Si}_{\text{sub}} + 2\text{O}_{\text{int}} \leftrightarrow \text{SiO}_2 + \text{Si}_{\text{int}} \quad (8.5)
\]

\[
2\text{Ge}_{\text{sub}} + 2\text{O}_{\text{int}} \leftrightarrow \text{GeO}_2 + \text{Ge}_{\text{int}} \quad (8.6)
\]

and

\[
\text{GeO}_2 + \text{Si} \leftrightarrow \text{SiO}_2 + \text{Ge} \quad (8.7)
\]

where the subscripts "sub" and "int" indicate substitutional and interstitial lattice positions. From a knowledge of the heat of formation and decomposition of SiO\(_2\) and GeO\(_2\), shown in tables 8.3 [85] and 8.4 [92], respectively, it is evident that SiO\(_2\), which has a lower free heat of formation and higher heat of decomposition, is the more stable of the two oxides (equation 8.7) and that the O-Si reaction will dominate with equation 8.5 tending to the right hand side for the system to accommodate the implanted oxygen (Ommen 1989) [87]. Consideration of the law of mass action shows that equation (8.6) will tend to the left due to the reduced concentration of O\(_{\text{int}}\) following the preferential formation of SiO\(_2\). However, it must be remembered that inferences drawn from equilibrium dynamics can only provide pointers to the way in which a system will respond under non equilibrium ion bombardment. In this case the low heat of decomposition of GeO\(_2\) compared to SiO\(_2\) will ensure a low concentration of GeO\(_2\), as we have observed experimentally. The reaction (8.7) has a negative free energy of reaction which signifies that this reaction will tend to the right rather than to the left side.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Heat of decomposition (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>880.1</td>
</tr>
<tr>
<td>GeO(_2)</td>
<td>540.1</td>
</tr>
</tbody>
</table>

The reduction of GeO\(_2\) and the redistribution of Ge during the anneals at 1000°C is consistent with parallel studies of the thermal oxidation of Si\(_{0.5}\)Ge\(_{0.5}\) in which the trapping of GeO\(_2\) to form mixed oxides (Si\(_{0.5}\)Ge\(_{0.5}\)O\(_2\)) during wet oxidation at 700°C and 800°C has
been observed (section 5.4). Upon increasing the temperature (≥ 900°C), Ge is rejected from the oxide during both wet and dry oxidation. This behaviour has been discussed by many authors in terms of the balance between the diffusivity of Ge in the alloy and the oxidation rate [23, 28, 36, 37, 45]. Only a few studies of the thermodynamics of the Si-Ge-O ternary system have been reported with Paine et al (1991) [25] being the first to carry out isothermal phase equilibrium calculations. They considered the stability of the system 

\[
\text{GeO}_2 + \text{Si} \rightarrow \text{SiO}_2 + \text{Ge}
\]

and found that it is energetically favourable for \(\text{SiO}_2\) to form when \(\text{GeO}_2\) is in contact with free Si (not oxidised). In contrast, layers of \(\text{SiO}_2\) on SiGe are stable for all alloy compositions. The reduction of \(\text{GeO}_2\) leading to a rejection of the Ge is a consequence of this reaction.

Samples prepared by the author have been investigated by Castle et al (1993) [41] using XPS techniques [29,30,33]. The Si-Ge-O system has been used to determine the role of thermodynamics in controlling the redistribution of the constituent elements when O\(^+\) ions are implanted into SiGe. To simplify the analysis, Castle et al [41] assumed that the synthesis of the oxide is a two step process; firstly, implantation of oxygen into the SiGe alloy with no redistribution and secondly, diffusion of the constituents to achieve thermodynamic equilibrium. Chemical activities of Si, Ge and O following implantation were calculated using the programme THERMO-CALC [93]. Figure 8.2 shows the changes of relative chemical potential of Si, Ge and O versus the depth in the as-implanted sample (this is taken from reference 41). The data are calculated using as input the XPS depth profiles and the chemical activity [29,30,33,41]. The results from the calculation indicate that the chemical potential of Ge is higher in the buried oxide layer and as the experimental observations show that Ge is ejected from the oxide, it was concluded that the driving force for the mass transport is the chemical potential. The process was successfully modelled assuming Si to be the mobile species which migrates into the buried oxide where it replaces Ge according to the reaction (8.7) (free energy -349 kJ/mol). The proposal was that the free Ge then diffuses out of the oxide due to its higher chemical potential, with the process continuing until all of the \(\text{GeO}_2\) has been reduced.

The reordering during the 1000°C anneal of these SiGe structures is dominated by the net thermally driven segregation of oxygen to the buried oxide layer [30] which results in a
Figure 8.2 (a) Changes of relative chemical potential of Si, Ge and O versus the depth in the as-implanted sample with high oxygen dose and (b) enlargement of the ordinate from 0 to -10 kJ/mol [41].
reduction in the total Ge volume concentration from 18% atomic (as implanted) to 10% atomic (annealed at 1000°C for 1 hour see figure 7.9 (a) and (d)). As in the case of SIMOX (Si-O) this reordering may be described in terms of the system moving to minimise the interfacial energy associated with oxide precipitates [94], which XPS shows consists of stoichiometric SiO₂ in both systems [30,33]. The reduced concentration of Ge atoms in the buried layer after annealing arises from the relative thermal instability of oxides of Ge which was observed in bulk Ge by Sjoreen et al [74], who found that an anneal at 650°C for 30 minutes was sufficient to cause the decomposition of a synthesised oxide with a total loss of oxygen from the samples. For SiGe samples the presence of Si acts as a trap for the implanted oxygen due to the thermodynamically favoured formation of stoichiometric SiO₂. However, the low solubility of Ge in SiO₂ leads to precipitation and rejection of Ge atoms from the synthesised oxide. It is evident from XPS analysis that Ge is predominantly elemental (not oxidised) and thus must exist as inclusions within the SiO₂ matrix. Similar structures have been reported by other authors for analogous systems, for example Si in SiO₂ and As in SiO₂ (Celler et al [66]). The segregation of elemental Ge has been previously mentioned in section 8.1.1 during thermal oxidation of wafer #1, Si₉₃Ge₂₅/Si₉₅, when Ge atoms were found to accumulate in the alloy layer just beneath the interface of the oxide/alloy. The segregation behaviour of implanted metallic impurities in SIMOX has been reported by Delin et al [64] and Kilner [65] who have also proposed that the segregation can be attributed to a thermodynamic driving force arising from differences in the enthalpies of formation of the relevant oxides. Kilner [65] has plotted the enthalpy of formation with respect to SiO₂ as shown in figure 2.3, and proposed that the positive relative enthalpy of formation leads to the observed strong segregation. This relative value of the enthalpy of formation for GeO₂ was calculated by the author to be 3.17 eV/O₂, which is more positive than that for SiO₂. It is consistent with their findings and supports our premise that the system is driven by chemical thermodynamics.

