Defect-Mediated Nanostructures and Luminescence Centres in Silicon

Supakit Charnvanichborikarn

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Declaration

I certify that the work contained in this thesis, except where explicitly stated, is original research conducted by the author.

Supakit Charnvanichborikarn
To my parents and grandparents

for instilling in me the value of education
Acknowledgements

Finally, it's time for me to write these few pages. Yes, it is getting close to the end of this long journey. "Hang in there, mate!", I said to myself. These five years of my Ph.D. program will be my lifetime memory. Overall, it has been a great experience and I could not have hoped for more.

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Abstract

Research over the past decade has indicated that ion implantation provides an attractive way of forming nanocrystals in solids that exhibit some exciting new material properties. However, the size and size distribution of these nanoparticles are both very difficult parameters to control, especially when a subsequent thermal anneal is needed to form well-defined precipitates. This usually leads to somewhat uncontrolled growth by the Ostwald ripening effect. In addition, ion implantation is known to create structural damage to crystals (especially semiconductors such as silicon), which evolves into many types of defects depending on the annealing regime and degree of damage. Some of these defects in silicon are optically active and can be detected by photoluminescence (PL), while others are inactive and may act as non-radiative recombination centres.

The first part of this thesis concentrates on the encapsulation of Au nanoparticles in silicon and SiO₂ using a combination of ion implantation, high temperature annealing, and wet oxidation. Structural analysis was undertaken by Rutherford backscattering spectrometry and channeling (RBS-C) in conjunction with transmission electron microscopy (TEM). The final structure of Au embedded at a precise depth in SiO₂ was achieved by wet oxidising the top silicon layer of a silicon-on-insulator (SOI) wafer containing Au precipitates. Several interesting phenomena including the segregation of Au precipitates at the oxidising interface, Au-enhanced oxidation, and preferential reprecipitation of Au on the Si–SiO₂ interface after dissolution are observed. The role of excess silicon-interstitials, which are injected into the underlying silicon during the oxidation process and mechanisms have been proposed to explain the results.

In the second part, Si implantation to a range of fluences and subsequent annealing under various conditions were used to form different types of interstitial-based defects
in crystalline silicon. Results show that low dose implantation \(10^{10}\) to \(10^{13}\) \(\text{cm}^{-2}\) and a low thermal budget annealing process (up to 525 °C for 2 minutes) are favourable for the observation of luminescence from small interstitial-related defect clusters (principally as the \(W\)-line at 1218 nm and the \(X\)-line at 1193 nm). Higher fluences create higher damage levels that lead to a formation of extended \(\{311\}\) defects and dislocations by annealing at higher temperatures, as can be identified by the \(R\)-line luminescence (at 1375 nm), as well as D-bands (around 1428 nm and 1530 nm), respectively. The \(W\)-line, in particular, is so sharp and bright that it was exploited to realise a sub-bandgap silicon light emitting diode (LED). The quantum efficiency of the fabricated LEDs is, however, poor especially when additional boron is introduced to create a \(p^+\) layer that serves the purpose of making a good electrical contact at low temperature. An extended study on the effect of boron is consequently carried out in the last experimental chapter, where the competing formation between optically active silicon-interstitial defects and boron-interstitial clusters (BICs) is argued for this luminescence intensity loss. The results presented in this thesis have provided a better understanding of defect-defect and defect-impurity interactions and may inspire future research on silicon-based applications.
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General Introduction and Background

The aim of this chapter is to provide the motivation behind this thesis, which investigates two methods for potentially enhancing light emission from silicon. An outline of the thesis is also provided at the end of this chapter.
1.1 Motivation: silicon as a light emitter

Figure 1.1: The number of publications on silicon-related topic in the past 10 years. (From ISI Web of Knowledge database as of July 2010.)

Silicon is the second most abundant element in the earth’s crust (27.7%) after oxygen (46.6%) [1] and the semiconductor material that dominates the microelectronics industry. As a result, it is economically inexpensive [2]. After more than half a century of intense research effort into silicon processing, silicon is considered a mature technology, yet an active research topic of interest. Figure 1.1 shows that the number of silicon-related publications has continued to increase steadily in the last 10 years. In Australia, there has also been considerable research interest in silicon, as indicated by the fact that over $2.5 million has been funded by the Australian Research Council (ARC) in 2009 on a range of silicon-related discovery projects. Such a growing interest in silicon is due not only to the excellent mechanical, electrical, and thermal properties of silicon, but also to a lack of understanding of a number of process-related issues on the nanoscale as device dimensions are scaled down. Specific crystalline silicon properties can be found in Ref. [3]. In addition, silicon naturally forms a high quality oxide, which is necessary for the fabrication of electronic devices and has been one of the most attractive features of silicon for electronic applications.

The device size has progressively shrunk to a submicrometre scale to satisfy rigorous
1.1. Motivation: silicon as a light emitter

Figure 1.2: Electronic band diagram of (a) indirect bandgap Si and (b) direct bandgap InP. The arrows illustrate the bandgap in $k$ space. (After Chelikowsky et al. [4])

demands for higher packaging density and enhanced speed of devices as driven by the industry and following the famous Moore's law [5]. Despite better manufacturing techniques, this miniaturisation poses several problems that were not present with the functioning of the devices in the micrometre scale. Some issues that have become more important as a consequence of the shrinkage are, for instance, the diffusion of metals (for contacts) into the device active layer during thermal processing, the redistribution of impurities during dopant activation, defects and their interactions during thermal processing that subsequently deteriorate device performance, and the overheating problem as the number of transistors on an integrated circuit exponentially increases.

The problem of overheating may be overcome to some extent by a development of optoelectronic or photonic devices for optical interconnects. However, this route for silicon is not straightforward. This is because silicon is not a good optoelectronic semiconductor material. Intrinsic bulk silicon is usually regarded as an inefficient light emitter (long radiative carrier recombination lifetime) due mainly to its indirect bandgap. That is, a carrier transition from the conduction band to the valence band requires participation of (at least) a phonon with appropriate momentum. Figure 1.2 shows the electronic band structure in a wave-vector $k$ space of (a) bulk silicon and (b) a direct bandgap compound semiconductor indium phosphide (InP), as calculated by an
empirical non-local pseudopotential method [4]. Several approaches have been used to get around this hurdle for strong silicon luminescence and these are reviewed separately in Chapter 6.

Since novel applications of ion implantation are a particular focus of the Electronic Materials Engineering (EME) department at The Australian National University (ANU), a focus of this thesis was to explore whether ion implantation (or irradiation) could be used innovatively to assist more efficient light emission from silicon. Initially, implantation-induced nanoparticles formed in SiO₂ in an attempt to obtain different optical properties from those of the bulk material. In most cases, such properties are critically dependent on the particle size and size distribution, which are two very difficult factors to control. The use of cavities or voids to form metal nanoparticles of tight size distribution via the gettering process has been successfully demonstrated by group members in silicon, but remains a challenge in SiO₂. This provides motivation for the first part of this thesis: to start with a simple scheme of Au nanoparticles in silicon and then progress to SiO₂ to look at the feasibility of obtaining a tight nanoparticle size distribution.

Partly since the optical characterisation of the samples containing Au nanoparticles of tight size and depth distribution in SiO₂, [see Chapter 4] did not exhibit the expected promise, another pathway for exploring the uses of ion implantation as a means for enhancing light emission was pursued through the investigation of radiation-induced defects.

Defects are natural constituents in solid matters including semiconductors. It is, therefore, necessary to understand their behaviours and be able to control them in order to create functional materials. Defects in silicon can be incorporated during the crystal growth (intrinsic defects) [6] or inevitably produced during the process of ion implantation and subsequent thermal annealing (extrinsic defects) [7–9]. Other defect-generated processes include reactive ion etching (RIE) [10], mechanical deformation [11], and even oxidation [12, 13]. Defect-defect interactions occur upon thermal annealing and lead to both annihilation of small point defects such as vacancies and interstitials and agglomeration into larger defect clusters or complexes, extended defects, and dislocations [7], which in turn play a significant role in the diffusion and trapping of impurity atoms in silicon – processes that are covered more fully in Chapters 3 and 4.

Implantation-induced defects also provide localised energy states in the forbidden gap of the silicon band structure, as shown in Fig. 1.2(a). They, therefore, directly influence not only the physical but also the electronic and optical properties of the material. Indeed,
previous studies have shown that some of these defects are optically active and give rise to luminescence. However, they have not been examined in detail for possibility of light emitting devices since radiation damage as well as defects and impurities are generally undesirable artifacts of ion implantation that limit application performance and reliability [14, 15]. As a consequence, not many studies have been conducted to understand the effects of common dopants in silicon such as boron (for p-type) and phosphorus (for n-type) on the luminescence intensity from radiation-induced defect complexes. Chapter 7 of this thesis addresses the gap in the literature pertaining to the interactions between impurities and interstitial-related luminescence centres.

1.2 Thesis structure

This thesis contains the following chapters. General experimental techniques used in this work and some particular analysis examples are described in Chapter 2. Chapter 3 begins with the introduction of some previous works on the process of metal gettering to H-induced cavities in silicon. Those achievements constituted the inspiration for the first part of this thesis, namely to obtain Au nanoparticles of a desired size in silicon and ultimately in SiO₂. From an application perspective, such a structure may benefit from nanoscale properties that do not occur in bulk materials, thus opening up an opportunity for the development of novel silicon-based optoelectronic devices. The results of Au nanoparticles formed in silicon and SiO₂ are also given in Chapter 3. Based on some intriguing observations relating to Au behaviour under oxidation of silicon that emerged in Chapter 3, further detailed studies to understand the underlying mechanisms are given in Chapter 4. The poor optical performance of Au nanoparticles in SiO₂ resulted in the focus of the thesis turning to defect-mediated luminescence. An overview of luminescence signatures from defects in silicon observed under various post-implantation annealing conditions is provided in Chapter 5, where new information on the luminescent behaviour of different defects is presented. In Chapter 6, one of the luminescence lines with a sharp and intense peak at 1218 nm (the so-called W-line) is selected to demonstrate a working light emitting diode (LED). This device exhibited a decrease in external quantum efficiency (EQE) when boron was implanted into the structure to create a buried contact or electrode. Chapter 7 subsequently investigates this boron effect in detail using p-type silicon wafers with different boron background concentrations as well as phosphorus-doped n-type silicon wafers for comparison. The results are discussed and compared with theoretical
predictions of boron interstitial cluster (BIC) formation. Finally, Chapter 8 summarises the important issues addressed in this thesis and indicates future research directions that have arisen from this work and may provide further stimulus for the development of silicon-based applications.

References


Experimental Techniques

Basic principles and general descriptions of sample preparation and characterisation employed in this study are provided in two major sections: processing and characterisation. The former includes ion implantation, thermal annealing, pulsed laser melting, and wet oxidation, while the latter consists of Rutherford backscattering spectrometry and channeling, transmission electron microscopy, luminescence spectroscopy, and electrical measurements. More specific details of the experiments undertaken are beyond the scope of this chapter and will be given later in the separate chapters that deal with results.
2.1 Processing

Throughout the processes of fabrication, all the samples were handled with plastic tweezers to minimise metal contamination and its effects during annealing.

2.1.1 Ion implantation

Ion implantation is a standard technique in the fabrication of silicon microelectronic devices. Ion implantation was used for three main purposes: (1) to introduce certain elements such as Au, B, P, and S into the silicon matrix; (2) to create an amorphous layer for liquid/solid phase epitaxial growth; and (3) to create radiation damage, which evolves into point defect clusters, extended defects, and dislocations after appropriate thermal treatment.

The ion implanted ranges ($R_p$) and distributions are crucial for the fabrication of nanostructures and can be pre-determined by a Monte Carlo based SRIM (Stopping and Range of Ion in Matter) simulation. [1] The calculations take into account the interactions between energetic ions and atoms in the targets. In general, the $R_p$ of the ions can be determined in any material from their atomic mass, implantation energy, and the ion incident angle. However, the amount of irradiation damage which destroys crystallinity of the substrate depends also on other additional parameters. Specifically, the ion fluence, ion mass, and implantation temperature control damage accumulation. In addition to SRIM, FASTRIM [2] was used to calculate damage-depth distributions as well as numbers of excess Si interstitials and vacancies generated by ion implantation.

Unless stated otherwise, the implantations were carried out at 7° from the surface normal in order to minimise channelling effects. The two ion implanters used in this research are described in the following subsections.

2.1.1.1 Low energy implantation

This ANU in-house implanter was mainly used for implants at energies ranging from 10 to 150 keV depending on ion species. The ion source is an NEC (National Electrostatics Corporation) SNICS (Source of Negative Ions by Cesium Sputtering) where the ion beam is produced by Cs sputtering of a solid cathode. In this work, all the cathodes were pressed powders. The ions were accelerated through an Einzel lens and along the beam line. The desired species was then resolved using a 90° magnet. Figure 2.1 illustrates the schematic of the low energy ion implanter. The beam was scanned over the sample
through an aperture in both vertical and horizontal directions to ensure the uniformity of the fluence over the implanted area. A cylindrical Cu cold shield was also used to suppress secondary electrons. The beam profile was monitored via a Tektronix TAS 465 cathode ray oscilloscope (CRO). To avoid the possibility of beam contamination, the implants were carried out when the average pressure along the beam line was in $10^{-7}$ Torr range.

2.1.1.2 High energy implantation

The NEC 1.7 MeV Tandem Pelletron Accelerator (model 5SDH-4) coupled with the same type of sputter source was used for implantation in the higher energy regime. Figure 2.2 shows the schematic of the high energy ion implanter. The negatively charged ions (atomic or molecular species) were extracted out of the source by Cs sputtering and accelerated by a combination of cathode, extractor, and bias voltage to the energy of up to 100 keV. Certain ion species were chosen according to the charge-to-mass ratio before entering the high voltage terminal, of which the maximum potential is 1.7 MV, by adjusting the magnetic field intensity of the $90^\circ$ mass analysing magnet $B_{\text{anal}}$ to the value given by
Figure 2.2: Schematic of the high energy ion implanter
\[ B_{\text{anal}} = 0.628 \cdot \frac{\sqrt{M_i \cdot E_{\text{src}}}}{q_i}, \] (2.1)

where \( M_i \) is the atomic mass of injected ion, \( q_i \) is the injected ion charge, which in our case is always a single-charge state. The source energy \( E_{\text{src}} \) is a product of ion charge and source voltage \( V_{\text{src}} \):

\[ E_{\text{src}} = q_i \cdot V_{\text{src}}, \] (2.2)

where \( V_{\text{src}} \) is the sum of cathode voltage \( V_{\text{cat}} \), extractor voltage \( V_{\text{ext}} \), and source bias \( V_{\text{bias}} \) (\( V_{\text{src}} = V_{\text{cat}} + V_{\text{ext}} + V_{\text{bias}} \)). For the implantation energy above 100 keV, nitrogen gas was used to strip electrons off the negative ions, creating neutrally, singly, and multiply charged positive ions. Molecular ion species are split up in the stripper with the energy of the various species proportional to their mass as below. Consequently, the positive ions generated in the stripper were further accelerated away from the positively charged terminal, \( V_T \). The (implantation) energy of (positive) ions after this final acceleration is given by:

\[ E_{\text{imp}} = \left( q_i \cdot \frac{M_f}{M_i} + q_f \right) V_T + q_i \cdot \frac{M_f}{M_i} \cdot V_{\text{src}}, \] (2.3)

where \( E_{\text{imp}} \) is the implanted energy (in MeV), \( M_f \) and \( q_f \) are the atomic mass and charge state of the accelerated positive (implanted) ion, respectively, and \( M_i \) is the negative ion mass before stripping. For atomic ion species and single charge states which is the usual situation for the studies of this thesis, \( M_i = M_f \) and \( q_i = q_f = 1 \), leading to \( E_{\text{imp}} = 2V_T + V_{\text{src}} \).