In summary, the experimental results clearly indicate that the oxidant preferentially reacts with Si rather than Ge during oxidation of the SiGe alloy and this can be attributed to the lower standard heat of formation of SiO₂. The driving force for ejection of Ge from the oxide layer is the chemical potential.
8.3.2 Kinetic considerations

8.3.2.1 Formation of GeO$_2$ during thermal oxidation

The experimental data clearly shows that GeO$_2$ forms during high temperature oxidation at 900°C and 1000°C when the samples are not preheated. This observation has not been reported previously [8-18], however, the alloy samples used in those earlier experiments contained lower concentrations of Ge (Ge $<< 50\%$). In contrast, when the samples (Ge=50%) are preheated the oxide layer contains only SiO$_2$. To explain these differences we note that a uniformly mixed layer of Si$_{0.5}$Ge$_{0.5}$O$_2$ is formed during oxidations at 700°C and 800°C both with and without preheating. It seems that at 900°C and 1000°C the diffusion of Ge is fast compared to the motion of the oxidation front [28,36,37]. Thermodynamics controls the outcome and only SiO$_2$ forms (as discussed in 8.2.1.1). At 700°C and 800°C Si and Ge are immobile compared to the O diffusivity [28,36,37]. In these cases Ge and Si are both oxidised and we speculate that the mass transport of the reacting species controls the supply of Si and Ge, thus the oxidation of SiGe alloy is controlled by kinetic mechanisms. We propose that the effect of Ge on the kinetics of the oxidation of SiGe alloy must be considered in addition to the three fluxes described and numbered $F_1$, $F_2$ and $F_3$ by Deal-Grove [46] (figure 2.1). Therefore, we have added a new component ($F_4$) which is a Ge flux as schematically presented in figure 8.3 (a). The Deal-Grove linear-parabolic model is well known so that it is only briefly described here. The flux $F_1$ is the flux of oxidant atoms from the gas phase to the top surface of the oxide and is dependent upon the gas-phase mass transfer coefficient, and the equilibrium and actual concentration of oxidant in the oxide. The solid state diffusional flux $F_2$ is dependent upon the effective diffusivity of the oxidant in the oxide, oxidant concentration near the SiO$_2$/Si interface and the thickness of the oxide. The flux $F_3$ represents the flow of oxidant to the SiO$_2$/Si interface where the first order oxidation reaction occurs. The values of the three fluxes depend upon the oxidation method (wet or dry or steam), temperature and time. For a particular experiment the fluxes $F_1$ and $F_2$, should be independent of the substrate material if the thickness of the oxide layer is the same, therefore, the flux $F_3$ is strongly related to the substrate material being oxidised. The component $F_4$ takes into account the difference between Si and SiGe alloy and is defined schematically in figure 8.3 (a), which shows a schematic diagram of the oxidation process. The schematic diagrams of the resulting depth
dependent Ge concentration profiles are also shown in figure 8.3 (lower) for the cases (b) \( F_4 \leq F_3 \), (c) \( F_4 > F_3 \), and (d) \( F_4 \leq F_3 \) initially which then changes to \( F_4 \geq F_3 \). In the case of the oxidation of bulk Si (chapter 2), the three fluxes are equal \( F_i = F_2 = F_3 \) when the steady-state condition is established [46]. During the oxidation of SiGe alloy whether Ge is trapped or ejected by the oxidation front is determined by the Ge diffusivity in SiGe alloy and the flow of the oxidant to the SiO\(_2\)/SiGe interface. If the oxidation temperature is low \((<900^\circ\mathrm{C})\) Ge is immobile compared with the motion of the oxidation front [36, 37] and this can be presented as \( F_4 \leq F_3 \) and \( F_i = F_2 = F_3 \) (figure 8.3 (b)). In this case, Ge is incorporated in the growing oxide and the oxidation of Ge can proceed. This is in good agreement with the experimental results obtained during wet oxidation of Si\(_{0.5}\)Ge\(_{0.5}\) alloy at 700°C and 800°C. In contrast, during oxidation at high temperature the diffusivity of Ge is higher than the flux of oxygen \( (F_4 > F_3) \) so that Ge is rejected (figure 8.3 (c)). This can be used to explain the oxidation behaviour in this experiment when the samples were oxidised after preheating at 900°C (dry) and 1000°C (wet and dry), in which case only pure SiO\(_2\) was formed. The oxidation of Si\(_{0.5}\)Ge\(_{0.5}\) at high temperature, without preheating, is a complicated non equilibrium process because initially the samples are at a low temperature where \( F_4 \leq F_3 \). Upon reaching the final oxidation temperature, the condition \( F_4 \geq F_3 \) is achieved. We conclude that two oxide layers will be formed (mixed Si\(_{0.5}\)Ge\(_{0.5}\)O\(_2\) located near the surface and pure SiO\(_2\) located beneath this mixed oxide, figure 8.3 (d)), which indeed is observed experimentally (figures 5.3, 5.4, 6.4 and 6.6 full circles).

During both wet and dry oxidation at 900°C and 1000°C without preheating the alloy samples pass transiently through the lower temperature range, especially the critical range of 700°C to 800°C when \( F_4 \leq F_3 \), as they warm up. During this warm up period Ge is incorporated in the growing oxide. The concentration of trapped Ge is higher for wet oxidation than for dry at the same temperature (tables 5.3 and 6.2 ) as \( F_4 \) is greater during wet oxidation, in other words, \( F_4 \ll F_3 \) in the case of wet oxidation. As the temperature rises further, the diffusivity of Ge in the oxide increases and \( F_4 > F_3 \) so that Ge can escape from the oxide front and only pure SiO\(_2\) is formed. The above discussion shows that the formation of GeO\(_2\) depends critically upon the temperature-time profile. The oxide which includes trapped Ge near the surface is only formed when there is no preheating or the
Figure 8.3 Schematic diagrams of (a) modified Deal-Grove [46] description of the oxygen flux (F₁, F₂ and F₃) to the interface. F₄ describes the Ge flux at the interface and (b), (c) and (d) the concentration of Ge versus depth.
oxidation temperature is lower than 900°C. However, with preheating oxidation can only occur at the equilibrium temperature (900°C or 1000°C) so no Ge is trapped. We speculate that this is because the Ge oxide does not form at temperatures greater than 900°C, but instead, elemental Ge is ejected from the growing oxide layer and builds up below the oxide/alloy interface (in the case of wet oxidation), or during the (slow) dry oxidation Ge diffuses into the alloy layer and then into the Si substrate. If the sample is in the oxidising ambient during warm up over the critical temperature range 700°C-800°C, it is found that the oxidation of Ge and consequential trapping does occur. It is evident that the composition of the oxide layer depends upon the balance between Ge diffusion and the velocity of the oxidation front.

It can be concluded that Ge is trapped in the oxide during stage one of oxidation, whilst the sample is warming up, that is, whilst the temperature of the sample is below 900°C when Ge and Si are relatively immobile compared to the reaction velocity of the oxidation front.

8.3.2.2 Oxidation rate - wet and dry

In this project we have studied the dependence of the oxidation rate upon the time at 1000°C for wet and dry oxidation and 900°C for dry oxidation. From the experimental results in sections 5.2, 6.1.1 and 6.2.1 it is clear that both wet and dry oxidation can be considered to be a two stage process where the first and second stages are described at the beginning of this chapter. It is noted that the oxidation rate during stage one is faster than during stage two.

——— Stage one ———

In general, for wet and dry oxidation it is found that Ge atoms are trapped in the region near the surface during the initial period of oxidation when the sample is not preheated as discussed in section 8.1.1.

- For wet oxidation -

It has been found that during wet oxidation the oxidation rate is about three times faster than that for bulk Si (figure 5.5 for 5 minutes and 10 minutes). Kinetic data for wet oxidation at 1000°C, which is given in figure 5.6 and table 5.4, confirms that the values of
the linear rate constant B/A for alloy (wafer #1) and bulk Si (wafer #4) are different, being higher during the oxidation of the alloy. This result agrees with previous reports [8-18].

- For dry oxidation -

In the case of dry oxidation at 1000°C and 900°C, the oxidation rate is the same for both Si_{0.45}Ge_{0.55} alloy (wafer #3) and bulk Si (wafer #4) when the sample is preheated, which is consistent with previously published work [16, 17, 20] though preheating was not employed in those experiments and no Ge was incorporated in the growing oxide. In contrast, the rate for the alloy is about twice that for bulk Si when the sample is not preheated. This result is at variance with previously published work in which the oxidation rate was found to be the same for both SiGe alloy and bulk Si when preheating was not used [16, 17, 20]. It appears that no other data is available in the literature that shows a faster rate during dry oxidation for SiGe alloy than for bulk Si, however, it must be pointed out again that the previous work was carried out using a Si_{1-y}Ge_{y} alloy with a lower Ge content (y<<0.5) and trapped Ge in the oxide was not observed.

Various mechanisms have been proposed to explain the enhanced oxidation rate during wet oxidation. One of these includes the lower binding energy of Si-Ge than that of Si-Si [8,9,17,49]. However, it has been argued by others that this is unlikely to be the explanation as the oxidation rates are the same for both Si and SiGe alloy during dry oxidation [15,16]. In the present experiment it is clear that the oxidation rate (for both wet and dry without preheating) is higher when Ge is trapped in the oxide layer. It is noted that from the experimental results (figures 6.2 and 6.7), that the enhancement of the oxidation rate for dry oxidation only occurs when there is GeO_{2} in the oxide layer (without preheating), whilst when GeO_{2} is not formed (with preheating) the oxidation rate is the same as bulk Si. The oxidation behaviour of wafer #2, also, shows that the oxidation rate of capped SiGe alloy can be the same as bulk Si (figures 5.5 and 5.6). In the case of this wafer, only the Si cap was oxidised and Ge was not involved in the oxidation during the stage one and the oxidation rate is consistent with that of bulk Si. However, the formation of GeO_{2} is not the only explanation for the increased wet oxidation rate. If the enhancement depends upon the formation of GeO_{2} then the thickness of the oxide, which does not contain GeO_{2}, grown on Si_{0.5}Ge_{0.5} alloy with preheating, should be the same as bulk Si. Figure 5.10 shows that the thickness of the oxide (SiO_{2}) grown at 1000°C for 15 minutes
after preheating is about 1.5 times as thick as the oxide on bulk Si, therefore there must be some other reason why the oxidation rate is enhanced. In stage one according to the oxidation reaction (equations (8.1) to (8.4)) the oxidation rate depends upon the availability of both Si atoms and O atoms. The Si atoms come from bulk Si or SiGe alloy whilst the oxidant is due to the reaction:

$$H_2O \rightarrow OH + H \text{ (for wet oxidation)} \quad \text{(8.8)}$$
$$O_2 \rightarrow O + O \text{ (for dry oxidation)} \quad \text{(8.9)}$$

It is known that the reaction 8.8 is easier than 8.9 due to a weaker binding energy for H-O (section 2.2) than for O-O and, also, that the activation energy is lower for H$_2$O diffusion than for O$_2$. From theoretical [89] and experimental data derived from oxidation of bulk Si at 900°C and 1000°C the number of oxygen atoms, which react with Si to form SiO$_2$ during wet oxidation, is about 5 to 6 times greater than during dry oxidation. In the case of wet oxidation, the number of OH molecules is high enough to sustain the oxidation. In this case, the oxidation rate is only determined by the number of available Si atoms for oxidation, which is higher for SiGe alloy than for bulk Si due to the lower binding energy of Si-Ge. The enhancement of the oxidation rate during wet oxidation for 15 minutes (compared with oxidation of SiGe at 1000°C) of SiGe alloy at 700°C and 800°C (figure 5.11) with preheating also confirms that there is enough OH to react with Si and Ge during oxidation. However, in the case of dry oxidation the number of O atoms is smaller because the reaction 8.9 is less favoured and the oxidation rate now is limited by the supply of O atoms. The lower Si concentration in the alloy does not reduce the oxidation rate and we suggest that sufficient Si atoms, from broken Si-Ge bonds, are available to maintain the required number of Si atoms, as in the case of bulk Si. This implies that the lack of about 50 percent Si atoms in the alloy (compared to bulk Si) is balanced by the breaking of the weaker Si-Ge bonds. We suggest that during stage one the reaction Si+O$_2$→SiO$_2$ (dry oxidation) may be dominated by the number of O atoms whilst the reaction Si+H$_2$O→SiO$_2$+2H (wet oxidation) is controlled by the number of Si (or Si and Ge) atoms. We conclude that the results from this experiment support the concept of the weaker Si-Ge binding energy causing the enhancement of the wet oxidation rate. It should be realised that
the oxidation behaviour of SiGe alloy is very complicated. It may involve several different mechanisms, besides, the speculation that the breaking of the Si-Ge bonds is easier in the case of Si$_{0.5}$Ge$_{0.5}$ alloy. LeGoues et al [15,16,17] have proposed that the pile up of Ge at the oxide/SiGe interface suppresses the injection of interstitial Si$_{int}$ resulting in an increase of the wet oxidation rate, and others [14,20] who proposed that the presence of Ge speeds up the decomposition reaction of H$_2$O→OH+H during wet oxidation, or formation of the unstable oxide GeO encourages the decomposition of H$_2$O or Si-OH molecules during wet oxidation and this then increases the Si-O reaction to form SiO$_2$ and elemental Ge. However, it must be noted that the presence of Ge will affect the charge state and concentration of point defects which may also modify the oxidation rate [8,9,13]. The experimental results discussed here do not disagree with the above speculations.

— Stage two —

A common feature during stage two for both wet and dry oxidation is the absence of trapped Ge in the oxide layer (section 8.1.1). The oxidation rate is slower than during stage one.

- For wet oxidation -

Experimentally we found that the wet oxidation rate at 1000°C is similar for all of the samples prepared from the Si$_{0.5}$Ge$_{0.5}$ alloy (wafer #1), Si$_{0.5}$Ge$_{0.5}$ alloy with a cap (wafer #2) and bulk Si (wafer #4) (figure 5.5). This observation is in agreement with earlier published results [8,9,10,15,16,18]. Kinetic data shown in figure 5.6 show that the data from wafer #1 parallels that from bulk Si and wafer #2. This suggests that the diffusion rate constant B is the same during the oxidation of these three samples. However, a different behaviour is observed during oxidation of wafer #2. Figures 5.5 and 5.6 show that the data from the Si/Si$_{0.5}$Ge$_{0.5}$/Si$_{sub}$ structure (w2) is almost the same as that from bulk Si (w4). This implies that the oxidation parameters, namely the linear rate constant B/A and diffusion rate constant B, are the same for these two samples. This is not surprising because after the Si cap has been completely consumed and the oxidation front reaches into the SiGe alloy, the oxidation rate will slow down as oxygen must diffuse through the oxidised cap. From the Deal-Grove model we can assume that the reaction Si+H$_2$O→SiO$_2$+2H may be dominated by the number of O atoms which diffuse to the oxide/alloy or oxide/Si interface so that the
oxidation rate of capped SiGe alloy will be the same as bulk Si. The weaker binding energy of Si-Ge and the presence of a Ge rich layer at the oxide/alloy interface are not relevant in this case. This explanation can, also, be used to describe the oxidation behaviour of uncapped SiGe alloy when the oxidation is slowed down by diffusion of oxygen through the growing oxide layer. In this stage oxygen may be the dominant species in the process of oxidation.