Before implantation, the ions of desired species (and charge state) were selected by tuning the magnetic field intensity of the 15° switching magnet \( B_{\text{sw}} \) to

\[ B_{\text{sw}} = 3.808 \cdot \frac{\sqrt{M_f \cdot E_{\text{imp}}}}{q_f}. \] (2.4)

The beam was focussed onto the target in the target chamber using a combination of electrostatic, vertical (Y) and horizontal (X) steerers (including an Einzel lens), a further high energy Y steerer, and a quadrupole lens. Similar to the low energy implanter, the beam was scanned across an aperture located in front of the target. At operation, the average pressure inside the beam line was kept below 10^{-7} Torr to minimise the amount of neutral beam present. The amount of time needed for implantation \( t \) is dependent on the beam
current $i$, the required dose $\phi$, the charge state $q_f$, and the implanted area $A$ as described in the following equation:

$$ t = \frac{e \cdot q_f \cdot A \cdot \phi}{i}, $$

(2.5)

where $e$ represents the elementary charge of $1.6 \times 10^{-19}$ C. The nickel or stainless steel sample holders were designed such that they are interchangeable between the two implanters and are capable of temperature dependent implantation ranging from 77 K to several hundred Kelvin above room temperature.

Specifically for this study, our implantation experiments are in a keV range, from energies as low as 10 keV to as high as 600 keV. A range of ion species including H, Au (in Chapters 3 and 4), Si (in Chapters 4, 5, 6, and 7), B and P (in Chapters 6 and 7) were used. Although most of the implantation works were performed at room-temperature, some were specially carried out either at a liquid nitrogen temperature to promote amorphisation or at an elevated temperature of 275 °C to prevent amorphisation. In any case, the ion beam current was kept below 2 μA to minimise localised substrate heating that may lead to an unpredictable disorder or recrystallisation of the substrate.

### 2.1.2 Thermal annealing

Thermal annealing was a vital process for several aspects of this thesis. Depending on the annealing timescale, different types of thermal treatments were performed in an Ar ambient.

#### 2.1.2.1 Rapid thermal annealing

For abrupt heating and cooling rate, rapid thermal annealing (RTA) was used to anneal the samples for times under 5 minutes. The annealing experiments at ANU were performed with an AET Rapid Thermal Processor (RX Series) in an Ar ambient. The samples were rested on a piece of virgin Si wafer, to which the thermocouple was attached. The processing steps, including the annealing temperature and the amount of gas flow, were defined in the corresponding AET software. An external thermocouple reader was also used as a secondary source of temperature monitoring. Initially the furnace tube was purged with 5 lt/min Ar for 2-3 minutes. The sample temperature was brought up to the set point within 7 seconds and maintained during the annealing period in a low flow ($\leq 0.5$ lt/min) environment. The Ar gas flow was kept to 5 lt/min for at least 5 minutes at the end
of each annealing process to purge the tube. The samples were always left to cool down in the furnace and removed when the sample temperature was below 50 °C to reduce the possibility of surface oxidation.

2.1.2.2 Furnace annealing

Furnace annealing was used for all the anneals from 5 minutes and over. Most of the samples annealed at ANU were carried out in a Lindberg 1-zone furnace. For each particular annealing temperature, calibration at the centre of the furnace was performed to ensure that the variation of the sample temperature is maintained within ±5 °C of the required processing temperature. A typical example of the calibration plot is illustrated in Fig. 2.3. In this case, the temperature of the furnace was set to 900 °C, while the temperature at the centre of the furnace was measured to be about 921 °C.

![Temperature vs Time Graph](image)

**Figure 2.3:** An example of a furnace calibration plot for conventional annealing process. The temperature set point was 900 °C, whereas the stable temperature at the centre of the furnace was found to be about 921 °C.

Generally, the furnace was heated up beforehand and the tube was always purged with Ar flow for at least 2 hours prior to the actual anneals. The Ar flow rate was determined by a gas flow controller. The samples were placed face down in a quartz boat to minimise any undesirable oxidation and introduced into the furnace using a quartz rod to ensure rapid
ramp up of the sample temperature. At the end of each run, the samples were removed immediately from the furnace to the cold zone in the furnace tube to ensure rapid cooling rate.

2.1.3 Pulsed laser melting

![Diagram of pulsed laser melting setup](image)

Figure 2.4: Schematic of the Questek excimer laser and a typical melting profile of untreated Si wafer monitored by a TRR system.

Pulsed Laser Melting (PLM) or pulsed laser irradiation is a well-controlled process used to study the kinetics of solidification far from normal equilibrium conditions. In this study, the processing technique was particularly used to return the material to the crystalline state as well as to incorporate ion-implanted sulfur into the solidified silicon crystals at a concentration level well above the intrinsic solid solubility. Indeed, the rapid resolidification after an ultrashort laser pulse favours the formation of a supersaturated Si–S alloy. The 308-nm Questek XeCl⁺ nanosecond excimer pulsed laser at the Harvard School of Engineering and Applied Sciences [see Fig. 2.4] was used for all the PLM work. The full width half maximum (FWHM) of the laser pulse and the total pulse duration are 25 ns and 50 ns, respectively. A homogeniser is used to achieve better uniformity of the laser beam profile. The specimens were mounted on the sample stage, which can be translated in three independent orthogonal directions (X, Y, and Z). Metallic masks (not shown) were
often used to discard the edge of the laser shot, where the energy profile was more likely to be non-uniform, thus giving an actual melted spot of size of $3 \times 3$ mm$^2$ or $1.5 \times 3$ mm$^2$. Also illustrated in the figure is a typical temporal melting profile obtained by time-resolved reflectivity (TRR) using a low-power Ar$^+$ ion laser (488 nm). Such a profile is used to determine the experimental melt duration for each laser shot. Theoretical melt duration, melt depth, and the time evolution of the temperature profiles versus sample depth were also calculated for a given laser fluence by the Laser-Induced Melting Predictions (LIMP) code [3], a one-dimensional heat flow simulation for pulsed laser melting of thin films. The program requires a sample to be modelled by a stack of several homogeneous layers, where the composition of one layer may be different from others. The calibration of laser fluence was always performed before an irradiation of the actual sample by pulsed laser melting a virgin Si wafer under a given optics setting. The melt duration $\tau$ was recorded and the laser fluence for that particular melting condition was extrapolated from a plot of melt duration versus fluence produced by LIMP. This same setting is used to produce a laser shot with the calibrated fluence on the actual sample.

In this thesis, the process of PLM is introduced in Chapter 6 as a mean to fabricate a silicon light emitting diode. A range of fluences (0.8 to 1.8 J/cm$^2$) and pulse durations (70 to 150 ns depending also on the target structure) was used mainly to remove any existing extended defects and return the material to crystalline state. More detail will be given in the Chapter 6.

### 2.1.4 Wet thermal oxidation

![Figure 2.5: Schematic (not to scale) of the wet oxidation setup, where N$_2$ gas is used to initiate water vapour flow.](image)

Wet oxidation was used throughout this study as it offers a relatively high oxide growth
rate. The chemical process of wet thermal oxidation of silicon can be described by

\[ Si + 2H_2O \rightarrow SiO_2 + 2H_2. \]  

(2.6)

Figure 2.5 illustrates the schematic diagram of our wet oxidation setup. Wet oxidation was always performed using a Lindberg 1-zone furnace in a quartz tube, with a combination of flowing water vapour and nitrogen. The flow rate was controlled by an electrically tunable N\textsubscript{2} gas controller, which is bubbled through a hot de-ionised water reservoir and finally to the quartz tube in the Lindberg 1-zone furnace. For all of the oxidations reported throughout this thesis, the control voltage of N\textsubscript{2} flow was kept at 0.5 V. The other end of the quartz tube is open to air.

Similar to thermal annealing, a calibration was performed at the centre of the furnace for a desired oxidizing temperature. An example of the calibration plot is shown in Fig. 2.6.

![Figure 2.6: A typical example of a calibration plot for wet oxidation. The targeted temperature was set to 980 °C, whereas the measured temperature at the centre of the furnace after stabilisation was found to be around 935 °C.](image)

To ensure the steady-state temperature and flow of the vapour, the furnace was set at the calibrated temperature and left for at least 2 hours prior to commencing an oxidation. The samples were always rested with the side to be oxidised facing up in a quartz boat to allow uniform oxidation. At the end of the process, the samples were taken immediately out of the furnace to prevent any further oxidation.
Apart from the oxidation temperature and hydrostatic pressure [4], the thickness of the oxide layer is dependent on exposure time, substrate doping and type, and substrate crystal orientation [5]. The relationship between the oxidation time $t$ and the oxide thickness $x_o$ for a given oxidation temperature $T$ can be estimated by the well-established Deal-Grove model [6]:

$$ t = \frac{x_o^2}{B} + \frac{x_o}{\frac{B}{A}} - \tau, \tag{2.7} $$

where the experimentally obtained parabolic rate $B$ and linear rate coefficients $B/A$ are defined in Arrhenius form by

$$ B = C_1 e^{-E_1/kT} \tag{2.8} $$

and

$$ \frac{B}{A} = C_2 e^{-E_2/kT}, \tag{2.9} $$

and $\tau$ is the time that would have been used to form the pre-existing oxide of thickness $x_i$ under the current oxidising conditions and is expressed by

$$ \tau = \frac{x_i^2 + Ax_i}{B}. \tag{2.10} $$

The activation energy $E_1$ and $E_2$ and the coefficients $C_1$ and $C_2$ are extracted from earlier work [6] to be 0.71 eV, 1.93 eV, 188, and $5.8 \times 10^7$, respectively. The typical oxidation temperature in this work was 900 °C. Such estimates of oxide thickness were used as a guide only. The actual oxide thicknesses were measured using characterisation techniques that will be described in the following section.

### 2.2 Characterisation

In order to understand the structure of the samples, a vast range of characterisation techniques were employed. Brief descriptions, experimental methods, and procedures are provided in the following subsections.
2.2.1 Rutherford backscattering spectrometry and channeling

Rutherford backscattering spectrometry and channeling (RBS-C) is an ion beam analytical technique that is commonly used in material science especially in the area of surface and thin film analysis. The technique deploys the energy differences of scattered MeV particles (usually $^4$He$^+$ ions) to determine the compositional structure and the absolute depth profile.

![Diagram of Rutherford backscattering spectrometry and channeling](image)

Figure 2.7: Schematic of elastic collision of two masses $M_1$ and $M_2$ with an energy $E_0$ and at rest, respectively. After collision $M_1$ scatters with an energy $E_1$, while $M_2$ recoils with an energy $E_2$. The scattering angle $\theta$ and recoil angle $\phi$ are shown in the diagram.

From the kinematics of elastic collisions, the energy of the scattered particles is dependent on the masses of the incident particle $M_1$ and the target atom $M_2$ and the scattering angle $\theta$, as can be illustrated by the schematic in Fig. 2.7 and described by Eq. 2.11,

$$K = \frac{E_1}{E_0} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{\frac{1}{2}} + M_1 \cos \theta}{M_2 + M_1} \right]^2,$$

(2.11)

where the scattered $E_1$ to incident $E_0$ energy ratio $K$ is known as the kinematic factor. For direct backscattering ($\theta$ approaches 180°), the energy ratio is given by

$$\frac{E_1}{E_0} = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)^2.$$

(2.12)

From Eq. 2.12, unknown elements as well as sample composition can be determined from the energy and number of the backscattered ions. However, the energy loss due to particle-atom or ion-atom interactions has to be considered when the target elements
of interest are buried in the substrate. The incident particle or ion loses energy due to interactions between ion and target atoms as it penetrates a sample. In principle, the energy of the backscattered particle can be used to accurately provide depth information. The energy loss can be classified according to the energy loss mechanism into two groups, namely electronic stopping (inelastic collisions) and nuclear stopping (elastic collisions). The electronic stopping is a result of an interaction between an energetic incident ion and sample electrons, resulting in a gradual energy loss as the ion traverses the target, while nuclear stopping occurs when the incident ion experiences a ‘hard’ collision with sample nuclei and generates a sudden energy loss and is scattered. The probability of the latter is less likely for energetic He\(^+\) ions since the atomic nuclei are very small compared with the size of the atom itself (e.g. the scattering probability of 2 MeV He\(^+\) in silicon through an angle \(\theta > 90^\circ\) is \(\ll 10^{-4}\)). The rate of energy loss depends critically on the energy (or velocity) of the incident ion. Specifically, at the beginning of the process the total energy loss of a fast particle (with an energy of a few MeV) is dominated by the electronic stopping power. Later on, when the particle becomes slower (closer to the end of range of the ion), nuclear stopping is more important as the probability of Coulomb interactions between the particle and the sample nuclei increases.

![Diagram of energy loss components](image)

**Figure 2.8:** Schematic of energy loss components including electronic energy loss of incident ion on incoming \(\Delta E_{in}\), and outgoing \(\Delta E_{out}\) paths and nuclear energy loss, \(\Delta E_s\), due to scattering at a depth \(t\) from a target atom at an angle \(\theta\)

The total energy loss can be separated into three major components: (1) energy lost to the electronic stopping along the entrance path, \(\Delta E_{in}\); (2) energy transferred to the target atom, \(\Delta E_s\); (3) energy loss on the exit path \(\Delta E_{out}\). Hence, the energy of the product
particle $E_1$ is equal to $E_0 - \Delta E_{in} - \Delta E_s - \Delta E_{out}$. The corresponding schematic is shown in Fig. 2.8. From the figure, $\Delta E_{in}$ increases as the particle traverses the sample and thus can be written as an integral:

$$\Delta E_{in} = \int_0^t \frac{dE}{dx} \, dx,$$

(2.13)

where $t$ represents the depth where the scattering takes place. Therefore, the energy of the incident particle at depth $t$ just before scattering is $E_t = E_0 - \Delta E_{in}$. The energy loss during scattering at depth $t$, $\Delta E_s$ is given by

$$\Delta E_s = (1 - K) E_t$$

(2.14)

$$= (1 - K) (E_0 - \Delta E_{in}),$$

(2.15)

while $\Delta E_{out}$ is defined in a similar fashion as $\Delta E_{in}$ with a negative sign indicating the outward direction, and can be written as follows:

$$\Delta E_{out} = -\frac{1}{|\cos \theta|} \int_t^0 \frac{dE}{dx} \, dx.$$

(2.16)

For analysis of thin film (thickness $\lesssim 1 \mu m$), the energy loss along the trajectory can be considered constant and thus $dE/dx$ can be approximated as a constant. It should, however, be noted that the $dE/dx$ values along the inward ($dE/dx_{in}$) and outward ($dE/dx_{out}$) paths are significantly different as they are evaluated at different energies before and after scattering. This allows the energy of the backscattered particle to be described as a function of $t$, as given below:

$$E_1(t) = -t \left( K \frac{dE}{dx}_{in} \bigg|_{in} + \frac{1}{|\cos \theta|} \frac{dE}{dx}_{out} \bigg|_{out} \right) + KE_0.$$

(2.17)

Tabulations [7] can be used to estimate $dE/dx$ as a function of energy in various elemental and compound targets, and computer codes (e.g. SIMNRA [8, 9] or RUMP [10]) can be used to calculate energy losses. Energy loss is normally determined in terms of number of target atoms but can be converted to depth using known target densities.

Figure 2.9 shows a typical RBS spectrum of a silicon-on-insulator (SOI) wafer implanted with 40 keV Au to a nominal dose of $10^{15} \text{ cm}^{-2}$ and annealed at 900 °C for 30 minutes. In this case, the majority of the implanted Au is observed near the surface. The backscattering energy can be obtained from calibration via a channel-to-energy ratio. The energy of the particles backscattering from the Au at the surface, $dE/dx|_{in} = dE/dx|_{out} =$
Figure 2.9: Energy spectrum of 2 MeV $^4$He$^+$ ions backscattered from an SOI sample implanted with 40 keV Au to a nominal fluence of $10^{15}$ cm$^{-2}$ and annealed for 30 minutes at 900°C. Majority of the Au is found at the surface. The inset (a) shows the Au concentration in a depth scale. Note that a drop in Si yield at an energy of about 104.5 keV occurs at the depth of the buried SiO$_2$ layer. (double arrowed)

0, is given by $E_1 = KE_0$, where the kinematic factor $K = K_{Au}$ for $^4$He at a scattering angle of $167.9°$ is $\approx 0.923$. For 2 MeV $^4$He ions, the particle energy $E_1(t = 0 \text{ nm})$ is 1846 keV.