- For dry oxidation -

Compared to bulk Si a retarded dry oxidation rate has been observed during stage two. This unexpected result has been confirmed by repeating several of the experiments with and without preheating. However, it is noted that earlier oxidation studies, which show the same oxidation rate for bulk Si and SiGe alloy [15,16,19], have been carried out on alloys containing less Ge (y<<0.5) than in our samples and, therefore, they may be strained or only partially relaxed. Interestingly, Manukutla et al (1991) [26] have reported a retarded dry oxidation rate in relaxed layers of Si0.8Ge0.2. Tentatively they suggest that the oxidation rate may be strain dependent even though this seems not to be the case during wet oxidation of strained Si [99].

From the results generated in this study it is clear that the retarded oxidation rate is not due to trapped Ge in the surface region as the retardation is observed in all samples, with and without preheating, even though pure SiO2 forms when preheating is employed. The results from RBS analysis (figures 6.4 and 6.7) clearly show that during oxidation the Ge diffuses to the alloy layer and then subsequently diffuses into the Si substrate. The diffusion of Ge has not been reported in earlier work. In order to explain this abnormal oxidation behaviour we note that the main feature of dry oxidation is that the net areal density of oxygen atoms participating in the process of oxidation is smaller (figures 6.2 and 6.7) than for wet oxidation (figure 5.5) and, also, that significant Ge diffusion occurs. There are several possibilities which can be used to explain the retardation as listed below.

1. The diffusion of Ge into the underlying alloy may release interstitial Si which will slow down the oxidation rate.

2. The diffusion of Ge changes the composition of the SiGe alloy as shown in table 5.3, which will modify the band gap $E_g(y)$ as follows
\[ E_y = 1.12(1-y) - 0.74y \text{ (eV)} \]

where the alloy composition is \( \text{Si}_{1-y}\text{Ge}_y \) \([94]\).

Jorgensen \([55]\) has proposed that an external electrical field can modify the oxidation rate (figure 2.2). We speculate that the observed changes in the alloy composition (region III) during oxidation may change the internal electric field due to the oxide-semiconductor heterostructure which could retard the transport of the mobile (charged) species. In this case, the reaction \( \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \) may be dominated by \( \text{O} \).

In summary, the experimental results have been described in terms of two stages of oxidation. We speculate that during stage one the oxidation reaction is governed by the supply of Si during wet oxidation, where the weak binding energy of Si-Ge enhances the oxidation rate, whilst it is dominated by the availability of oxygen during dry oxidation when the weak Si-Ge binding energy does not affect the oxidation rate, which remains the same as bulk Si. This speculation supports the idea that the easier breaking of the Si-Ge bond increases the wet oxidation rate and importantly the model is not contradictory with the results from dry oxidation. During stage two, oxygen is probably the dominant species controlling the oxidation reaction for the wet oxidation. However, it is not clear whether Si or O controls the oxidation rate during dry oxidation. The identity of the dominant species controlling the reactions \( \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \) (dry) and \( \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2 \) (wet) are listed in table 8.5.

Table 8.5 Controlling species during the oxidation of \( \text{Si}_{0.5}\text{Ge}_{0.5} \) alloy.

<table>
<thead>
<tr>
<th></th>
<th>Wet</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage one</td>
<td>Si</td>
<td>O</td>
</tr>
<tr>
<td>Stage two</td>
<td>O</td>
<td>Si or O</td>
</tr>
</tbody>
</table>
CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 Conclusions

Oxidation of SiGe alloy is a complicated process. The thickness and composition of the oxide layer critically depend upon the temperature, time, ambient, thickness and composition of the alloy. Thick relaxed alloy layers have been used in this project to facilitate studies of the evolution of the oxide by RBS and IR analysis. The resulting data and ideas will assist in the interpretation of oxidation data generated by others from thinner layers. From this study of the oxidation behaviour of 320 nm Si$_{1-y}$Ge$_y$ ($y$=0.5) alloy at 1000°C and 900°C the following conclusions can be reached

1. As with bulk Si, the oxidation of Si$_{1-y}$Ge$_y$ ($y$=0.5) alloys can be qualitatively described by the Deal-Grove diffusion and reaction model. The oxidation of bulk Si is controlled both by the diffusion of the oxidant through the oxide and reaction of Si/O at the oxide/Si interface, however, in the cases of the alloy the three matrix components (Si, Ge and O) all contribute. (section 8.2.1)

2. Due to the low standard free energy of formation of SiO$_2$, the dominant component formed during oxidation (dry, wet and internal) is SiO$_2$ and Ge is rejected from the SiO$_2$ layer. The driving force for this Ge rejection is the higher chemical potential of Ge. (section 8.3.1)

3. GeO$_2$ is formed during thermal oxidation at temperatures less than 900°C (infinite source of O) when there is an insufficient supply of Si atoms to react with the excess O. (section 8.3.2.1)

4. For a finite source of O (internal oxidation) GeO$_2$ is only formed after the Si is fully reacted with O. The oxide is then a mixed Si$_{1-y}$Ge$_y$O$_2$ layer which is not thermally stable at temperatures above 900°C. In this case, the decomposition of GeO$_2$ occurs when the sample undergoes high temperature heat treatment. (section 8.3.2.1)
5. Thermal oxides grown on relaxed (without preheating), thick Si$_{0.5}$Ge$_{0.5}$ alloy contain three distinct layers of different composition: (i) region I, a mixed Si$_{0.5}$Ge$_{0.5}$O$_2$ layer, (ii) region II, a pure SiO$_2$ layer (for both wet and dry oxidation) and (iii) region III, where the composition of the initially homogeneous alloy below the oxide is modified. During dry oxidation the underlying alloy becomes Ge deficient and during wet oxidation the alloy becomes Ge rich. (section 8.2.1)

6. The oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy can be considered to be a two stage process for both dry and wet oxidation but with different dominant species limiting the reaction:

(i) stage one - Si during wet oxidation and O during dry oxidation,
(ii) stage two - O during wet oxidation and either Si or O during dry oxidation.

This interpretation supports the speculation that the weak binding energy of Si-Ge enhances the wet oxidation rate and, for the first time, we suggest that the idea of a weak binding energy is not contrary to the experimental results for dry oxidation. (section 8.3.2.2)

7. A retarded oxidation rate is observed during dry oxidation for time longer than 2 hours. We suggest that this may be a consequence of the diffusion of Ge away from the oxide/alloy interface deep into the alloy and then to the Si substrate although the reason for this deviation is not clear and needs to be further investigated. (section 8.3.2.2)

8. The kinetics of oxidation are very much dependent upon the oxidation temperature due to the formation of GeO$_2$ at low temperatures (<900°C). Thus, for high temperature oxidation it is necessary to preheat samples in order to ensure that oxidation occurs only at the pre-set temperature. It is clear that preheating in a non oxidising ambient up to the oxidation temperature will be an important consideration in future physics experiments and during the fabrication of SiGe devices. (section 8.3.2.1)

9.2 Suggestion for future work

As discussed above, the behaviour during oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy is complicated. A retarded oxidation rate during dry oxidation has been observed in this study, but the reason
for this retardation is still unclear. In future experiments it is recommended to concentrate on dry oxidation.

1. Different oxidation methods especially rapid thermal oxidation and plasma oxidation can be used to further understand the oxidation behaviour of Si\textsubscript{0.5}Ge\textsubscript{0.5} alloy.

2. The oxidation can be performed with different compositions of Si\textsubscript{\textit{y}}Ge\textsubscript{\textit{y}} alloy including \textit{y}<0.5 and \textit{y}>0.5 to study the effects of composition on oxidation behaviour and provide a fuller picture of oxidation from bulk Si to bulk Ge, especially wet oxidation at 900°C. It seems that 900°C is a critical temperature during wet oxidation of Si\textsubscript{0.5}Ge\textsubscript{0.5} alloy (figure 5.9 (c)) and the oxidation behaviour is very sensitive to the composition of the alloy.

3. The electrical properties of the oxide and interface state density should be studied in order to explore the possibilities of incorporating oxides in SiGe device structures.

4. It is necessary to have more data from TEM, SIMS and XPS analysis to directly explore the structures of the oxide, to study the effect of the structure, defects (point defect) and strain on the oxidation behaviour.
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RELEVANT PUBLICATIONS (written or partially written (*) by the examinee)

1. Behaviour of high dose O+ implanted Si/Ge/Si structures

2. Formation of buried SiO$_2$ layer by oxygen implanted into Si/Ge and Si/Si$_{0.3}$Ge$_{0.7}$ substrates
   Newstead, A.R. Powell, T.E. Whall, and E.H.C. Parker

3. The study of Si$_{0.3}$Ge$_{0.7}$ alloy implanted by high dose oxygen
   Nucl. Inst. and Meth., B55 (1991) 691

4. An investigation of Si$_{0.3}$Ge$_{0.7}$ alloy oxidation by high dose oxygen implantation
   Nucl. Inst. and Meth., B55 (1991) 697

5. Synthesis of oxides in Si$_{0.3}$Ge$_{0.7}$ alloy by high dose oxygen ion implantation
   * J.E. Castle, H.D. Liu, J.F. Watts, J.P. Zhang, P.L.F. Hemment, S.M. Newstead,
   A.R. Powell, T.E. Whall, and E.H.C. Parker

6. A comparison of the behaviour of Si$_{0.3}$Ge$_{0.7}$ alloys during dry and wet oxidation
   Thin Solid Film 222 (1992) 141
   Parker

7. Si$_{0.57}$Ge$_{0.43}$ alloy layers implanted with oxygen: sputtering yields and atomic
   composition depth profiles
   Whall, and E.H.C. Parker

127
8. Formation of germanium dioxide during wet oxidation of Si$_{0.5}$Ge$_{0.5}$ alloy
Proceeding of the MRS-93 vol. 326, P.73

9. Synthesis of a buried oxide in relaxed Si$_{0.5}$Ge$_{0.5}$ material using high energy oxygen implantation

10. Thermodynamic behaviour of GeO$_2$ formed by oxygen implantation into relaxed Si/Si$_{1-x}$Ge$_x$/Si structures
to be published in the proceedings of Tenth International Conference on Ion implantation Technology (June 1994, University of Catania, Italy)
Table A1.1(i) Samples used in wet oxidation experiments.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ambient</th>
<th>Wet $O_2$</th>
<th>Wafer number</th>
<th>Structure of wafer</th>
<th>Methods of analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$ (preheating)</td>
<td>$T(°C)$</td>
<td>$t$ (mins)</td>
<td>$T(°C)$</td>
<td>$t$ (mins)</td>
</tr>
<tr>
<td>w001</td>
<td>-</td>
<td>1000</td>
<td>5</td>
<td>$#1$</td>
<td>$Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<tr>
<td>w002</td>
<td>-</td>
<td>1000</td>
<td>5</td>
<td>$#2$</td>
<td>$Si/Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
</tr>
<tr>
<td>w003</td>
<td>-</td>
<td>1000</td>
<td>5</td>
<td>$#4$</td>
<td>$Si$</td>
</tr>
<tr>
<td>w004</td>
<td>-</td>
<td>1000</td>
<td>10</td>
<td>$#1$</td>
<td>$Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
</tr>
<tr>
<td>w005</td>
<td>-</td>
<td>1000</td>
<td>10</td>
<td>$#2$</td>
<td>$Si/Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<tr>
<td>w006</td>
<td>-</td>
<td>1000</td>
<td>10</td>
<td>$#4$</td>
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</tr>
<tr>
<td>w007</td>
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<td>1000</td>
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<td>20</td>
<td>$#4$</td>
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<tr>
<td>w010</td>
<td>-</td>
<td>1000</td>
<td>35</td>
<td>$#1$</td>
<td>$Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<tr>
<td>w011</td>
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<td>1000</td>
<td>35</td>
<td>$#2$</td>
<td>$Si/Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<tr>
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<td>-</td>
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<td>35</td>
<td>$#4$</td>
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<tr>
<td>w013</td>
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<tr>
<td>w014</td>
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<td>$Si/Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<td>60</td>
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<td>$Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
</tr>
<tr>
<td>w017</td>
<td>-</td>
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<td>60</td>
<td>$#2$</td>
<td>$Si/Si_{0.5}Ge_{0.5}/Si_{sub}$</td>
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<td>w018</td>
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Table AI.1 (ii) Samples used in wet oxidation experiments.

<table>
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<th>Sample number</th>
<th>Ambient N₂ (preheating) T(°C) t (mins)</th>
<th>Ambient Wet O₂ T(°C) t (mins)</th>
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<th>Structure of wafer</th>
<th>Methods of analysis</th>
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<td>700 15</td>
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<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS</td>
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<tr>
<td>w302</td>
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<td>700 15</td>
<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS, XPS</td>
</tr>
<tr>
<td>w303</td>
<td>800 15</td>
<td>800 15</td>
<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS</td>
</tr>
<tr>
<td>w304</td>
<td>- -</td>
<td>800 15</td>
<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS, XPS</td>
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<tr>
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<td>900 15</td>
<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS</td>
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<tr>
<td>w306</td>
<td>- -</td>
<td>900 15</td>
<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS, XPS</td>
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<td>w307</td>
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<td>#1</td>
<td>Si₀.₅Ge₀.₅/Si₉₂</td>
<td>RBS</td>
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<tr>
<td>w308</td>
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<td>Si₀.₅Ge₀.₅/Si₉₂</td>
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Table AI.2 (i) Samples used in dry oxidation experiments.