Particles lose more energy as they penetrate through the silicon. Here, the energy loss rate along the inward path $dE/dx|_{in}$ is approximated from the 2 MeV $^4$He stopping cross-section $\epsilon$ in silicon to be about 0.246 keV/nm. Therefore, the particle will have an energy of 1998 keV just before scattering with Au at a depth of 10 nm (assuming negligible energy reduction along the path). Immediately after scattering, the energy of the particle becomes 1845 keV. On the outward path, the rate of energy loss $dE/dx|_{out}$ is evaluated at 1845 keV to be about 0.251 keV/nm. Thus, the energy of the particle on the exit $E_1(t = 10 \text{ nm})$ is 1842 keV. Similarly, we can determine the particle energy as if it scattered from the Au at a different depth so long as it satisfies the thin film condition: thickness of the thin film is $\lesssim$ 100 nm. For thick films, the rate of energy loss cannot be treated as a constant. Alternatively, this can be easily done by inserting a Au monolayer (as a marker) in the
computer simulated model and then correlating the energy peak position of the Au to the depth. The energy scale can then be converted to a depth scale using Eq. 2.17. The result is plotted in the inset (a) of Fig. 2.9.

RBS can be conveniently used to estimate the impurity concentration as an alternative or a confirmation to Secondary Ion Mass Spectrometry (SIMS). The approximate concentration or atomic density of impurities \( N_i \), distributed uniformly in a substrate or a layer, whose atomic density is \( N_s \), can be established from scattering yields using the following relation:

\[
N_i = \frac{H_i}{H_s} \cdot \frac{\Delta E_i}{\Delta E_s} \cdot \frac{\sigma_s}{\sigma_i} \cdot N_s, \tag{2.18}
\]

where \( H \) represents the height (counts) of scattering yield, \( \Delta E \) is the energy shift due to the particles located below the surface and can be determined from Eq. 2.17, and \( \sigma \) is the scattering cross-section. The subscripts \( i \) and \( s \) denote whether the parameter is for impurity or substrate. In the present case [Fig. 2.9], \( \Delta E_{Au} \) is 1.94 keV and \( \Delta E_{Si} \) is 1.85 keV. The ratio of scattering cross-section of Si \( \sigma_{Si} \) to that of Au \( \sigma_{Au} \) is around 0.96 and the silicon atomic density is \( 5 \times 10^{22} \) atoms/cm\(^3\). The inset of Fig. 2.9 plots the Au concentration as extracted from the RBS spectrum in a depth scale. Integration of the area under the Au concentration peak also provides a verification of the implanted Au dose.

When the analytical He\(^+\) ion beam is properly aligned with the axis of a single crystalline target, a significant reduction of backscattering yield is observed. Such a phenomenon is known as channeling of He\(^+\) ions. In a perfect channeling condition, a yield as low as 2–3 % of that measured in a non-channeling mode may be achieved. An example of channeling spectrum is shown in Fig. 2.10. The figure illustrates both random and channeling spectra of a silicon sample implanted at room temperature with 95 keV \(^{32}\)S to a fluence of \( 10^{16} \) cm\(^{-2}\). The channeling spectrum shows a relatively low scattering yield in a crystalline region behind the implanted layer. The normal yield near the surface (from 1030 to 1130 keV) corresponds to scattering from an implantation-induced amorphous region (a-Si). The thickness of the amorphous layer is found to be about 200 nm.

All the RBS analyses were performed at the ANU using the NEC 5SDH 1.7 MV tandem pelletron to generate 2 MeV He\(^+\) ions as an analysing beam from a gas source. The ions are accelerated similarly to that described for the high energy ion implanter except that Rb is used for negative ionisation instead of Cs. The sample is mounted on the holder surrounded with a liquid nitrogen (LN\(_2\)) cooled Cu shield, which is biased to -300 V for secondary electron suppression, in the target chamber. The energy of the backscattered
particles is monitored by both back-angle and grazing-angle or glancing detectors. The geometry of the RBS system is illustrated in Fig. 2.11.

The spectra are acquired by Canberra MCAs (Multi-Channel Analyser), which in turn are controlled by an in-house acquisition program, DEI. The program operates on an OS/2 platform. Random spectra were collected using a randomising function, where the sample was rotated randomly in both X (α) and Y (β) axes. For channelling spectra, the sample was tilted until the minimum yield was achieved. An unimplanted area was often used to help identify channeling orientation especially for samples with a high damage level. The collected data are saved in RUMP format. The files were further analysed using either the RUMP [10, 11] or SIMNRA [8] software package. A channel-to-energy calibration was performed for each set of measurements using a piece of silicon wafer with trace amounts of Cu, Ag, Au, and oxide on the surface.

In regard to our study, the RBS-C was used to obtain various pieces of information including the depth profile of Au in silicon and SiO₂, the oxide thickness after oxidation,
the thickness of an amorphous silicon (a-Si) layer as a result of ion implantation, and the concentration and distribution of implanted species instead of SIMS, as described earlier.

2.2.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is an important analysis tool for materials characterisation. The TEM instrument has a series of electromagnetic lenses to focus the electron beam onto the sample, allowing us to perform both imaging and diffraction. The very short wavelength of electrons (≈ 2 pm for 300 keV), in contrast to a longer wavelength of visible light (≈ 500 nm for green colour), allows a much smaller resolving distance (i.e. better resolving power). The technique provides a range of structural information. As shown in Fig. 2.12, a conventional TEM column consists of an electron gun, sets of electromagnetic lenses and apertures, a eucentric goniometer, and a viewing chamber with binoculars and a fluorescent screen. Detailed explanations and further discussions on various aspects of TEM are excellently provided in a Transmission Electron Microscopy textbook by Williams and Carter [12].

For this study, all the observations were conducted at the Research School of Earth
Figure 2.12: Schematic of TEM showing the microscope column in cross section. (Image courtesy of http://upload.wikimedia.org commons/2/25/Scheme TEM en.svg)

Sciences (RSES), ANU, on a Philips CM300 microscope equipped with a LaB₆ filament and EDS (Energy dispersive X-ray spectrometry) system. The instrument was operated at 300 kV for most of the studies mentioned in this thesis. A computer-controlled eucentric goniometer, Philips Compustage double-tilt holder, was used in most cases and allowed the sample to be tilted along two orthogonal axes. Prior to exploring the sample, the physical height of the specimen (also called eucentric or Z-height) has to be adjusted. Two different standard imaging bright-field (BF) and dark-field (DF) modes have been used. As the name suggests, BF mode produces an image from the direct transmitted electron beam with a bright background, while DF mode from a diffracted beam produces the
opposite. The two imaging modes are selectively used for interpretation and analysis of the structures. For example, it is difficult to resolve whether the dark area observed in a BF image arises from a Bragg diffraction or mass-thickness contrast. The DF image, in which the Bragg contrast appears bright but the atomic mass \(Z\)-thickness contrast remains dark, clearly highlights regions of the sample showing the selected diffraction contrast (a silicon diffraction spot in this particular example). As shown in Fig. 2.13 (and used to interpret the results in Chapter 4), both imaging modes are operated to demonstrate that the elongated dark feature observed in the BF image is crystalline silicon, and not the gold.

![Figure 2.13: Cross-sectional TEM images showing the use of BF and DF imaging modes to differentiate between the crystalline Si and Au. The scale bars represent 50 nm.](image)

To obtain a strong contrast from one set of diffracting planes, the specimen is oriented such that the corresponding diffraction pattern (DP) shows only two strong spots from (i) the transmitted beam and (ii) a diffracted beam. This is known as a two-beam condition. An improved image resolution and contrast favourable for examination of defects and dislocations can be achieved under a weak-beam dark field (WBDF) condition. In this case, the specimen and the electron beam are tilted well away from Bragg positions and the image is produced from a weakly excited diffraction spot. As a result, only the distorted planes located from a narrow part of the dislocation cores bend back enough to satisfy the Bragg condition, hence are visible.
Good TEM sample preparation is crucial especially for lattice imaging. Typically, the rule of thumb is that thinner is better. The specimen in particular has to be electron transparent. The critical thickness depends on the electron energy and the atomic mass and density of the specimen. The standard procedures used to prepare cross-sectional and plan-view TEM specimens are different and described as follows.

### 2.2.2.1 Cross-sectional transmission electron microscopy (XTEM)

Figure 2.14 summarises the preparation process of a cross-sectional TEM sample. Initially, (a) the samples were cleaved into pieces of \(3 \times 1 \text{ mm}^2\). Then, (b) two pieces were glued face-to-face with Gatan epoxy adhesive and cured for about 30 minutes at 100 °C in an oven. The samples were mounted on a stub with Crystal Bond thermoplastic wax [Fig. 2.14(c)] and then mechanically polished on both sides of the sandwich with silicon carbide (SiC) polishing papers (P400, P800, P1200, 800/2400, and 1200/4000 grit) until their thicknesses were about 15 μm. Each sample was mounted on a Be-Cu support ring by Araldite epoxy adhesive [Fig. 2.14(d)] and left to cure for over 8 hours. After lifting the sample (still mounted on the support ring) from the stub, an ion-thinning process was performed at room temperature using a Gatan DuoMill 600 machine, as shown in Fig. 2.14(e). The top and bottom sides of the specimen were sputtered with 4 kV beams of Ar ions at incidence angles of 13° and 10° to the surface until the sample became perforated. The total ion current was maintained at 1 mA to minimise localised heating effects of the sample.

### 2.2.2.2 Plan-view transmission electron microscopy (PTEM)

PTEM samples were prepared by conventional methods of ultrasonic disc cutting, mechanical polishing and dimpling of the back of the sample, and chemical etching. In particular, the samples were first cut into small discs of 3 mm in diameter by a Gatan 601 ultrasonic disc cutter and polished down to about 100 μm. Each sample was then dimpled to further reduce the thickness at the centre of the sample to less than 10 μm. Subsequently, the samples were secured face down onto a Teflon strip and a special acid resistant, Lacomit varnish, was spread around the edges to stop the chemicals from seeping into the regions of interest. This ensured that the samples were etched from the back side by a mixture of hydrofluoric acid (HF), acetic acid (CH₃COOH) and nitric acid (HNO₃) in the ratio 1:1:5 by volume until a small hole was formed in the middle of the sample. Finally, the Lacomit varnish was removed with acetone.
Figure 2.14: Schematic showing steps in the cross-sectional TEM sample preparation process.
2.2.3 Luminescence spectroscopy

Figure 2.15: Schematic energy-momentum (E-k) diagram illustrating the luminescence process in (a) indirect-gap materials and (b) direct-gap materials. The red and blue arrows represent the radiative transition and the phonon-assisted transition, respectively, of an excited electron (filled circle) as it decays from the conduction band to the valence band to recombine with a hole (open circle), while \( E_g \) denotes the bandgap energy.

Luminescence or the spontaneous emission of light is a relaxation process whereby energy is released in a form of photons from a solid due to the process of electron-hole (e-h) pair recombination. Specifically, electrons in the valence band absorb energy and are excited to the conduction band, resulting in an e-h pair. The recombination of an e-h pair or the transition of the electrons in an excited state to lower energy states will result in optical or radiative transitions, which can be observed by a spectrometer. In this thesis, luminescence from silicon, which is an indirect bandgap material, is of interest. That is, the optical transition of intrinsic silicon requires phonon participation with an appropriate momentum, hence is inefficient (radiative lifetime is in millisecond range) [Fig. 2.15(a)]. The radiative band-to-band transition in direct bandgap materials (e.g. III-V compound semiconductors), on the other hand, is efficient with much shorter radiative lifetime in nanosecond range [Fig. 2.15(b)]. We shall show in Chapter 5 that some impurities and defects may provide localised energy states within the bandgap, allowing a phonon-less radiative transition in silicon, an indirect bandgap material.

The two kinds of luminescence techniques used in this study are described in the
2.2.3.1 Photoluminescence

Photoluminescence (PL) was used as a sensitive, quick, and non-destructive method to study the evolution of radiative centres in silicon formed by ion implantation and specific thermal treatments. A schematic diagram of the PL system at ANU is shown in Fig. 2.16. Unless otherwise stated, the samples were pumped by a solid-state laser operating at a wavelength of 532 nm ($\approx 2.33$ eV), with a power of about 15 mW. Such a wavelength has an absorption depth of around 1.27 $\mu$m in silicon. The absorption depth is a material property and is independent of the light intensity. It is generally defined as the depth where 63.2% of the photon energy is absorbed (i.e. $e^{-1}$ of the energy is not absorbed). The relationship between the optical absorption depth or penetrating depth in silicon and the excitation wavelength is shown in Fig. 2.17.

The emission from the sample was dispersed by a triple grating monochromator (model Acton SpectraPro-2500i) and collected using an InGaAs detector equipped with a temperature controller (not shown in the figure). To increase the signal-to-noise ratio, all the measurements were conducted using a standard lock-in technique, where a chopper operating at a 330-Hz chopping frequency and a lock-in amplifier from Stanford Research Systems (model SR830) were used to modulate and manipulate the signals. The monochromator was controlled and the PL spectra were recorded by SpectraSence, a data acquisition software developed by Princeton Instruments and Acton Research. The 532-
nm solid-state laser and InGaAs detector were replaced with a 325-nm He-Cd laser and a silicon detector for room-temperature PL measurement to produce some of the results presented in Sec. 4.7. For low-temperature PL measurements, the samples were adhered with silver paint to a cryostat holder, where the temperature of the block can be cooled to 12 K. It should be noted here that the temperature of the holder, particularly at low temperatures, could be different from that of the sample if vacuum grease with relatively poor thermal conductivity was applied instead of silver paint. All the components described above are mounted on an optical table for precision optics.

The recorded spectral wavelength $\lambda$ can be converted into photon energy $E$ using the following Planck-Einstein relation:

$$E = \frac{hc}{\lambda} \approx \frac{1240 \text{ (eV nm)}}{\lambda},$$

(2.19)

where $h$ is a Planck's constant and $c$ is the speed of light.

All of the PL results reported in Chapter 6 and part of the results in Chapter 7 were obtained by our research collaborator, Dr. Jiming Bao, at the Harvard School of Engineering and Applied Sciences. An Ar$^+$ ion laser emitting at 458 nm ($\approx 2.71$ eV), was used to optically excite the samples, which were placed inside a continuous flow optical cryostat. The minimum temperature of the cryostat was approximately 6 K in this case.
The luminescence was passed through a single grating spectrometer and detected by an InGaAs infrared detector.

2.2.3.2 Electroluminescence

Similar to PL, electroluminescence (EL) is a result of radiative recombination of electrons and holes. However, an electric current or a strong electric field is used to excite the material instead of a laser beam. In this study, all the EL measurements were performed by Dr. Jiming Bao at the Harvard School of Engineering and Applied Sciences. A light emitting diode (LED) was fabricated and spectra were taken from the cleaved edge of the device. Chapter 6 is dedicated to this device where the methods of fabrication will be described and further detail on the optical measurement techniques will be given.

2.2.4 Electrical measurements

Electrical measurements were performed to primarily obtain the wafer resistivity \( \rho \), which generally is defined as a reciprocal of conductivity \( \sigma \) or vice versa. In semiconductors, \( \sigma \) contains contributions from electron and hole conduction and is given by

\[
\sigma = q(n\mu_n + p\mu_p),
\]

where \( q \) is the electrical charge, \( n \) is the electron concentration, and \( p \) is the hole concentration. The carrier mobility is denoted by \( \mu \), where the subscripts \( n \) and \( p \) refer to the electron and hole, respectively. Therefore, \( \rho \) can be expressed as

\[
\rho = \frac{1}{\sigma} = \frac{1}{q(n\mu_n + p\mu_p)}.
\]

For extrinsic p-type silicon \( (p \gg n) \), one can reduce Eq. 2.21 to

\[
\rho = \frac{1}{qp\mu_p},
\]

which can be rewritten as

\[
p = \frac{1}{q\rho\mu_p}.
\]

Similarly, the following expression can be used for n-type silicon \( (p \ll n) \):

\[
\rho = \frac{1}{qn\mu_n},
\]
giving

\[ n = \frac{1}{q \rho \mu_n}. \]  

(2.25)

Substitution of the mobility values extracted from [14] and [15] into Eqs. 2.23 and 2.25 allows the carrier concentration or alternatively the dopant density, assuming complete ionisation, to be plotted as a function of resistivity as shown in Fig. 2.18.