<table>
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<th>Wafer number</th>
<th>Structure of wafer</th>
<th>Methods of analysis</th>
</tr>
</thead>
<tbody>
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<td>N&lt;sub&gt;2&lt;/sub&gt; (preheating)</td>
<td>Dry O₂</td>
<td>T(°C) t (mins)</td>
<td>T(°C) t (hrs)</td>
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<tr>
<td>d001</td>
<td>-</td>
<td>-</td>
<td>1000 1</td>
<td>#1 Si&lt;sub&gt;0.5&lt;/sub&gt;Ge&lt;sub&gt;0.5&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
</tr>
<tr>
<td>d002</td>
<td>-</td>
<td>-</td>
<td>1000 1</td>
<td>#4 Si</td>
</tr>
<tr>
<td>d003</td>
<td>-</td>
<td>-</td>
<td>1000 2</td>
<td>#1 Si&lt;sub&gt;0.5&lt;/sub&gt;Ge&lt;sub&gt;0.5&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
</tr>
<tr>
<td>d004</td>
<td>-</td>
<td>-</td>
<td>1000 2</td>
<td>#4 Si</td>
</tr>
<tr>
<td>d005</td>
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<td>-</td>
<td>1000 4</td>
<td>#1 Si&lt;sub&gt;0.5&lt;/sub&gt;Ge&lt;sub&gt;0.5&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
</tr>
<tr>
<td>d006</td>
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<td>-</td>
<td>1000 4</td>
<td>#4 Si</td>
</tr>
<tr>
<td>d007</td>
<td>-</td>
<td>-</td>
<td>1000 9</td>
<td>#1 Si&lt;sub&gt;0.5&lt;/sub&gt;Ge&lt;sub&gt;0.5&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
</tr>
<tr>
<td>d008</td>
<td>-</td>
<td>-</td>
<td>1000 9</td>
<td>#4 Si</td>
</tr>
<tr>
<td>d009</td>
<td>-</td>
<td>-</td>
<td>1000 24</td>
<td>#1 Si&lt;sub&gt;0.5&lt;/sub&gt;Ge&lt;sub&gt;0.5&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
</tr>
<tr>
<td>d010</td>
<td>-</td>
<td>-</td>
<td>1000 24</td>
<td>#4 Si</td>
</tr>
<tr>
<td>d401</td>
<td>1000 15</td>
<td>1000 1</td>
<td>#3 Si&lt;sub&gt;0.2&lt;/sub&gt;Ge&lt;sub&gt;0.8&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
<td>RBS</td>
</tr>
<tr>
<td>d402</td>
<td>1000 15</td>
<td>1000 1</td>
<td>#4 Si</td>
<td>RBS</td>
</tr>
<tr>
<td>d403</td>
<td>-</td>
<td>-</td>
<td>1000 1</td>
<td>#3 Si&lt;sub&gt;0.2&lt;/sub&gt;Ge&lt;sub&gt;0.8&lt;/sub&gt; /Si&lt;sub&gt;sub&lt;/sub&gt;</td>
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<td>1000 4</td>
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<td>d408</td>
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<td>1000 18</td>
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<td>RBS</td>
</tr>
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<td>d410</td>
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<td>1000 18</td>
<td>#4 Si</td>
<td>RBS</td>
</tr>
<tr>
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<td>-</td>
<td>1000 18</td>
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<tr>
<td>d412</td>
<td>-</td>
<td>-</td>
<td>1000 18</td>
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Table A1.2 (ii) Samples used in dry oxidation experiments.

<table>
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<tr>
<th>Sample number</th>
<th>Ambient</th>
<th>Dry O₂</th>
<th>Wafer number</th>
<th>Structure of wafer</th>
<th>Methods of analysis</th>
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<td></td>
<td>N₂ (preheating) T(°C) t (mins)</td>
<td>Dry O₂ T(°C) t (hrs)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>d413</td>
<td>900 15</td>
<td>900 1</td>
<td>#3</td>
<td>Si₀.₄₅Ge₀.₅₅ /Si₇₅</td>
<td>RBS</td>
</tr>
<tr>
<td>d414</td>
<td>900 15</td>
<td>900 1</td>
<td>#4</td>
<td>Si</td>
<td>RBS</td>
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<td>d415</td>
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<td>900 1</td>
<td>#3</td>
<td>Si₀.₄₅Ge₀.₅₅ /Si₇₅</td>
<td>RBS</td>
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<td>RBS</td>
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<td>RBS</td>
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<td>d418</td>
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<td>900 6</td>
<td>#4</td>
<td>Si</td>
<td>RBS</td>
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<td>900 6</td>
<td>#3</td>
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<td>900 12</td>
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<td>d423</td>
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<td>900 24</td>
<td>#4</td>
<td>Si</td>
<td>RBS</td>
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Table AI.3 Samples used in internal oxidation experiments.

All samples implanted with 200keV O⁺ ions

<table>
<thead>
<tr>
<th>Sample number</th>
<th>O⁺ implantation dose (10¹⁸/cm²)</th>
<th>Anneal details</th>
<th>Wafer number</th>
<th>Methods of analysis</th>
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<tr>
<td>i7a</td>
<td>0.6 (low)</td>
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<td>RBS, XPS, IR</td>
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<td>i7b</td>
<td>1.8 (high)</td>
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<td>RBS, XPS, IR</td>
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<td>#2</td>
<td>RBS, XPS, IR</td>
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<td>i7a8</td>
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<td>RBS, IR</td>
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<td>1.8 (high)</td>
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<td>RBS, XPS, IR</td>
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<td>#2</td>
<td>RBS, XPS, IR</td>
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<td>0.6 (low)</td>
<td>900 1</td>
<td>#2</td>
<td>RBS, IR</td>
</tr>
<tr>
<td>i7b9</td>
<td>1.8 (high)</td>
<td>900 1</td>
<td>#2</td>
<td>RBS, XPS, IR</td>
</tr>
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<td>i7c9</td>
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<td>900 1</td>
<td>#2</td>
<td>RBS, IR</td>
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<td>1.8 (high)</td>
<td>1000 1</td>
<td>#2</td>
<td>RBS, XPS, IR</td>
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<td>1000 1</td>
<td>#2</td>
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<tr>
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<td>-</td>
<td>#5</td>
<td>RBS,</td>
</tr>
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<td>i14b</td>
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<td>#5</td>
<td>RBS</td>
</tr>
<tr>
<td>i14c</td>
<td>1.2 (medium)</td>
<td>-</td>
<td>#5</td>
<td>RBS</td>
</tr>
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</table>
APPENDIX - II

BASIC PRINCIPLES OF RUTHERFORD BACKSCATTERING SPECTROMETRY

Rutherford backscattering spectrometry (RBS), named after Ernest Rutherford who correctly interpreted large angle Coulomb scattering of alpha particles from thin metal foils in 1911 [95], has been a standard analysis technique in material sciences since the late 1960's. The method consists of irradiating the unknown target with mono-energetic ions (MeV range of energies) using light elements such as hydrogen or helium. The elastically backscattered particles that are emitted from the target are detected and energy analysed (usually using a solid state detector such as Si with a Au/Al Schottky barrier) and presented as an energy spectrum. This technique enables the composition of an unknown target to be determined in terms of the atomic mass and concentration depth profile of the constituent. In this appendix the fundamental concepts of RBS analysis are introduced.