**Figure 2.18**: Carrier concentration versus resistivity for phosphorus-doped n-type and boron-doped p-type silicon. (Chart courtesy of Solecon Laboratories)

### 2.2.4.1 Four-point probe

Four-point probe is a simple method used to measure the sheet resistance of a thin conductive layer. The Jandel four-point probing equipment used in this study consists of four equally spaced \( (s \approx 1 \text{ mm}) \) metal contacts as illustrated schematically in Fig. 2.19. A
current $I$ is supplied through the outer two contacts while the voltage drop $V$ is measured across the inner two contacts. The resistivity of the wafer is given by

$$\rho = \frac{\pi}{\ln 2} \cdot CF \cdot \frac{t}{I} \cdot \frac{V}{I},$$

(2.26)

where $t$ is the specimen thickness and $CF$ is the correction factor, which is $\sim 1.00$ when the specimen is sufficiently thin ($t/s \leq 1$) and large ($b/s \geq 20$) [16] in comparison with the probe spacing. Subsequently, the corresponding dopant concentration can be estimated from Fig. 2.18. The method was found to be more favourable for the samples with low ($\approx 0.005 \Omega \text{ cm}$) to medium ($\approx 5 \Omega \text{ cm}$) resistivity due to the limitation of the current source, non-ohmic contacts at higher resistivities, as well as the voltmeter resolution.

### 2.2.4.2 Capacitance-voltage

The capacitance-voltage or C-V technique was used to determine the carrier density. The method was used when the (high) resistivity of the specimen is beyond the four-point probe limit. The native oxide was initially removed by HF etching. A series of 200 nm thick Ti circular dots with an average diameter of $\approx 1 \text{ mm}$ were subsequently deposited
Figure 2.20: (a) A cross-sectional schematic diagram of the diode structure, where the Ti contact was deposited on the specimen surface by e-beam evaporation to form a Schottky contact and an In-Ga eutectic was used for an Ohmic contact. (b) An optical image showing the actual structure from top view.

on the specimen surface by electron beam (also known as e-beam) evaporation to form a Schottky diode. A liquid metal In-Ga eutectic was applied on the bottom side of the diode to form an Ohmic contact. The corresponding schematic diagram is shown in Fig. 2.20(a), whereas Fig. 2.20(b) illustrates a typical image of the front side of the sample from an optical microscope.

In this case, assuming a uniform doping density, the contact can be considered as a one-sided p-n abrupt junction where the width of the depletion region $W$ is expressed by [17]

$$W = \left[ \frac{2\epsilon(V_{bi} - V_R)}{q N_A} \right]^{\frac{1}{2}},$$

(2.27)

where the permittivity $\epsilon$ is a product of relative dielectric constant $\epsilon_r$ (11.9 for silicon) and vacuum permittivity $\epsilon_0$ (8.85×10$^{-12}$ F/m) and is equal to 105×10$^{-12}$ F/m or 1.05 pF/cm, $V_{bi}$ is the built-in voltage at the junction, voltage $V_R$ is an applied negative reverse bias, $q$ is the electronic charge, and $N_A$ is the constant doping density. The capacitance $C$ is given
for a contact of area $A$ by

$$C = \frac{qA}{W}. \tag{2.28}$$

Considering Eqs. 2.27 and 2.28 together yields

$$C = A \left[ \frac{2qN_A}{(V_{bi} - V_R)} \right]^{1/2}, \tag{2.29}$$

which can be rearranged in a linear form to find

$$\left( \frac{A}{C} \right)^2 = -\frac{2}{\epsilon q N_A} V_R + \frac{2V_{bi}}{\epsilon q N_A}. \tag{2.30}$$

The $N_A$ can be derived from the slope of the $(A/C)^2$ versus $V_R$ plot and the corresponding resistivity can be obtained from the chart in Fig. 2.18.

### 2.2.4.3 Current-voltage

Current-voltage or I-V measurements were conducted to complement C-V measurements to determine the diode characteristics, which is reflected by the ideality factor $\eta$. The ideality factor is incorporated in the forward bias current-voltage characteristics as follows:

$$I = I_s e^{qV/\eta kT}(1 - e^{-qV/kT}), \tag{2.31}$$

where $I_s$ is the (constant) saturation current, $k$ is the Boltzmann's constant, and $T$ is the measurement temperature. This expression can be rewritten in a linear form by taking logarithms of both sides, giving

$$\ln \left( \frac{I}{1 - e^{-qV/kT}} \right) = \frac{q}{\eta kT} V + \ln(I_s). \tag{2.32}$$

From the slope of the plot of $\ln(I/(1 - exp(-qV/kT)))$ against the bias voltage $V$, $\eta$ can be determined:

$$\eta = \frac{qV}{\text{slope}(kT)}. \tag{2.33}$$

We note that the thermal energy $kT \approx 0.026$ eV at 300 K. An ideal diode has $\eta = 1$, while a practical diode normally yields $1 < \eta < 2$. A relatively large $\eta$ indicates significant undesirable carrier recombination in comparison to the carrier diffusion. In this study, we consider $N_A$ to be reliable when $1 \leq \eta \leq 1.1$ [18].
2.3 Summary

This chapter has provided a brief introduction to the processing and characterisation techniques used in this study. Some examples of the results are provided to give an idea of how they can be characterised and analysed. More specific experimental detail is supplied in following chapters.

References


[2] H. J. Hay, unpublished, **FASTRIM** is a modified version of TRIM-90 which takes into account the multilayer target (interfaces) problems inherent with TRIM.


Formation of Self-Assembled Au Nanoparticles

This chapter presents results on the formation of Au nanoparticles in silicon and silicon dioxide (SiO$_2$) materials. Ion implantation, thermal annealing, and wet oxidation have been employed to produce encapsulated gold particles in SiO$_2$. The samples were characterised by Rutherford backscattering spectrometry (RBS) and transmission electron microscopy (TEM).
3.1 Introduction and brief literature review

In the last decade, nanocrystals embedded within a low refractive index matrix have generated significant scientific interest. Metallic nanoparticles have been shown to possess some interesting properties that substantially differ from those in the bulk when they are embedded in a dielectric matrix. Silicon dioxide (SiO$_2$) stands among the favourite choices of host material for its optical transparency, thermal stability, mechanical strength, and chemical resistance. The differences in optical [1], electrical, and magnetic [2] properties arise from the small dimension of the particles and associated quantum confinement effects of electrons and holes. The surface plasmon resonance (SRP) is one of the extraordinary optical phenomena that has been utilised to create coloured glass objects long before the underlying principles were properly understood. Some examples are the famous Lycurgus cup [3] in the British museum and the Gothic stained glass rose window of Notre Dame. Recently, the SRP has been experimentally observed and characterised for nanoparticles of various metallic species including copper (Cu) [4], silver (Ag) [5, 6], and gold (Au) [5, 7]. Their fast response and nonlinear optical properties are attractive for many applications such as optical biosensors [8–10], optical switches [11], and silicon solar cells [12]. By tailoring the size and shape of these particles, the absorption peak due to the SRP can be tuned [13, 14]. Photoluminescence (PL) is another interesting effect that is uncommon in bulk metal due to the lack of bandgap. The observed luminescence was assigned to the radiative recombination of electrons in the $s$–$p$ conduction band and holes in the $d$ bands with the estimated quantum efficiency of about $10^{-10}$ [15]. However, later studies have shown that a much higher quantum efficiency (of the order of $10^{-4}$) may be obtained from metal nanoclusters [16] or nanorods [17] with size-dependent optical properties.

The above reasons have led to a strong demand for uniform particle size distribution in most metal nanoparticle-based photonic applications. Additionally, the formation of metal nanoparticles at a precise depth in a dielectric host is essential in many applications especially when tuning the optical properties of devices in nanocomposite materials [18]. Although a considerable effort has been made, gaining control over the size, shape, and depth distribution of metal nanoparticle inclusions in solids has proven difficult to date and remains a challenge.

Several approaches have been pursued to synthesise Au nanoparticles in silicon and silica glass. The sol-gel process is one of the favourite wet-chemical techniques used for
fabrication of glass/ceramic materials or, more specifically, metal oxide nanocomposites. The process generally involves dissolution of very fine solid (usually inorganic) particles in a solvent to obtain liquid ‘sol’ and a subsequent method to convert the ‘sol’ into a solid ‘gel’ phase. The main advantage of the sol-gel process is that it can be used to form various structures and components, opening up opportunities for a diverse range of applications. Because low viscosity liquid solutions are normally used in the preparation of liquid sol mixtures, the final products are highly homogeneous [19]. For this same reason, the embedded particles are usually distributed over a wide depth range. Some (Au embedded in SiO₂) structures prepared by this method show reasonably small Au particles confined within a broad depth distribution [20–22]. Furthermore, the gel network usually suffers a significant shrinkage due to the gelation process (solidification of liquid sol) and contains a number of pores.

Deposition of Au onto silicon or SiO₂ by thermal evaporation and subsequent annealing was reported to produce Au nanoparticles with an average diameter of about 15 nm on the SiO₂ layer or elongated Au nanoparticles grown epitaxially below the silicon surface [23]. Despite limited statistical information available, we can clearly see from the provided cross-sectional images that the shape of Au precipitates in both cases (on the SiO₂ and at the silicon surface) is not uniform. The elongated Au particles were specifically observed to facet along (111), (311), (711), and (-111) planes of the silicon lattice.

Alternate radio frequency (RF) sputtering of Au and SiO₂ was employed to fabricate a sandwich structure of SiO₂-Au-SiO₂ nanocomposite films [24]. The method allows formation of Au particles with average diameters ranging from 2 to 10 nm. The size of Au precipitates is shown to be smaller for thinner sputtered Au layers, while the distribution of the precipitates becomes broader with precipitate size. A few Au particles with a relatively large size are not spherical, but rather elongated. A combination of RF sputtering of Au and plasma enhanced chemical vapour deposition (PECVD) of SiO₂ was also reported to produce an array of not-so-spherical Au nanoparticles within the SiO₂ layer [25]. The characterisations and analyses show that a longer deposition time leads to a growth of Au particles as well as a broader size distribution.

Among the different processing techniques, implantation provides an attractive way of fabricating metal nanoparticles due in part to the spatial controllability and the compatibility with current semiconductor fabrication technology. Experiments on direct keV [26] and MeV [1] Au-implantation followed by thermal annealing have been shown to form small Au particles (below 5 nm in diameter for keV implant and below 30 nm for MeV
implant), however, with relatively broad depth distributions. An extremely low energy 1 keV Au-implantation into a thin SiO₂ layer followed by a subsequent 1-hour anneal at 900 °C has been reported to demonstrate Au particles of a much narrower depth distribution (but still not a single depth distribution) [27].

In general, the size of particles is largely dependent on the thermodynamics of the system during annealing, namely the Ostwald ripening process, where larger particles are growing at the expense of smaller ones. The fabrication of Au nanoparticles, as evidenced in most of the techniques reviewed above, usually involves high temperature thermal processing. For this reason, achieving particles of a desired size and a narrow size distribution is very difficult since significant Ostwald ripening is apparent.

Earlier observations on the use of gas-induced nanocavities or voids in silicon for gettering and trapping of a range of metals opened up the possibility of the formation of metal nanoparticles of a tight and controlled size distribution in silicon. High dose H [28] and He [29] (in the order of 10¹⁶ cm⁻²) ion-implantation followed by high temperature annealing have been successfully used to produce cavities of nanometre size in silicon. The process of cavity formation takes place in the early stage of annealing when the gas atoms diffuse to occupy implantation-induced vacancies in silicon and subsequently agglomerate into tiny gas bubbles. The gas is expelled out in the later stage of annealing (e.g. by ≈ 800 °C, 10 minutes for He [30] or 750 °C, 60 minutes for H [31]), leaving empty well-faceted cavities [32] in the crystalline silicon matrix. The formation of nanocavities is temperature dependent. A series of XTEM micrographs in Fig. 3.1 illustrates the evolution of the H-formed nanocavities in silicon as a function of post-implantation annealing temperature. It is clear from the images that a minimum threshold temperature of 750 °C is necessary to reduce a significant amount of implantation-induced damage/disorder and introduce a strain-free band of cavities slightly beyond the projected range (R_p) of the H ions.

In an attempt to vary the size of these H-formed cavities, Zhu et al. have demonstrated by in-situ TEM analyses that the diameter of a cavity decreases with the increase of a subsequent silicon-implantation dose [33]. The shrinkage of the cavities was explained by (i) annihilation of self-interstitials (that were introduced by the Si-implantation) at the cavity in a crystalline phase or (ii) liberation of vacancies from the cavity in an amorphous phase as well as the flow of amorphous silicon into the cavity during the implantation. This shrinking process has been shown to not only reduce cavity size but tighten up the size distribution [34].
Figure 3.1: Cross-sectional TEM images of H-implanted silicon showing the formation of cavities after 1-hour isochronal annealing at different temperatures. The scale bar represents 100 nm. (adapted from [31])
Previous works on the interactions of impurities with open volume defects [28, 30, 35–38] have shown that the cavities formed within crystalline silicon are attractive sinks or effective gettering sites for several metal species including Cu, Au, and Pt. This gettering process is typically applied to semiconductor devices in order to remove metal impurities from the active region. The RBS spectra in Fig. 3.2(a) reveal that a large fraction of Au impurities diffuses to the cavities during the post-metal-implantation anneal. The XTEM shown in Fig. 3.2(b) suggests that the Au initially decorates the cavity walls and subsequently occupies these cavities to form spherical Au precipitates when there is an adequate supply of Au. The size of these registered Au particles is determined by that of the cavities. The loss of the well-faceted structure is noteworthy when the cavities are completely saturated with Au.

![RBS profile and XTEM micrograph](image)

**Figure 3.2:** (a) RBS profiles showing the redistribution of implanted \((7 \times 10^{14} \text{ cm}^{-2})\) Au in cavity-containing samples before (as-implanted) and after isothermal 750 °C annealing for various times. (b) An XTEM micrograph illustrating the decoration and precipitation of Au at H-formed cavities after a 1-hour anneal at 850°C. The scale bar represents 20 nm. (adapted from [31])

A detailed study on the Cu and Au gettering mechanism has indicated that, during the gettering process, the system first attains pseudo-equilibrium after short-time annealing [39], in which the concentration of the metal impurities in the bulk of a cavity-containing sample is way below the solubility limit of cavity-free silicon (since almost all the metal is trapped at cavity sites). Together with the ability to tailor the cavity size, the
method of metal gettering to form nanoparticles of a desired size in a low disorder and low impurity level silicon looks very promising. The question to be answered in this and the following chapters is whether we can replace silicon with SiO₂ and apply the same experimental procedures to obtain cavities and ultimately Au precipitates within SiO₂? If it is not possible to directly form Au decorated cavities in SiO₂, is there an alternative approach to get around this problem?

In this chapter, several methods were carried out in an attempt to obtain a narrow size and depth distribution of Au nanoparticles in SiO₂. Structural analyses were performed in order to demonstrate the precipitate formation processes, while more details and a complete explanation of mechanisms are given in the following chapter.

### 3.2 Experimental procedures

The experimental conditions of the samples whose results are presented in this chapter are summarised in Table 3.1. Some single crystalline p-type (100) silicon wafers were initially oxidised in a conventional furnace at 900 °C for 6 hours to form a SiO₂ overlayer of about 400 nm thick (sample A) or implanted with 125 keV oxygen ions (O⁻) to the dose of $1.8 \times 10^{18}$ cm⁻² at 500 °C and annealed for 2 hours at 1100 °C to form a buried oxide (BOX) layer (samples O and P). Alternatively, commercially available silicon-on-insulator (SOI) wafers obtained from Soitec were used to provide a high quality BOX layer with well-defined Si–SiO₂ interfaces (samples B, C, H, I and N). The thicknesses of the top p-type (100) silicon layer and the BOX layer are 180 nm and 200 nm, respectively. Most samples were then implanted with 10 or 12 keV hydrogen ions (H⁻) to a dose of $3 \times 10^{16}$ cm⁻² at either a conventionally tilted angle of 7° to minimise channelling or specially tilted by 60° away from normal beam incidence to reduce the $R_p$ of the ions by about a factor of 2. An optional 60-minute anneal at 850 °C was performed in flowing Ar gas to remove the irradiation damage and simultaneously form a band of nanocavities in the proximity of $R_p$. Au was subsequently introduced near the surface by implantation at room temperature to a nominal dose of $1 \times 10^{15}$ cm⁻², followed by annealing at either 850 or 900 °C for 30 minutes in a conventional quartz tube. Finally, about half of the samples were selectively wet oxidised for up to 6.5 hours at 900 °C in water vapour flow. Control samples (I for B and C, N for H, and P for O) were prepared without H-implantation and a subsequent anneal but followed all other processing steps as above.
Table 3.1: Summary of the samples presented in this chapter and their processing sequences starting from left to right.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Starting material</th>
<th>Oxide preformation</th>
<th>H⁻ implant Energy (keV)</th>
<th>Angle (deg)</th>
<th>60-minute annealing (°C)</th>
<th>Au⁻ implant energy (keV)</th>
<th>30-minute annealing (°C)</th>
<th>900 °C oxidation (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Si</td>
<td>pre-oxidation</td>
<td>10</td>
<td>7</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
</tr>
<tr>
<td>B</td>
<td>SOI</td>
<td>No</td>
<td>10</td>
<td>7</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
</tr>
<tr>
<td>C</td>
<td>SOI</td>
<td>No</td>
<td>10</td>
<td>60</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
</tr>
<tr>
<td>H</td>
<td>SOI</td>
<td>No</td>
<td>10</td>
<td>60</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>6</td>
</tr>
<tr>
<td>I</td>
<td>SOI</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>80</td>
<td>850</td>
</tr>
<tr>
<td>N</td>
<td>SOI</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>80</td>
<td>850</td>
</tr>
<tr>
<td>O</td>
<td>Si</td>
<td>O⁻ implant</td>
<td>12</td>
<td>7</td>
<td>No</td>
<td>80</td>
<td>850</td>
<td>6.5</td>
</tr>
<tr>
<td>P</td>
<td>Si</td>
<td>O⁻ implant</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>80</td>
<td>850</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The depth profiles of Au following each processing step were extracted from RBS spectra using the SIMNRA programme [40]. Microstructure analyses in plan view and cross-sectional view were carried out using a Philips CM300 instrument operated at 300 kV. The methods of sample preparation are outlined in chapter 2.

### 3.3 Implantation into SiO₂

The first experiment attempted to form a narrow band of Au precipitates of narrow size distribution. The experimental procedure involved the following (in sequential order): (i) implantation of H ions to try to form cavities directly in SiO₂ and (ii) gettering of Au to these cavities. The results of this experiment are presented in Fig. 3.3. Figure 3.3(a) illustrates a random RBS spectrum of sample A as identified in Table 3.1. It should be noted that both H⁻ and Au⁻ implant ranges are well within the oxide layer, with the $R_p$ of 10 keV H⁻ ≈ 150 nm and the $R_p$ of 40 keV Au⁻ ≈ 25 nm. The RBS analysis reveals the majority of the Au at the depth of around 25 nm, in good agreement with the cross-sectional TEM (XTEM) images shown in the inset of Fig. 3.3(a) and Fig. 3.3(c). In particular, the XTEM images show a band of Au clusters distributed from ≈ 20 to 40 nm below the sample surface. The shape of Au precipitates is not well defined and therefore the average size is difficult to determine. However, they are generally ≲ 5 nm in diameter with a relatively broad size distribution, consistent with results from a previous study of direct Au implantation into SiO₂ [27]. The agglomeration of Au particles close to $R_p$ arises from the local supersaturation of Au in the implanted region and the very low diffusivity of Au in SiO₂ [41]. The magnified XTEM image of the sample after H-implantation and a subsequent anneal [see Fig. 3.3(b)] did not show any cavities in SiO₂, in contrast to what
3.3. Implantation into SiO₂

Figure 3.3: (a) A typical RBS spectrum of sample A showing Au located at the depth corresponding to the $R_p$ of 40 keV Au−. The inset displays the corresponding XTEM micrograph of the same sample, whereas the areas around the $R_p$ of 10 keV H− and 40 keV of Au− are magnified and shown in (b) and (c), respectively. The scale bars are 20 nm in both images.

has been observed in silicon [31]. In fact, this is consistent with the results reported in the study of noble gas implantation in SiO₂ [42], where no voids were observed. Specifically, a previous study has shown that the formation of implantation-induced cavities in SiO₂ is only possible with heavy species such as krypton (Kr) and xenon (Xe) [43]. On the other hand, light species such as helium (He) and neon (Ne) are suggested to be very mobile in SiO₂ and hence cannot be used to form implantation-induced cavities, regardless of implantation temperature [42]. Although there have been no previous attempts to form cavities in SiO₂ using H ions, we believe the same explanation (high solubility and diffusivity of H in SiO₂) also contributes to the lack of H-formed cavities.

These results clearly demonstrate that the same method of forming H-implantation-induced nanocavities and gettering of Au in silicon does not work in SiO₂. According to the existing literature, it is reasonable for one to contemplate the gettering of Au to either Kr- or Xe-induced nanocavities in SiO₂. However, it is evident that Au does not diffuse appreciably within SiO₂ upon thermal annealing. In addition, it is not clear from
the literature that Kr or Xe gas-free, well-defined cavities can be formed in such cases. Therefore, the prospect of Au gettering to Kr or Xe-formed cavities in SiO₂ does not look promising. The following sections present the results from alternative approaches to form encapsulated Au particles in SiO₂ of narrow size and depth distributions. The method involves first gettering of Au to preformed cavities in silicon and then a subsequent wet oxidation to encapsulate the Au in SiO₂.

3.4 Gettering of Au in silicon (on insulator)

![Graph showing RBS spectra](image)

Figure 3.4: RBS spectra showing the sample structure after one (solid square) and two (open circle) cycles of 5-hour wet oxidation at around 900 °C. The inset specifically compares the Au redistribution before (solid square) and after (open circle) the oxidising interface reaches the Au precipitates at the cavities, where (1) and (2) denote the buried Si-SiO₂ interfaces of the sample after the first and second oxidations, respectively.

A different approach to obtain Au particles in SiO₂ is to initially form Au precipitates in silicon and then wet oxidise in an attempt to surround the Au precipitates with SiO₂. As briefly described in Sec. 3.1, a number of different experiments have previously been
performed to address various aspects of the Au precipitate formation in silicon. Hence, the results of gettering of Au to cavities in silicon in this study are not shown here. In fact, they are generally similar to the results in Fig. 3.2. An interesting Au segregation behaviour during oxidation, which was noticed earlier [44] but has not previously been investigated in any detail, is observed in the current study after a subsequent high temperature wet oxidation. We illustrate this effect in Fig. 3.4, where our preliminary experiments on wet oxidation of a Au-at-cavity sample (not included in Table 3.1) were conducted with the aim to incorporate Au precipitates into a growing SiO$_2$ layer. Initially, the Au precipitates were formed during annealing near the surface and at a depth corresponding to the expected cavity band (around 110 nm from the surface) by gettering. The first cycle of wet oxidation was subsequently performed for 5 hours at approximately 900 °C, leading to the formation of 230-nm thick surface oxide shown in Fig. 3.4. We note in this case that the Si–SiO$_2$ interface proceeds very close to the band of Au precipitates at the cavities, while a fraction of the Au appears to diffuse further into the silicon substrate but this may possibly be a Au tail from the Au precipitates [see inset of Fig. 3.4]. An extended oxidation was carried out for 5 hours on the same sample after 30 minutes at 850 °C. By this stage, the buried interface has now advanced beyond the precipitate band but no Au is observed to remain at the band [open circles in Fig. 3.4]. Instead, much of the Au appears to reside behind the oxide or deeper in the silicon substrate [see the Au profile increasing beyond the buried oxide in the inset of Fig. 3.4]. It is important to note that the Au has not been incorporated into the oxide layer. Such a result is consistent with the previous finding from the study of Williams and Christodoulides [44] that reports segregation of the Au behind a thermally grown oxide. From this perspective, an alternative strategy might be to use a preformed buried oxide (BOX) layer to prevent the Au particles from diffusing further into the silicon, trap them at the BOX interface, and hence encapsulate them within an SiO$_2$ layer once the thermal oxide had grown down to the BOX layer. This strategy was pursued and the results presented in the remaining part of this chapter.

In this study, the insulating BOX layer was obtained either by elevated temperature O-implantation to the fluence of $1.8 \times 10^{18}$ cm$^{-2}$ followed by an anneal at 1100 °C for 2 hours or otherwise is readily available in commercial Soitec’s (UNIBOND) wafers [45]. The former method is known as SIMOX (separation by implantation of oxygen) whereby the product is often referred to as a SIMOX wafer.

Firstly, let us consider a home-made SIMOX structure. Figure 3.5 shows an RBS-C spectrum and, in the inset, a corresponding XTEM image of sample O (as per Table 3.1)
after H-implantation but prior to Au-implantation. Both characterisation techniques indicate that a BOX layer with a thickness of about 300 nm was successfully formed underneath a 240-nm silicon film. The displacement distribution due to 12 keV H-implantation was determined by a Monte Carlo SRIM simulation [46]. The profile matches quite nicely with the presence of the damage arising from O- and H-implantation, as observed in the silicon overlayer [see insert of Fig. 3.5]. Although the fabricated SIMOX wafer contains the necessary BOX layer, the micrograph in particular reveals relatively poor quality (non-uniform and blurry) interface for Si–SiO₂ boundaries.

Sharp Si–SiO₂ interfaces are typical of commercial wafers such as Soitec SOI wafers. In fact, these wafers were primarily used to process the remaining samples whose results are reported in this chapter [see Table 3.1]. Without the need to preform BOX layer, the
3.4. Gettering of Au in silicon (on insulator)

![Graph showing Au redistribution in silicon layer](image)

**Figure 3.6:** Random RBS spectra showing the Au redistribution in the top 180-nm silicon layer of the samples with different processing conditions. Sample B was prepared by 12 keV H-implantation to a fluence of $3 \times 10^{16}$ cm$^{-2}$ followed by a 60-minute anneal at 850°C, and 40 keV Au-implantation to a dose of around $10^{15}$ cm$^{-2}$ followed by a second anneal at 900°C for 30 minutes. The preparation steps of sample C are identical to those of sample B except that the H-implantation was carried out with a special ion incident angle of 60°. Sample I is a control sample, free of H-formed cavities.

Sample preparation steps consist of 12 keV H-implantation to a dose of $3 \times 10^{16}$ cm$^{-2}$ and an 850°C anneal for 60 minutes to form a band of cavities at a depth of $\approx 100$ or 130 nm (i.e. within 180 nm of the top silicon layer) depending on the ion beam angle of incidence. The Au was subsequently introduced by ion implantation (40 keV, $10^{15}$ cm$^{-2}$) and diffused to precipitate at the cavities by 30-minute annealing at 900°C. Here, the impurity gettering process in an SOI wafer with a thin silicon overlayer was analysed. Random RBS spectra of the samples (B, C, and I) are compared in Fig. 3.6, where we note the relocation of the implanted Au to three different depths: surface, middle of the silicon layer, and at or close to the Si–SiO$_2$ front interface. When the sample was tilted by 7° towards the direction of the H-ion beam (sample B), most, if not all, of the Au is observed near the Si-SiO$_2$
interface, which corresponds closely with the expected depth of the cavity band in this case. With a specially tilted angle of 60° (sample C), the Au appears at all three locations but predominantly in the middle of the layer where the cavities are expected to have been formed. All of the implanted Au is relocated to the surface of sample I in the absence of preformed cavities. The results are qualitatively consistent with XTEM observations, of which the micrographs are shown in Fig. 3.7.

The XTEM image in Fig. 3.7(a) shows the cross-sectional structure of sample B as per Table 3.1. In this case, the cavity band is found to locate at or very close to the Si–SiO₂ interface. We note that these cavities are usually best observed with TEM in an underfocused condition, noting that the Au-decorated internal walls of these cavities can be observed because of their high z-contrast. The trapezoidal and hexagonal faceted cavities are observed at the interface and in the vicinity of the BOX layer, respectively. Similarly, Au precipitates appear in an island-like or hemispherical shape at the interface and in a normal spherical shape near the oxide layer. Indeed, the cavities and precipitates appear at a depth corresponding closely to the \( R_p \pm \delta R_p \) of 10 keV H⁻, where \( \delta R_p \) represents the straggling of the ions and is around 40 nm. The average lateral dimension of Au nanoislands at the buried SiO₂ interface is around 20 nm across with a height of less than 10 nm, while the average diameter of spherical precipitates is approximately 15 nm with a standard deviation of about 4 nm (27% deviation). It is noteworthy that the faceted cavities and Au precipitates are only observed in silicon, consistent with our previous findings that nanocavities in SiO₂ cannot be formed by H-implantation.

Implantation-induced voids or nanocavities in silicon typically facet along the \{111\} and \{001\} planes, whereas those at the buried Si–SiO₂ interface have similar faceting in the silicon but are truncated on the (00-1) plane at the front interface of the BOX, thus giving rise to a trapezoidal shape. Such a structure is presumably a result of forming cavities too close to the BOX layer. Gettering of Au to nanocavities in bulk silicon as mentioned earlier results in Au decoration of cavity walls and ultimately leads to the formation of spherical or nearly spherical Au precipitates provided that Au is adequately supplied. The situation is different at the oxide interface, where the Au precipitates elongate and usually exhibit in a hemispherical or an island-like shape, possibly due to a combination of gettering and preferential wetting processes of Au on the SiO₂ interface.

Sample C was prepared under identical processing conditions as sample B except for the H-implantation step, where the ion bombardment was carried out at an angle of 60° instead of the conventional 7°, resulting in a significant reduction of the projected range
Figure 3.7: Typical XTEM images illustrating the microstructure of (a) sample B, (b) sample C, and (c) control sample I. Note that sample B is subjected to a conventional H-implanted angle of 7°, whereas sample C was tilted to 60° away from the beam direction and sample I is free from H-implantation. The sample identification is shown at the top-right corner of each TEM image.
R$_p$ of H ions and consequently the depth of the cavity band. Figure 3.7(b) shows a typical XTEM image of sample C. The image reveals that both Au precipitates and empty faceted voids (as shown in the inset) are contained strictly in the top silicon layer. Indeed, the precipitates are also occasionally observed at the surface and the Si–SiO$_2$ interface, with a large fraction in the middle of the layer. This is indicative of a relatively low surface free energy for Au in contact with SiO$_2$, giving rise to competing precipitation of Au at the cavities and the oxide interfaces. In other words, the result supports an argument that the Si–SiO$_2$ interface is a potential nucleation site for Au precipitates. Our finding is somewhat analogous to Au wetting of silicon surfaces where the lowest free energy surface was identified as {111} [47].

A [004] two-beam bright field TEM image of the sample I is shown in Fig. 3.7(c). Rather than precipitating at the BOX interface, the implanted Au was entirely segregated to the surface during the post-implantation annealing which resulted in solid phase epitaxial growth (SPEG) of the amorphous surface layer that formed as a consequence of the Au implantation [37]. Such a process results in preferential precipitation of Au at the surface or precisely at the interface between silicon and any existing surface oxide. The presence of the surface oxide may be attributed to the following three factors: (i) a native oxide film, (ii) unintentional oxidation during the annealing process, and (iii) Au-enhanced oxidation as will be elaborated on in Chapter 4. A similar Au–Si structure has previously been demonstrated for the case of Au evaporation onto a p-type (100) silicon substrate followed by thermal annealing [23].

### 3.5 Encapsulation of Au precipitates in SiO$_2$

Wet oxidation was applied to the samples discussed in the previous section in an attempt to confine Au precipitates within SiO$_2$. Our results presented earlier and experimental studies on thermal oxidation of ion implanted silicon [44] have shown that Au is segregated at the Si–SiO$_2$ interface. This suggests that a BOX layer is required to stop the advancing Au precipitates at the BOX interface, hence trapping the Au within a single layer. Figure 3.8 shows the RBS spectra of different samples containing (samples O and H) and not containing (samples P and N) preformed cavities after 900 °C wet oxidation. The profiles displayed in Figs. 3.8(a) and (b) were obtained from the SIMOX-based and commercial SOI-based structures, respectively. In all the cases, the Au precipitates are essentially segregated behind the oxidising interface and encapsulated between the thermally grown
Figure 3.8: Random RBS spectra showing the Au distribution after wet oxidation of the samples with and without the initial step of Au gettering to the cavity band, where the BOX layer is either (a) formed by SIMOX or (b) available in commercial SOI wafers.
and buried oxide layers. No significant difference (as observed by RBS) is found between the samples with and without cavities. The RBS measurements in Fig. 3.8(a) show that the top silicon layer is close to completely oxidised for SIMOX-based O and P samples, with a small amount of silicon remaining near the original BOX interface. Figure 3.8(a), however, shows that the top silicon layer has been completely oxidised, with thermal oxide combining continuously with the BOX layer for commercial SOI-based H and N samples.