AII.1 Mass and depth

When analysing a sample many scattering events will occur including large angle (scattering angle >90°) scattering (i.e. backscattering) which has a small probability. In general, typically ~$10^{14}$/cm$^2$ He$^+$ particles will be incident upon the sample of which, typically, ~$10^8$/cm$^2$ He$^+$ particles will be backscattered and a small proportion of them will enter the detector. Rutherford backscattering analysis provides an ability to distinguish the atomic mass of elements in a target and their depth profile from the energy spectrum of the backscattered particles. As an example, figure AII.1 illustrates a typical backscattering energy spectrum of 1.5 MeV $^4$He$^+$ particles ($E_0=1.5$ MeV) with an incident angle $\theta_i=0$ scattered from a Si$_m$O$_n$ film (here $m=1$ and $n=2$ for SiO$_2$) on a Si substrate and analysed at a scattering angle $\theta=160^\circ$. The energy scale conversion from the channel scale was described in section 4.4.2. Figure AII.2 (a) and (b) shows, (a) a schematic diagram of the geometry and notation of energies at the surface and interface between Si$_m$O$_n$ film and Si substrate and (b) a schematic spectrum constructed from figure AII.1. For simplicity, the contribution of the
Figure AII.1 A typical non-channelling RBS spectrum of 1.5 MeV $^4$He$^+$ particles scattered from a 320 nm SiO$_2$ film on a Si substrate.
Figure AII.2 Upper, a schematic diagram of the geometry and notation of energies at the surface and interface between SiO₂ film and Si substrate and lower, the schematic spectrum constructed from figure AII.1.
Si substrate to the spectrum is not shown. When a particle of mass \( M_1 \) (for example, a \(^4\)He\(^+\) particle with \( M_1 = 4 \)) with incident energy \( E_0 \) collides elastically with a target atom of mass \( M \), the energy of the particle is reduced to \( E_{0,0}(M) \) after scattering from the surface (figure AII.2 (a)). Here \( E_{0,0} \) represents a particle with an energy \( E_0 \) which is scattered from the surface (depth 0-the right side of subscript, 0). This energy is proportional to the kinetic recoil factor \( K_M \) [83,97]

\[
E_{0,0}(M) = K_ME_0
\]  

(AII.1)

where the kinetic recoil factor \( K_M \) is a function of the mass \( M \) of the target atoms, the mass \( M_1 \) of the analysing particles and the scattering angle \( \theta \) [83,97].

\[
K_M = \frac{\left[M_1\cos\theta + \left(M^2 - M_1^2 \sin^2\theta\right)^{1/2}\right]}{M_1 + M}
\]  

(AII.2)

The energy spectrum can be converted to a mass scale using equations AII.1 and AII.2 as shown in figure AII.1. The lower abscissa gives the energy scale of the backscattering spectrum whilst the upper abscissa gives the mass \( M \) associated with positions \( K_ME_0 \). As an example, a few elements are indicated in the upper abscissa. Note that the mass to energy conversion established via \( K_M \) is unique, but nonlinear.

There are two elements in this experiment, as shown in figure AII.1, between the arrows labelled \( \downarrow \) Si and \( \downarrow \) O. As the particles penetrate the \( \text{Si}_{\text{in}}\text{O}_{n} \), there is an energy loss \( \Delta E/\Delta x \) along the path. The magnitude of their energy loss is a function of energy, stopping material and projectile. When the \( \text{He}^+ \) particles penetrate the total thickness of the film (\( x = 320 \text{ nm} \)), before suffering a large angle scattering, they have energy \( E_x \) (figure AII.2):

\[
E_x = \int_{x=0}^{320} \frac{\Delta E}{\Delta x} \, dx
\]  

(AII.3)

Since \( \Delta E/\Delta x \) is a slow function of energy, an average value \( \Delta E/\Delta x|_{\text{in}} \) can be used for the entire inward path without introducing unacceptable errors [83] and equation (AII.3) can be simplified to
\[ E_x = E_0 - [x][dE/dx]_{in} \]  \hspace{1cm} (AII.4)

After the He\(^+\) particles have been scattered through a scattering angle \( \theta \) from the Si or O located at \( x = 320 \) nm, they will have an energy \( E_{xx}(M) \) (see figure AII.2 (a) and (b)). Here \( E_{xx}(M) \) represents the particle with an energy \( E_x \) and scattered at depth \( x \).

\[ E_{xx}(M) = K_m E_x \]  \hspace{1cm} (AII.5)

On the outward path, the He\(^+\) particles lose energy again and emerge from the target with an energy \( E_{x0}(M) \) (figure AII.2), where

\[ E_{x0}(M) = E_{xx} - [x/|\cos \theta|][dE/dx]_{out} \]  \hspace{1cm} (AII.6)

where \( [dE/dx]_{out} \) represents an average value along the outgoing path. From figure AII.2 (a) it is clear that the energy width \( \Delta E(M) \) is given by

\[ \Delta E(M) = E_{00} - E_{x0}(M) \]  \hspace{1cm} (AII.7)

From equations AII.1 - AII.6 the equation AII.7 can be rewritten as

\[ \Delta E(M) = \{K_m[dE/dx]_m + [1/|\cos \theta|][dE/dx]_{out}\}[x] \]  \hspace{1cm} (AII.8)

or

\[ \Delta E(M) = [S]^M[x] \]  \hspace{1cm} (AII.9)

where the backscattering energy loss factor \([S]^M\) is dependent on \( K_m \) and the energy loss per unit path length, \( dE/dx \), and is defined as

\[ [S]^M = \{[K_m[dE/dx]_m + [1/|\cos \theta|][dE/dx]_{out}\} \]  \hspace{1cm} (AII.10)

As the He\(^+\) particles penetrate to different depths an energy spectrum will be built up due to the loss of energy along the inward and outward paths (figure AII.2 (b)). Because of the energy loss of the He\(^+\) ions in the target material, the He\(^+\) ions scattered from a larger depth will have lower energy. The low energies labelled, \( \downarrow \text{Si}_x \) and \( \downarrow \text{O}_x \) in figure AII.1, represent scattering from the interface of \( \text{Si}_m\text{O}_n \) film and the Si substrate at depth \( x \), respectively. The He\(^+\) particles backscattered (the signals) from Si and O within the Si\_m\_O\_n layer have energies which fall between energy \( \sim 700-860 \) keV and \( \sim 383-556 \) keV, labelled A(Si) and A(O),

A-10
respectively (figure AII.1). A continuous part of the spectrum between energies 233keV and 700 keV (dashed line) corresponds to the Si substrate. The oxygen signal overlaps this continuous part of the spectrum. The energy difference, \( \Delta E(\text{Si}) \) and \( \Delta E(\text{O}) \), represents the amount of energy lost by the \( \text{He}^+ \) particles during their inward and outward passage through the layer. From a knowledge of \( \Delta E(M) \) (AII.8) the total thickness of the layer can be calculated by

\[
x = \frac{\Delta E(\text{Si})}{\left\{ K_{\text{Si}}(dE/dx)_{\text{in}} + [1/|\cos\theta|](dE/dx)_{\text{out}} \right\}} \quad \text{(AII.11)}
\]

or

\[
x = \frac{\Delta E(\text{O})}{\left\{ K_{\text{O}}(dE/dx)_{\text{in}} + [1/|\cos\theta|](dE/dx)_{\text{out}} \right\}} \quad \text{(AII.12)}
\]

Usually the values of \( dE/dx \) are given in terms of the stopping cross section \( \varepsilon = (1/N)(dE/dx) \), where \( N \) is the atomic density of the material. The values of the stopping cross section \( \varepsilon \) of \( \text{H}^+ \) and \( \text{He}^+ \) for all energies and all elements have been compiled by Anderson and Ziegler [96]. When one deals with compound targets, an attention to the stopping cross section (Bragg's Rule) must be applied [83, 97], i.e.

\[
\varepsilon \text{SimO}_{n} = n\varepsilon \text{Si} + n\varepsilon \text{O} \quad \text{(AII.13)}
\]

The thicknesses of the films can then be calculated by using the following equations:

\[
x = \frac{\Delta E(\text{Si})}{\left\{ N_{\text{SiO}_2}\left[ (K_{\text{Si}}\varepsilon \text{SimO}_{n}(E_{\text{in}})) + [1/|\cos\theta|]\varepsilon \text{SimO}_{n}(E_{\text{out}}) \right) \right\}} \quad \text{(AII.14)}
\]

or

\[
x = \frac{\Delta E(\text{O})}{\left\{ N_{\text{SiO}_2}\left[ (K_{\text{O}}\varepsilon \text{SimO}_{n}(E_{\text{in}})) + [1/|\cos\theta|]\varepsilon \text{SimO}_{n}(E_{\text{out}}) \right) \right\}} \quad \text{(AII.15)}
\]

AII.2 Determination of Composition

In RBS analysis, the number of atoms per square centimetre of target, i.e. the areal density of the target \( (N_x) \), where \( N \) is the atomic concentration (atom cm\(^{-3}\)), can be determined by RBS analysis. The areas \( A(\text{O}) \) and \( A(\text{Si}) \) in figure AII.1 are proportional to the total number of atoms per unit area \( (N_x) \) of each element and to the Rutherford Differential Scattering Cross Section \( \sigma_R \). According to the Rutherford formula, \( \sigma_R \) is given as [83, 97],
\[ \sigma_R = (Z, Ze^2/E_r)^2 (\sin^4 \theta/2)^{-1} \] (AII.16)

where \( Z_i \) and \( Z \) are the atomic numbers of the incident particles (\( Z_i = 2 \) for \( ^4\text{He}^+ \)) and the target atoms (\( Z = 8 \) for O and \( Z = 14 \) for Si), respectively. For an integrated charge \( Q \) of \( ^4\text{He}^+ \) particles, and a detector solid angle \( \Omega \), the total area \( A \) (in counts) under the peak is given by [83, 97]

\[ A = Q \Omega \sigma_R [N_x] \] (AII.17)

The yield of the spectrum is also defined by the number of scattering events in an incremental target thickness \( \delta x \). Figure AII.3 (a) and (b) [97] includes a schematic energy spectrum, (a) at the surface and (b) in the target at depth \( x \), to define the yield. From figure AII.3 (a) \( \delta x \) is the incremental thickness in the target from which backscattering into the energy interval \( \delta E \) takes place (from equation AII.9 \( \delta E = [S] \delta x \)). The increment \( \delta E \) is the energy width of one channel which is fixed by the gain of the electronic system and is set to be 3.10 keV/ channel in our experimental system (see section 4.4.2). Thus, the spectrum yield evaluated at the surface can be written as [83,97]

\[ H_{M}(E_0) = Q \Omega \sigma_R N \delta x \] (AII.18)

or

\[ H_{M}(E_0) = Q \Omega \sigma_R N \delta E/[S] \]

\[ = Q \Omega \sigma_R \delta E/[K_m E_x (E_0)] + [1/(\cos \theta)] e(E_{out}) \] (AII.19)

It should be noted in figure AII.3 (b) that \( \delta E \) is defined as the energy width of one channel of the detecting system (pulse height analyser), which is set to be constant when the detector system is set up, and \( \delta(K_m E_x) \) is the corresponding energy width within the target at the scattering depth \( x \). It is known that [83,79] \( \delta(K_m E_x) = [e(K_m E_x)/e(K_m E_{x,0})] \delta(E) \).

Similar to equation AII.19, the spectrum yield at energy \( E_{x,0}(M) \) is given by

\[ H_{M}(E_{x,0}) = Q \Omega N(M) \sigma_R (M) \delta(K_m E_x)/(S) \]

\[ = Q \Omega \sigma_R (M) \delta(K_m E_x)/[K_m E_x (E_0)] + (1/(\cos \theta)] e(H_{out}) \] (AII.20)

In the case of \( \text{Si}_m \text{O}_n \), the area \( A \) and the yield \( H \) are given by
Figure AII.3 A schematic diagram of the energy spectrum, (a) at the surface and (b) in the target at a depth \( x \), to help with the description of the definition of the yield [97].
\[ A(\text{Si}) = Q \sigma_r(\text{Si}) [xN(\text{Si})] \]  
\[ A(\text{O}) = Q \sigma_r(\text{O}) [xN(\text{O})] \]

Thus

\[ H_{\text{Si}}(E_x) = \frac{\Omega Q [m_x] \sigma_r(\text{Si}) \delta(K_{\text{Si}}E_x)}{K_{\text{Si}} e^{\text{SimOn}(E_x)} + e^{\text{SimOn}(K_{\text{Si}}E_x)}/|\cos\theta|} \]  
\[ H_{\text{O}}(E_x) = \frac{\Omega Q [n_x] \sigma_r(\text{O}) \delta(K_{\text{O}}E_x)}{K_{\text{O}} e^{\text{SimOn}(E_x)} + e^{\text{SimOn}(K_{\text{O}}E_x)}/|\cos\theta|} \]

The average composition of the film defined as \( \text{Si}_m\text{O}_n \) can be obtained by comparing the yield or the area of the signals \( A(\text{Si}) \) and \( A(\text{O}) \) (see figure AII.1) where

\[ m/n = [A(\text{Si})/A(\text{O})] [\sigma_r(\text{O})/\sigma_r(\text{Si})] \]  
\[ \text{and the composition of the film at depth } x \text{ is given by} \]

\[ [m/n]_x = \frac{H_{\text{Si}}(E_x) \sigma_r(\text{O}) \delta(K_{\text{O}}E_x) [K_{\text{O}} e^{\text{SimOn}(E_x)} + e^{\text{SimOn}(K_{\text{O}}E_x)}/|\cos\theta|]}{H_{\text{O}}(E_x) \sigma_r(\text{Si}) \delta(K_{\text{Si}}E_x) [K_{\text{Si}} e^{\text{SimOn}(E_x)} + e^{\text{SimOn}(K_{\text{Si}}E_x)}/|\cos\theta|]} \]

where the ratio of \( \sigma_r(\text{O})/\sigma_r(\text{Si}) \) is proportional to the ratio of the atomic numbers of O and Si. Taking data from \( \sigma_r(\text{O})/\sigma_r(\text{Si}) = [8/14]^2 \), \( e^{\text{SimOn}} \) from the stopping cross section data [96] and \( H_{\text{Si}}(E_o)/H_{\text{O}}(E_o) \) from the spectrum as indicated in figure AII.1, we find a value of \( m/n = 0.5 \pm 0.04 \). When experimental uncertainties are taken into account, we assume the composition of oxide to be \( \text{SiO}_2 \).