Figure 3.9: XTEM micrographs showing Au distribution after the oxidation at 900 °C. The images (a) and (b) on the left column show the microstructures produced in SIMOX wafers, while those (c) and (d) on the right column show typical images of the samples formed in Soitec SOI wafers. The samples with preformed cavities are exhibited in the top row, whereas the equivalent control samples (without cavities) are shown in the bottom row. The sample identification is specified at the top-right corner of each image and the scale bar corresponds to 200 nm.
Figure 3.10: Plan-view TEM images showing an almost identical structure of encapsulated Au particles in SiO₂ of (a) cavity-containing sample H and (b) cavity-free sample N. The sample identification is denoted at the top-right corner of each corresponding image. The scale bars represent 300 nm in both images.

The corresponding XTEM micrographs are displayed in Fig. 3.9. The TEM observation is consistent with the RBS spectra in that all the Au particles are pushed back to the BOX layer and sandwiched in between the two oxide layers. Au clusters or precipitates appear along the line at a single depth corresponding to the original front interface of the BOX layer. Typical plan-view TEM (PTEM) images of samples H (with cavities) and N (without cavities) shown in Fig. 3.10 confirm the structural similarity of the samples with and without preformed cavities, although the average precipitate size appears to be a little smaller for the cavity-containing sample (H). Such results suggest that the cavities and subsequent Au precipitation within them may not be particularly beneficial under these experimental conditions where segregation of Au precipitates behind a growing oxide occurs. The images [see Figs. 3.9(a) and (b)] also confirm that, although samples O and P were oxidised longer than samples H and N, there is a thin silicon layer (or isolated silicon pockets) left unoxidised (as detected by RBS) and, additionally, the shape and arrangement of Au precipitates or clusters is found to be rather peculiar compared with spherical precipitate shape in Figs. 3.9(c) and (d) following complete oxidation. This may be explained by competing processes of recrystallisation, metal precipitation, and oxidation [48], taking into account a heavily damaged oxide interface as a consequence of O-implantation and the absence of post H-implantation annealing. Because the shape of the Au clusters in SIMOX samples (O and P) is somewhat arbitrary, determining
their size is very difficult. However, it is possible to estimate the size of spherical Au precipitates in the SOI samples (H and N). The mean values of the Au precipitate size after completing the oxidation process were found to increase from 15 nm as observed before oxidation at the cavity band to about 30 nm in sample H and 40 nm in sample N with the corresponding standard deviations of $\approx 12$ nm (40% deviation) and $\approx 17$ nm (42.5% deviation), respectively. The average precipitate density was determined from PTEM images to be around 5.17 $\mu$m$^{-2}$ for cavity-containing sample H and 4.21 $\mu$m$^{-2}$ for cavity-free samples N. The results imply that the Au precipitates initially formed in silicon may have undergone segregation, dissolution, diffusion, and re-precipitation processes at the BOX interface so that they eventually failed to preserve the original precipitate size as well as the tight size distribution. It is interesting and equally important to identify when such processes are operative. Extended experiments were undertaken to scrutinise the Au precipitate formation during wet oxidation in Chapter 4 where the results are presented and the mechanisms are discussed.

3.6 Summary

In this chapter, different approaches have been used to form Au nanoparticles in SiO$_2$. In particular, the gettering of Au to fill H-induced nanocavities was expected to overcome the broad particle size distribution generally associated with nanoparticles formed by implantation and annealing. We have shown that such nanocavities cannot be formed directly in SiO$_2$ due partly to the high mobility of H atoms in SiO$_2$. However, they are possible in silicon and become useful in obtaining a narrow size and depth distribution of Au precipitates. A subsequent wet oxidation of the precipitate-containing silicon allows the Au to be rearranged in a sharp array of spherical or irregular shape, depending on the method of BOX formation (i.e. the quality of BOX layer as well as the Si–SiO$_2$ interfaces), within a SiO$_2$ layer where the depth of the particles is correlated precisely to the original front interface of the BOX layer. The growth and relocation of Au precipitates lead us to speculate that there are several processes involved during the oxidation including segregation, dissolution, diffusion, and re-precipitation. We will concentrate and discuss the associated mechanisms based on these processes in the following chapter.
References


Oxidation of Au Nanostructures in Silicon: The Mechanisms

This chapter provides details of the behaviour of Au nanoparticles as they are progressively segregated and encapsulated within SiO₂ during oxidation. The role of silicon interstitials produced from wet oxidation is discussed in proposing mechanisms for the observed phenomena.
4.1 Introduction

In the previous chapter, we have demonstrated that H-induced cavities can be formed within the top silicon layer of an SOI wafer, whereby Au precipitation at such cavities (by metal gettering) leads to the formation of Au precipitates with a rather tight size and depth distribution. A subsequent wet oxidation was carried out to segregate and eventually embed the Au nanoparticles at a precise depth within an SiO\textsubscript{2} layer. At the completion of oxidation, comparisons of the sample structures with and without preformed cavities suggest that the final size distribution of Au precipitates is unexpectedly little different for the two cases. Thus, the evolution of Au nanoparticles during wet oxidation is therefore worthy of investigation. In addition to that, a good understanding of Au–Si and Au–SiO\textsubscript{2} interactions, especially near the surfaces and interfaces (and during oxidation) is essential as Au is commonly used for contacts and interconnects in packaging processes of many silicon-based microelectronic devices. Such studies are outlined in this chapter.

In this chapter, further examination on the evolution of Au particles was carried out through a series of thermal wet oxidation experiments. Structural characterisation was performed using RBS, TEM, EDS, and photoluminescence (PL). Responsible mechanisms are proposed, based on the results presented in this chapter and other earlier observations.

4.2 Experimental procedures

The experimental conditions used to prepare the samples whose results are presented in this chapter are summarised in Table 4.1. We note that some of the already reported samples (from chapter 3) are revisited in this chapter for comparison purposes. All the samples were fabricated using commercially available Soitec SOI wafers. The top layer is a 180-nm thick boron-doped (100) silicon, while the underlying layer is a 200-nm thick thermally grown SiO\textsubscript{2}. Initially, the samples were irradiated with 10 keV H\textsuperscript{−} ions to the fluence of $3 \times 10^{16} \text{ cm}^{-2}$. The implantation was carried out at a special tilting angle of 60° in order to minimise channeling and reduce the ion range without sacrificing ion flux, which tends to drop rapidly with decreased implantation energy below 10 keV (irrespective of the implantation area that increases by twofold at the 60° tilt angle). The samples were then annealed at 850 °C for 60 minutes followed by a 40 keV Au\textsuperscript{−} implant to a fluence of about $1 \times 10^{15} \text{ cm}^{-2}$. A post-implantation thermal anneal at 900 °C for 30 minutes in a
Table 4.1: Summary of the samples used in this chapter and their processing sequences starting from left to right.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>10 keV H⁺ implant dose (cm⁻²)</th>
<th>60-minute annealing (°C)</th>
<th>Au⁺ implant energy (keV)</th>
<th>30-minute annealing (°C)</th>
<th>300 keV Si⁺ implant dose (cm⁻²)</th>
<th>900 °C oxidation (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>D</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>0.5</td>
</tr>
<tr>
<td>E</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>1</td>
</tr>
<tr>
<td>F</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>2</td>
</tr>
<tr>
<td>G</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>4</td>
</tr>
<tr>
<td>H</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>6</td>
</tr>
<tr>
<td>I</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
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</tr>
<tr>
<td>J</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
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<tr>
<td>K</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
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</tr>
<tr>
<td>L</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
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</tr>
<tr>
<td>M</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>4</td>
</tr>
<tr>
<td>N</td>
<td>No</td>
<td>No</td>
<td>40</td>
<td>900</td>
<td>No</td>
<td>6</td>
</tr>
<tr>
<td>Q</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>2×10¹⁶</td>
<td>2</td>
</tr>
<tr>
<td>R</td>
<td>3×10¹⁶</td>
<td>850</td>
<td>40</td>
<td>900</td>
<td>2×10¹⁶</td>
<td>6</td>
</tr>
</tbody>
</table>

A quartz tube was performed to getter the Au to the H-induced cavities and ultimately to form Au precipitates or clusters as shown earlier in Fig. 3.7(b). Some selected samples (Q and R as per Table 4.1) were irradiated with 300 keV Si⁺ prior to the final process of single step wet oxidation at a temperature of 900 °C from 30 minutes to 6 hours in water vapour flow. This was carried out to inject vacancies into the silicon layer prior to oxidation as discussed below. A control set of cavity-free samples (I, J, K, L, M, and N) was prepared as a counterpart to the experimental set.

### 4.3 Diffusion mechanisms of Au in silicon

The diffusion of metallic impurities in silicon, where the metal in solution is predominantly substitutional, has been explained by the following two mechanisms: namely Frank-Turnbull or dissociative mechanism [1] represented by:

\[ V + M_s \leftrightarrow M_i, \]  

(4.1)

and kick-out mechanism [2] represented by:

\[ M_s + I \leftrightarrow M_i, \]  

(4.2)
where $M_i$ is an interstitial metal atom, $M_s$ is a metal atom in a substitutional site (or on cavity walls), $I$ and $V$ represent a lattice self-interstitial and a lattice vacancy, respectively. In general circumstances where the number of $I$ is comparatively equivalent to that of $V$, it is very difficult to explicitly identify which mechanism is in play. The Frank-Turnbull mechanism is expected to control the metal diffusion kinetics when the system contains a relatively large number of vacancies. The kick-out mechanism, on the other hand, prevails when there is a considerable amount of self-interstitials. The Frank-Turnbull mechanism has formerly been proposed to explain the diffusion behaviour of Au in silicon [3–5]. However, the results from specific silicon systems with a low level of internal sinks showing that the Au concentration in the middle of the wafer increases in proportion to the square root of diffusion time [6] and the fact that silicon interstitials are predominantly observed during high temperature annealing [7, 8] have disproved the possibility of the vacancy-mediated Frank-Turnbull mechanism. Several other successive works are also in favour of the kick-out model [9, 10]. It is now widely accepted that the diffusion of Au in silicon is determined by the kick-out mechanism [2].

### 4.4 Kinetics of Au particles encapsulated in SiO₂

#### 4.4.1 Evolution of Au particles: sequential oxidation

In this section, we concentrate on the evolution of Au precipitates during progressive oxidation of the top silicon layer. Figure 4.1 compares the RBS spectra of the samples with preformed cavities (represented by solid lines with open circles) and without preformed cavities (represented by solid lines with no symbol) for different exposure times. Shown in Fig. 4.1(a) are random RBS profiles of samples C and I prepared as per Table 4.1. Since the thickness of the BOX layer is maintained until the top silicon layer is completely oxidised, the Si-BOX interfaces of the experimental and control samples are used as a common reference and therefore vertically aligned in each subfigure. The depth profile analysis clearly shows the difference in Au redistribution of the cavity-containing and non-cavity-containing samples after 30-minute annealing at 900 °C as reported in the previous chapter [see Fig. 3.6]. The majority of the Au is essentially observed either at the cavity band when the cavities (effective sinks) were primarily formed within the silicon layer ($\approx$ 100 nm deep) or at the surface by solid phase epitaxial growth (SPEG) in the absence of cavities. A smaller fraction of the Au remains in the surface vicinity of sample C, presumably due to trapping in its own residual implantation damage or disorder [11].
Figure 4.1: Random RBS spectra showing the Au distribution of the samples with (top panel) and without (bottom panel) cavities (a) before wet oxidation and subsequently after wet oxidation at 900 °C for (b) 30 minutes, (c) 1 hour, (d) 2 hours, (e) 4 hours, and (f) 6 hours. Note that the profiles are aligned with respect to the Si-BOX boundary.

After 30-minute wet oxidation at 900 °C, the distribution profiles of the Au in experimental and control samples D and J are compared in Fig. 4.1(b). It is obvious that all the Au is segregated into the silicon layer and specifically behind the oxidising interface. The depth profile of sample J in particular reveals the distribution of the Au close to the back interface of the thermal oxide (note that limited RBS resolution accounts
for the 'broad' Au distribution). We also note the slight volume expansion of the samples, which is due to the difference in atomic density of silicon (≈ 5 × 10^{22} \text{ atoms cm}^{-3}) and molecular density of SiO_2 (≈ 2.3 × 10^{22} \text{ molecules cm}^{-3}). The thickness of the oxide layer is approximately equal to 2.2 times (220%) that of the original silicon layer consumed by the oxide.

As the oxidation progresses, the Au is segregated further into the silicon layer. Figure 4.1(c) also shows an increasing amount of Au (that was initially at cavities within the silicon layer) accumulating at the BOX front interface of sample E, while a high concentration of the Au is still observed within the top silicon layer. For the corresponding cavity-free sample K, most of the Au is distributed close to the thermal SiO_2–Si interface.

By 2 hours [see Fig. 4.1(d)], the oxidising interface has reached the original cavity/precipitate band. Almost all of the Au in sample F with preformed cavities is clearly observed to migrate to the Si–BOX interface, with less than 10% of the Au detected elsewhere. This intriguing observation warrants further investigation, as outlined later. In the case of the cavity-free sample L, the Au is confined within the unoxidised silicon layer. However, due to the limitation of the RBS resolution and the unoxidised silicon layer being very thin (≤ 50 nm), it is difficult to determine whether the Au has remained at the thermal SiO_2–Si interface. A thickness difference of about 50 nm between the thermal oxide layers of samples F and L should also be noted here. This observation will again be discussed later.

The top silicon layer is found (within the resolution of the RBS) to be completely oxidised after 4 hours of oxidation, whereby Fig. 4.1(e) illustrates the Au profiles of the corresponding samples with and without cavities (G and M). The distributions of the Au in the two samples are qualitatively identical, indicating that all the Au particles are confined within an SiO_2 matrix at a depth corresponding to the original front interface of the BOX. A single oxidation for 6 hours does not further change the Au distribution profiles in both experimental and control samples as shown in Fig. 4.1(f). Indeed, the RBS measurements of sample H and N [see Fig. 3.8(b)] only reveal an overall increase in the thickness of the oxide layers to ≈ 620 nm.

TEM analyses were additionally performed in order to obtain specific structural information. The cross-sectional transmission electron micrographs (XTEMs) of the samples with and without cavities are placed side by side on the left and right panels of Fig. 4.2, respectively. The front interface of the BOX layer is aligned vertically to aid visual comparison. The sample identification (as used in Table 4.1) is tagged at the top-right
Figure 4.2: A series of snapshots showing the cross-sectional microstructures of the samples after wet oxidation at 900 °C for various time intervals from 30 minutes to 6 hours. The left column [(a)–(f)] shows the samples with preformed cavities, while the right column [(g)–(l)] shows the control samples without preformed cavities.
corner of each image. It should be noted that the structures prior to wet oxidation are omitted here, as they have already been shown in the subfigures (b) and (c) of Fig. 3.7. In general, our XTEM images are consistent with the RBS results. Figure 4.2(a) portrays a cross-sectional structure above the BOX layer of the cavity-containing sample after a 30-minute oxidation (sample D). A high density of the Au precipitates is observed in the middle of the unoxidised silicon layer, in agreement with the quantitative RBS analysis [see Fig. 4.1(b) for comparison]. Besides that, the mean size and shape of these precipitates in silicon (originally formed in cavities) are essentially maintained during the oxidation process. In contrast, in the absence of cavities, the oxidation process causes segregation of all the Au particles originally at the surface [see Fig. 3.7(c)] behind the thermal SiO2–Si interface as exemplified in Fig. 4.2(f). In addition, protrusions of the oxide into the underlying silicon layer can also be seen in this micrograph at the oxidising interface and adjacent to the Au particles. Such protrusions at the interface are not observed in Fig. 4.2(a) where Au precipitates are initially formed away from the surface (e.g. at the cavities).

A longer oxidation of 1 hour results in a thicker thermal oxide layer regardless of the preformed cavities. Similar differences as observed after 30 minutes, however, can be seen in the 1 hour case as shown in Fig. 4.2(b) and Fig. 4.2(f), when comparing the cavity-containing and cavity-free samples, E and K, respectively. Similar to sample D, sample E shows mostly spherical Au precipitates in the silicon layer whereas those at the oxidising interface (as shown in sample K) are larger and segregated further into the silicon, a clear evidence of Au-enhanced oxidation. This process of Au-enhanced oxidation [12] will be discussed in more detail in Sec. 4.5. It should be noted for the cavity-containing sample that at this stage of the oxidation process, few Au decorated (or empty) cavities remain visible and the majority of the Au precipitates are still at the depth of the cavity band in the middle of the silicon layer. Although the limited resolution of the RBS analysis of sample E [see Fig. 4.1(c)] suggests a reasonable amount of Au at the Si-BOX interface, very few Au precipitates were observed at this interface across the XTEM specimen. This strongly suggests that most of the Au has not relocated but some Au particles may have agglomerated at the interface and are lower in density than can be observed by TEM.

A 2-hour wet oxidation leads to an intriguing Au diffusion behaviour as previously realised from RBS measurements. Figures 4.2(c) and (h) exhibit typical cross-sectional images of the specimens with (sample F) and without cavities (sample L) after the oxidation for 2 hours. Lower magnification images are shown in Fig. 4.3 for a better
4.4. Kinetics of Au particles encapsulated in SiO$_2$

Figure 4.3: Low magnification XTEM micrographs of (a) sample F and (b) sample L showing the morphology and depth distributions of Au precipitates after 2-hour oxidation.

representation of both samples. Figure 4.3(a) in particular, where the growing oxide interface of sample F has proceeded to the depth of the Au precipitate band, shows that the cavities are no longer observed. Interestingly, most of the Au precipitates have been transferred to the Si-BOX interface in contrast to the corresponding control sample L, where the precipitates are still segregated behind the growing SiO$_2$ layer. This seems to indicate that the Au particles originally located at the surface (or native oxide-Si interface) remain segregated under extended oxidation. In contrast, the majority of the Au in the sample with cavities was originally at the precipitate band and these precipitates were mostly relocated to the Si-BOX front interface when the oxidising front moved through the cavity band. We address this intriguing effect in detail later in Sec. 4.6. The slightly thicker thermal oxide layer (i.e. thinner sandwiched silicon) of sample L as observed by TEM is consistent with the RBS measurements. We attribute this small thickness difference either
to the non-uniformity of the oxide thickness, which is known to be influenced by water vapour flow rate, temperature, and pressure, or the possible Au-enhanced oxidation.

By 4 hours, the TEM analysis shows that the silicon layer is almost completely oxidised, in agreement with the random RBS spectra. The thermal oxide is continuous with the BOX and all the Au is confined within an oxide layer at the depth of the original BOX interface. Figures 4.2(d) and (i) are representative cross-sectional micrographs of samples H and N, respectively. Indeed, both cavity-containing and control samples are structurally similar, indicating that the size and shape of Au precipitates appear to be no longer determined by the geometry of the H-induced cavities as pointed out earlier in the previous chapter. The Au particles line up along the original front interface of the BOX layer and their spherical shape is driven by interfacial surface energy minimisation (i.e. minimum surface area for a given volume). The average precipitate size was measured to be around 30 nm, denoting a significant growth over the original mean size ($\approx 15$ nm in diameter), presumably due to Ostwald ripening\textsuperscript{1} at the oxidation temperature. However, this is not the case when the Au precipitates are not dissolved (i.e. remain trapped in the cavities). Our previous work shows that the size of cavity-induced Au precipitates in silicon marginally increase after a prolonged anneal (900 °C for 6.5 hours) [14]. We also observe sparse thin layers of unoxidised silicon sandwiched in between the two oxide layers along the array of Au precipitates. This tiny amount of silicon could not be resolved by the RBS method but was detected by TEM, as illustrated in Figs. 4.2(d) and (i). We confirmed that it is silicon and not Au using two imaging techniques: (i) by bright field (BF) imaging with and without the objective aperture (in both cases, only the Au should always appear dark due to Z-contrast while the thin unoxidised silicon shows no diffraction contrast) and (ii) using BF and dark field (DF) modes to identify whether the thin layer could be imaged in dark field selecting crystalline silicon reflections [see Sec. 2.2.2 for details]. These results suggest that slightly over 4 hours wet oxidation at 900 °C is required to completely trap the Au precipitates in a continuous single SiO$_2$ layer.

A 6-hour wet oxidation at 900 °C for both samples with (H) and without cavities (N) results in Au particles embedded in SiO$_2$ as previously shown in the last chapter and here again in Fig. 4.2(e) and Fig. 4.2(j). The top silicon layer of each sample is now completely oxidised and continuous with the BOX. The precipitates are successfully confined within a single SiO$_2$ layer. The excessive oxidation yields a thicker oxide layer overall. The structures of samples H and N are now qualitatively identical in term of precipitate depth and shape.

\textsuperscript{1}A coarsening process in which large precipitates are growing at the expense of the smaller ones [13].
However, the average size of Au precipitates in sample H (with cavities) is slightly smaller and the density of Au precipitates is marginally higher than those in sample N, as reported earlier in Chapter 3.

### 4.4.2 Further experiments: the influence of vacancies

![Graph showing depth distribution of excess vacancies and interstitials](image)

**Figure 4.4:** **FASTRIM simulation of 300 keV Si⁺ implantation showing a depth distribution of excess vacancies and interstitials in a 180-nm SOI wafer.**

Possible explanations for the observed redistribution of the Au precipitates under oxidising conditions may be involved with the liberation of silicon interstitials. It is well known that during thermal oxidation a fraction of silicon interstitials I are injected into the underlying silicon layer [15–17] and these can potentially interact with (and possibly dissolve or displace) Au that is either in solution within the silicon layer or in the precipitate form via the kick-out mechanism. Another experiment was carried out to demonstrate the role of silicon interstitials on the dissolution of Au precipitates. An additional 300 keV Si⁺ room-temperature implantation to a fluence of $2 \times 10^{16}$ cm$^{-2}$ was specifically performed after Au precipitate formation but prior to 2- or 6-hour wet oxidation in order to generate excess vacancies or vacancy clusters in the silicon overlayer.
at the depth of up to 250 nm from the surface (the total depth of the top silicon layer, plus part of the SiO$_2$ layer) and generate excess interstitials beyond the BOX layer [18–20]. Figure 4.4 illustrates this situation, in which the program FASTRIM [18] has been used to generate the distribution of vacancies and interstitials in the Si–SiO$_2$–Si structure for the implantation conditions used. The resulting profile, in contrast to that produced by SRIM 2010, obeys the simplistic +1 model [21]. These samples are labelled in Table 4.1 as Q and R. The two following points are important for the discussion and should be noted: (i) highly mobile silicon interstitials effectively recombine with excess vacancies [22, 23] or voids [24], in analogy to the annihilation of Frenkel pairs, and (ii) the expected location of excess interstitials is well beyond the BOX layer and therefore will not influence the kinetics in the silicon overlayer. The results are given below.

![TEM micrograph](image)

Figure 4.5: XTEM micrograph of sample Q showing the Au precipitate distribution after 2-hour wet oxidation in the presence of excess vacancies produced by 300 keV high fluence Si$^+$ irradiation.

Figure 4.5 illustrates the XTEM micrograph of sample Q (wet oxidation for 2 hours). In this case, a few Au precipitates remain in the unoxidised silicon layer, whereas the corresponding cavity sample F (in Fig. 4.2(c)) that has been oxidised under similar conditions has all of the Au at the BOX interface. Nonetheless, a large fraction of the precipitates in sample Q (in Fig. 4.5) is still observed at the front interface of the BOX layer, suggesting that the injection of vacancies by high fluence Si$^+$ bombardment has
retarded but not completely stopped the dissolution of Au precipitates. After a 6-hour wet oxidation, the cross-sectional structure of the specially prepared sample R (with preformed cavities and pre-oxidation high fluence Si-implantation) is compared with the cavity-containing (H) and cavity-free (N) samples, as shown in Fig. 4.6. Overall, the structures of all three samples are almost identical. That is, all the Au precipitates are encapsulated within the SiO₂ at the depth of the original Si-BOX interface. The only obvious difference was the presence of loops and dislocations in the silicon below the BOX layer in the cross-sectional micrograph of sample R [see Fig. 4.6(c)]. This is not surprising as this region corresponds to the depth where most of the excess silicon interstitials from the 300 keV implant were dumped as can be seen in the fastrim simulation [see Fig. 4.4]. In the inset of Fig. 4.6(c), the image contrast was adjusted to clearly show the dislocations in the crystalline silicon beyond the oxide layer. However, we have found that the average diameter of the Au precipitates is statistically different in these three samples. Figure 4.6(d) shows the histogram of the size distribution of Au precipitates in these three samples. It was observed that the size of Au precipitates in sample R (with extra Si-implantation to create excess vacancies in the surface silicon layer) is smallest (∼20 nm) and is closest to those in the cavities measured prior to the oxidation. In addition, the precipitate size distribution was found to be narrower than those in the other two samples. This behaviour is suggested to be as a result of suppression of the dissolution process by preferential annihilation of oxidation-produced interstitials at vacancies.

The above results clearly show that the injection of excess vacancies into the silicon layer prior to the oxidation reduces the final size and size distribution of Au precipitates. The contribution due to a variation of the nucleation sites at the buried interface is expected to be minimal as the damaged interface should recover to an equilibrium structure rapidly by annealing during the early stage of thermal oxidation. The density of other interface defects such as voids at the bonding interface produced in the SOI fabrication process [25] and recoiling oxygen atoms from the buried oxide layer due to collision cascades are presumed to be small and uniformly distributed. We, therefore, conclude that the injected vacancies have provided additional preferential traps (other than H-induced cavities, interface defects, and Au precipitates) for the silicon interstitials released from the oxidation reaction. The additional Si-implantation step will effectively suppress the amount of silicon interstitials present at the Au precipitates, and thus limit the rate of precipitate dissolution and Au diffusion (as controlled by the kick-out mechanism). This allows the Au precipitates to retain their original dimensions during the
Figure 4.6: Typical XTEM images of (a) sample H, (b) sample N, and (c) sample R, where the inset with the scale bar of 100 nm shows particularly the implantation-induced dislocations behind the oxide layer. (d) Statistical comparison illustrating the Au precipitate size (in diameter) distribution of samples H, N, and R.
oxidation process. Increasing the silicon fluence used to inject vacancies should increase the vacancy concentration and may further suppress the dissolution. The implantation-induced damage may, however, be undesirable from the application perspective. Trapping the silicon interstitials with substitutional carbon [26] instead of silicon-vacancies may be a preferable alternative approach. We discuss the mechanism for the interstitial-mediated dissolution process in Sec. 4.6.

4.5 Au-induced phenomena during wet oxidation

Figure 4.7: EDS spectra of the Au-induced oxide protrusion (red) and the thermally grown oxide (solid outline), where the XTEM micrograph in the inset shows the corresponding analytical areas. The scale bar represents 20 nm. [Images courtesy of J. Wong-Leung]

From a number of samples (whose processing conditions may be different from those described in Table 4.1), we have observed interesting enhanced oxidation and Au–SiO₂ wetting behaviours that are worthy of discussion. As briefly introduced in the previous section, a Au-enhanced oxidation effect was observed at the thermal SiO₂–Si interface near the Au precipitates originally formed at the surface prior to the oxidation. In this section,
we will show evidence that the protrusions showing contrast close to the Au precipitates are protrusions of SiO$_2$ embedded in the silicon layer. First, EDS spectra obtained from the interesting protrusion area and the thermally grown oxide are compared in Fig. 4.7 and clearly show that the protrusions have some oxygen (O) content. These protrusions are three dimensional features which are embedded in silicon. Thus, the beam spot focused in this region will give a signal averaging over the oxide protrusions embedded in silicon. It is not surprising that the EDS spectra from these protrusions show an O peak lower in intensity than the O-to-Si ratio observed in thermal oxide and do not reflect the true stoichiometry of the protrusions themselves. Figure 4.8 gives further confirmation of the fact that these protrusions are a result of Au enhanced oxidation. Figure 4.8(a) is used to demonstrate the three-dimensional nature of these protrusions. The image shows a region of the sample which is thin enough to show the thickness fringes from the silicon surrounding the protrusions. The contours of the thickness illustrate the three-dimensional contours of these protrusions without strain in the surrounding crystalline silicon near the oxide and three-dimensional Au precipitate. Strain is responsible for the strong diffraction contrast, as displayed in Figs. 4.2(f) and (g). Figure 4.8(b) shows a thinner cross-section of the oxide protrusion. In this case, the oxide observed is not embedded in the underlying silicon and there is no distinction in contrast between the thermal oxide and the oxide protrusion. From the figure, the region of enhanced oxidation is clearly observed to extrude from the oxidising layer and extend laterally beyond the contact area of the Au precipitate and thermal oxide. The geometry of such Au precipitates is about 40 nm across with a height of around 30 nm.

Figure 4.8: Typical XTEM images displaying the effect of Au-enhanced oxidation (a) in a regular area and (b) in a very thin area. The scale bars measure 50 nm in both subfigures. The dashed line is a guide to the eye of the oxidising plane front. [Images courtesy of J. Wong-Leung]

The Au-enhanced oxidation effect has been reported previously after dry-oxidising
Au-covered silicon (111) samples at a much lower oxidation temperature ($\leq 400^\circ$ C) and pressure ($< 1$ Torr) [12]. This same phenomenon was also evident following dry and wet oxidation in the study of silicon nanowires [27], where the proposed mechanism can be used to explain our observation. When Au is in contact with the oxide layer, the main oxidation reaction takes place at the Au-oxide interface, whereby the oxidation process dissociates Au–Si bonds in the Au silicide eutectic droplet and consumes the silicon atoms in order to grow the oxide. The Au–Si eutectic droplet in turn absorbs silicon atoms from the underlying silicon substrate to maintain the stoichiometry within the droplet. Such a chemical process allows the oxide to form progressively on top of the Au precipitate and consequently segregate the Au precipitate behind the oxidising interface at a rate faster than that of the conventional silicon oxidation. The previous observation of buried Au precipitates in silicon after thermal evaporation of Au and annealing in a residual oxygen-containing nitrogen gas ambient has also been explained similarly [28]. The catalytic behaviour of Au, which is responsible for the enhanced oxidation reported here and in the oxidation study of silicon nanowires [27], is accounted for by replacement of Si–Si bonds at the SiO$_2$–Si interface with weaker Au–Si bonds [12, 29]. We also speculate that the effect of Au-enhanced oxidation by interdiffusion of silicon through Au droplets becomes less important for longer oxidation times, where the diffusion of the oxidant through thicker oxides is a rate-limiting factor [30]. On top of that, this process is aided by the increasing number of liberated silicon interstitials (proportional to the oxide thickness [31]) that facilitate the oxidation process.

Additional evidence of Au preferentially wetting the oxide layer was observed when the growing oxide approaches the BOX. Figure 4.9 illustrates cross-sectional structures of a sample after wet oxidation for 6 hours at a temperature slightly under 900$^\circ$ C. In this case, the silicon overlayer was almost completely oxidised and the Au precipitates were about to be confined within an SiO$_2$ layer. Figure 4.9(a) shows that one of the Au precipitates is wetting both oxide interfaces when the silicon layer is sufficiently thin. Figure 4.9(b) is a two-beam bright-field XTEM image, exhibiting a similar wetting behaviour of Au. It can be confidently stated that these precipitates were initially formed at the surface as distinguished by the Au-induced oxide protrusion. This observation strongly supports an argument that the surface free energy of the Au–SiO$_2$ interface under the oxidising condition is lower than that of the Au–Si interface. Moreover, a range of Au–SiO$_2$ interfacial free energy values $\gamma_{\text{Au-SiO}_2}$ from 1.186 to 1.503 J m$^{-2}$ has been reported in [32], while a value for the Au–Si free energy $\gamma_{\text{Au-Si}}$ was also reported in [33] to be 1.25 J m$^{-2}$. Our
Figure 4.9: XTEM images captured when the top silicon layer is close to completely oxidised showing interesting Au wetting behaviour. The scale bars are 50 nm.

The conclusion that $\gamma_{\text{Au-SiO}_2} < \gamma_{\text{Au-Si}}$ does not contradict these previous observations.

### 4.6 Dissolution and reprecipitation mechanism

In this section, we will consider the Au dissolution and reprecipitation mechanism during the wet oxidation process. The results in the previous section show that the segregation, dissolution and precipitation behaviours of Au are location dependent. That is, during wet oxidation the behaviour of Au precipitates initially formed at the surface is different from those that are originally formed at the cavity band and at the Si-BOX front interface. Our proposed mechanism of Au dissolution and reprecipitation is summarised as shown in Fig. 4.10.

By gettering of Au to H-implantation-induced cavities in the top silicon layer of the 180-nm SOI wafer, the Au precipitates were essentially observed at three different regions within the layer: (i) a small fraction at the surface, (ii) mostly at the cavity band, and (iii) a very small amount at the BOX interface [see Fig. 4.10(a)]. Determined by the free energy, the Au precipitates at the cavities take a spherical form, while those at the surface or interfaces are of island-like or lens-like shape. Let us first consider the near-surface Au precipitates, which are primarily observed in the cavity-free sample. The oxidation process allows these Au precipitates to progressively segregate precisely behind the growing interface [see Fig. 4.10(b)], in agreement with an earlier study [34]. An
increase in the overall sample thickness with oxidation time as depicted in the schematic is a result of the difference in atomic density of silicon and the molecular density of SiO₂. Indeed, the thickness of the thermally grown oxide is approximately twice that of the consumed silicon. Concurrently, a large number of silicon interstitials are released. Theoretical studies on silicon-interstitial diffusion during thermal oxidation of silicon suggest that the silicon interstitials concentrate at the interface between silicon and the growing SiO₂ [17, 35, 36]. A small fraction of the interstitials diffuses into the underlying silicon, generating a flux of self-interstitials towards the BOX layer, while a larger fraction diffuses back into the thermal SiO₂. Those interstitials that remain in SiO₂ or close to the interface (also known as surface regrowth flux) are almost immediately removed by re-oxidation with incoming oxygen and thus have no significant effect on the Au evolution. Therefore, the flux of silicon interstitials diffusing in silicon towards the BOX layer is the
only component considered in our regime for possible Au dissolution.

We suggest that the oxidation-induced silicon interstitials, if not annihilated at any existing nucleation sites (e.g. voids, dislocations, stacking faults, and interfaces), play a crucial role in dissolution and reprecipitation of Au precipitate clusters. This effect is pronounced and becomes more effective when the oxidising interface approaches the Au precipitate band (i.e. cavity band), consistent with the models proposed previously in [17, 35, 36] to explain the interactions of point defects and oxidation-induced stacking faults with Si–SiO₂ interfaces during the oxide growth. As the oxidation progresses, the silicon interstitials build up in the top silicon layer close to the Si–SiO₂ interface. The amount of silicon interstitials in the silicon overlayer near the interface will eventually exceed the equilibrium solubility, leading to a strong driving force for their annihilation at appropriate sinks for silicon interstitials. This concentration gradient of silicon interstitials towards the BOX layer will saturate empty cavities as well as dissolve the Au at the cavity band. The silicon layer, especially near the thermal oxide interface, will therefore become supersaturated with interstitial Au \((Au_i)\). The diffusion of Au in silicon and related Au interstitial and substitutional solubility in silicon depends on several parameters and is therefore rather complex [2, 37]. We note that the diffusivity of \(Au_i\) is considerably higher than that of substitutional Au \((Au_s)\). The \(Au_i\) solubility, in contrast to the diffusivity, is about two orders of magnitude lower than that of the \(Au_s\) [37]. In our case, the high concentration of silicon interstitials near the 'moving' Si–SiO₂ interface will prevent Au precipitates from coalescing at that interface. The supersaturation of Au will therefore force the Au atoms (primarily \(Au_i\)) to diffuse and reprecipitate at a more favourable lower-free-energy site such as the BOX interface, as shown in Fig. 4.10(c).

To assess the viability of our model for relocation of Au to the BOX interface during oxidation, an estimate of the number of silicon interstitials \((I)\) injected into the underlying silicon layer is needed. The absolute flux of injected \(I\) into the underlying silicon under different oxidation conditions has not been established but Raineri et al.[31], who measured the shrinkage of nanocavities as a monitor of trapped interstitials, were able to estimate the number of injected \(I\) under oxidation conditions that are not too different from those that we used. During the growth of 160 nm of oxide (similar to our case) at 1100°C, Raineri et al. determined that \(\approx 1 \times 10^{16}\) to \(4 \times 10^{16}\) Si cm\(^{-2}\) are liberated into bulk silicon. These authors also noted that the number of the \(I\) was proportional to the oxide thickness and that there was little dependence of this number on oxidation temperature although they did indicate that the number of \(I\) trapped at cavities depended on the
availability of other traps for silicon interstitials. Hence, it is reasonable to estimate that
the number of \( I \) liberated into the underlying silicon layer after 2 hours is \( \approx 2 \times 10^{16} \) Si
\( \text{cm}^{-2} \) under our oxidation conditions. In our model for the relocation of Au, we argue that
such injected interstitials both shrink cavities and kick out \( \text{Au}_s \) (to liberate fast diffusing
\( \text{Au}_i \)) according to Eq. 4.2. Firstly, the total amount of implanted Au in our samples is
around \( 10^{15} \) \( \text{cm}^{-2} \), located prior to oxidation in precipitates, on cavity walls and a very
small fraction in substitutional sites. Thus, there is an order of magnitude more \( I \) available
to displace Au so long as the silicon interstitials are not depleted by trapping at more
favourable sites (e.g. nanocavities). In order to account for that amount of \( I \), we estimate
the number of \( I \) required to completely fill our cavities. TEM observation and analysis was
used to determine the cavity density before Au implantation. Assuming that all the cavities
are spherical and distributed at a precise depth within the silicon overlayer, we determined
the cavity band to have an average (areal) density of about \( 2.06 \times 10^{10} \) \( \text{cm}^{-2} \) and an average
diameter of \( \approx 15 \) nm. Hence, the average volume of a cavity or void is approximately
equal to \( 1.8 \times 10^{-18} \) \( \text{cm}^3 \). Recalling that the atomic density of silicon is \( 5 \times 10^{22} \) atoms
\( \text{cm}^{-3} \), a single void of average diameter can accommodate around \( 9 \times 10^4 \) silicon atoms.
Therefore, the number of \( I \) needed to saturate our cavities (without Au precipitation) is
about \( 1.85 \times 10^{15} \) \( \text{cm}^{-2} \). This calculated value puts an upper limit on the number of \( I \) that
possibly annihilate at the cavities in our case (i.e. when considering Au precipitates are
formed within most cavities), but is still an order of magnitude lower than the number
of silicon interstitials available from our oxidation conditions. Hence, in the absence of
alternatively more favourable trapping sites for the flux of diffusing silicon interstitials,
our proposed model for silicon-interstitial-driven Au relocation seems plausible.

The envisaged role of \( I \) as a mediator of Au diffusion under an oxidising ambient is
well justified by the kick-out mechanism and the results from our partial oxidation and
injection of vacancies experiments. That is, the surface Au precipitate clusters are found
to accelerate the oxidation rate, whereas those at the cavity band (well within the silicon
layer and away from the high silicon-interstitial concentration region) are not influenced
by the oxidation process until approached by the oxidising interface. The former, Au-
enhanced oxidation process, was explained in Sec. 4.5. The top panel of Fig. 4.10(b)
shows a schematic model of the corresponding enhanced oxidation. The process (1)
(interaction of oxygen with silicon within Au eutectic) stimulates the oxidation of silicon,
resulting from a preferential dissociation of a weaker Au–Si bond as compared to a Si–
Si bond. This usually causes a local decrease in silicon concentration in the Au eutectic
precipitates and sets up the need for a continual supply of silicon (interstitials) from the silicon layer underneath (note that the silicon and the Au eutectic precipitates are in intimate contact) [see process (2) in the top panel of Fig. 4.10(b)]. This enhanced oxidation process, which consumes silicon interstitials, accounts for the fact that Au precipitates at the growing oxide interface are not dissolved [see Sec. 4.4 for results and Sec. 4.5 for further explanation].

The bottom panel of Fig. 4.10(b) and Fig. 4.10(c) illustrate that the segregation and dissolution of the Au precipitates does not occur until they are approached by the oxidising interface. A different experimental study on the diffusion of silicon generated by oxidation at an Si–SiO₂ interface using isotopic heterostructures (natSiO₂ on ²⁸Si) has shown agreement with the theoretical predictions that the excess silicon-interstitial flux is largely concentrated close to the advancing interface and decays exponentially away from it [38]. This effectively explains why the dissolution of Au precipitates is only observed near the growing oxide layer. The attempt to suppress the silicon-interstitial effect on the Au dissolution by injection of vacancies into the silicon layer prior to the oxidation via Si-irradiation has shown some success in preserving the geometry of Au precipitates. This result provides additional support for our silicon-interstitial-induced Au dissolution model. The low solubility of Au in the silicon oxide yields the formation of stable Au precipitates at the Si-BOX interface until they are completely confined by the thermally grown oxide in a spherical shape as depicted in Fig. 4.10(d) to satisfy the minimum free energy conditions.

4.7 Photoluminescence of Au particles encapsulated in SiO₂

Photoluminescence (PL) was selectively performed on oxidised samples with and without embedded Au particles. We note that these samples were characterised by RBS prior to the PL measurement. A 325-nm line from He-Cd laser was used to excite the samples at room temperature. The PL spectra recorded from a few different spots on an SOI wafer oxidised at 900 °C for 6 hours and the equivalent sample containing embedded Au particles (sample N) are shown in top and bottom panels of Fig. 4.11, respectively. In both cases, the PL signals vary from one spot to another, implying a non-uniformity of the origin of the photoluminescence peaks. A broad spectral feature (possibly consists of several luminescence peaks at 420, 438, and 465 nm) extending from 400 to 475 nm appears in both samples regardless of the presence of Au particles. A peak at about 500 nm exists
Figure 4.11: Room-temperature PL spectra from several different locations on the same samples (a) oxidised at 900 °C for 6 hours and (b) irradiated with 40 keV Au⁺ followed by a 30-minute anneal at 900 °C and oxidation at 900 °C for 6 hours (sample N).

in both samples usually with relatively low intensity except in one measurement of a Au-containing sample where the peak has relatively high intensity and is accompanied by a peak at 645 nm. Overall, these results suggest that the Au particles are not responsible for most of the above-mentioned luminescence peaks.

Photoluminescence studies on silica glasses [39] and nanowires [40, 41] have reported several luminescence bands in the wavelength range of 290 to 650 nm. The peaks centred around 420 nm (2.95 eV) and 435 nm (2.85 eV), and 465 nm (2.65 eV) have previously been observed from amorphous silica nanowires synthesised by carbothermal reduction under 260-nm excitation [41] or by excimer laser ablation under 325-nm excitation [40], and are linked to the oxygen deficient defects. In addition, the peak at around 460 nm has been observed from Si-implanted SiO₂ films and was ascribed to the oxygen vacancy [42]. The 650-nm (1.9 eV) band was reported after examination of high-purity silica glasses and tentatively assigned to the non-bridging oxygen hole centre (NBOHC) [39, 43]. Indeed, the
PL spectrum of encapsulated Au particles in SiO$_2$ structure is simply a weak and broad luminescence band centred around 600 nm [44]. The results of these previous works, together with the fact that the luminescence peaks are observed irregularly on the same specimen, have led us to believe that the presented PL signatures are not associated with encapsulated Au particles but rather originate from defects or oxygen deficiency localised in the oxide. The relatively low concentration of Au particles in our sample (compared to the Au-embedded SiO$_2$ structure in reference [44]) may be responsible for the absence of Au-related PL signals.

![Photon energy (eV)](image)

**Figure 4.12:** Low-temperature PL spectrum (open square) of an SOI wafer after 1-hour wet oxidation at 900 $^\circ$C and RBS characterisation. The spectrum from the same area but after 2-minute anneal at 275 $^\circ$C (solid circle) exhibits a very sharp and bright luminescence at 1218 nm (so-called W-line), where the inset shows a plot of temperature dependent PL intensity of the line.

Low-temperature PL measurements were also performed in an infrared region on some oxidised samples without Au particles using a 532-nm laser line. The results were initially surprising, as can be seen in Fig. 4.12. Although several luminescence peaks can
be identified, they only come from some specific areas of the specimen. This suggests, in a similar manner to the above observations of the defect formation in SiO₂, that the luminescence may originate from defect-related centres. A thorough check of the sample history and some repeated experiments have been able to confirm that the observed luminescence peaks arise from the RBS measurement spots, where a 2 MeV He⁺ beam was used to examine the sample structure. A subsequent anneal (RTA) at 275 °C for 2 minutes was found to activate an overall PL intensity and especially a peak at 1218 nm (1.018 eV), as shown in Fig. 4.12. The intensity of the 1218-nm emission was found to decrease with increasing measurement temperature, as displayed in the inset of Fig. 4.12. Our results are consistent with the previous photoluminescence study of silicon implanted with noble gases [45], where a similarly strong emission (usually referred to as W-like line) appears at a slightly longer wavelength of 1226 nm (1.012 eV) after 200 °C annealing of 350 keV He-implantation to the dose of 10¹⁶ cm⁻². A further literature survey has indicated that the emission at 1218 nm is normally observed following radiation damage and is known as I₁ or W-line. The line is so sharp and intense that it is attractive for silicon-based light emitting devices. In the next chapter, several other defect luminescence centres are systematically explored by photoluminescence under various implantation and annealing conditions.

4.8 Summary

This chapter provides further insight into the evolution of implantation-induced Au precipitates in the top silicon layer of an SOI wafer under sequential wet oxidising conditions. Several intriguing phenomena, including segregation of Au particles, Au-enhanced oxidation, and dissolution of Au precipitates at the cavities and reprecipitation at the front interface of the BOX layer are identified. A key role of silicon interstitials in these processes is discussed. A mechanism is proposed based on the interaction of silicon interstitials (continuously released during the oxidation process) and Au precipitate clusters. An array of spherical Au precipitates is observed at the depth corresponding to the front interface of the original BOX layer at the completion of oxidation. The introduction of vacancies into the silicon overlayer is found to inhibit the Au dissolution effect of silicon interstitials and hence preserve to some extent the original precipitate size (i.e. tight size distribution of around 20 nm in average diameter). The optical characterisation by photoluminescence does not show a promising effect from the encapsulated Au particles.
However, an intense luminescence line was unexpectedly observed at a wavelength of 1218 nm after RBS measurements. This ‘serendipity’ led to a change of focus in the thesis to the study of optically active defects formed by ion-implantation.

References


[18] H. J. Hay, unpublished, \textsc{fastrim} is a modified version of \textsc{trim}-90 which takes into account the multilayer target (interfaces) problems inherent with \textsc{trim}.


Luminescence from Defects in Silicon

A combination of ion-implantation and subsequent annealing at different thermal conditions gives rise to several different kinds of optically active defect clusters. This chapter explores the possibilities of several defect-originated sub-bandgap luminescences using photoluminescence as a primary method of characterisation, where complementary information on the defect structure was provided by transmission electron microscopy.
5.1 Background and selected literature review

Disorder and defects are generally inevitable, following the process of ion implantation. These lattice imperfections and impurities are usually undesirable from an optoelectronic device perspective as they are known to degrade device performance and often lead to non-radiative recombination processes. However, some of them are recently shown to provide states in the silicon bandgap [1], giving rise to radiative recombination possibilities [2]. The resulting luminescence becomes observable mostly at low temperature when other non-radiative recombination pathways as well as thermal line broadening are suppressed. In fact, this kind of recombination process is the mechanism behind most of the silicon devices available to date.

5.1.1 Structure of crystalline defects

Four different types of common crystalline defects are (1) point defects, (2) line defects, (3) planar defects, and (4) volume defects [3]. The point defect is regarded as a zero-dimensional defect that exists under thermodynamic equilibrium conditions and is the simplest form of defects in a solid. According to lattice positions, it can be further divided into three categories: (i) vacancy, (ii) interstitial, and (iii) substitutional [see top view of the model in Fig. 5.1]. By definition, a vacancy is an empty lattice site, an interstitial is an atom occupying the interstices of regular lattice sites, and a substitutional atom is a foreign atom in a lattice site. Vacancies and self-interstitials are often referred to as native or intrinsic defects, whereas interstitials of different species and substitutional atoms are known as impurity-related defects.

In contrast to point defects, one-dimensional line defects or dislocations are microscopic and usually formed at the termination of an atomic plane under non-equilibrium conditions such as thermal treatment and mechanical deformation. The two noteworthy types of dislocations are (i) edge dislocation and (ii) screw dislocation. Fig. 5.1 illustrates the formation of an edge dislocation when a plane of atoms is shifted in a direction perpendicular to the dislocation line. The formation of an edge dislocation can alternatively be viewed as an extra plane of atoms bounded by normal lattice planes. A screw dislocation, on the other hand, appears when the shift is parallel to the direction of the dislocation. Previous studies have shown in regard to defect interaction that dislocations are preferential sinks for several transition-metal impurities [4, 5].

Planar defects are two-dimensional defects produced in a solid during thermal
Figure 5.1: A schematic illustrating point and line defects in a simple cubic lattice structure. Open circles represent host atoms; filled circles represent impurity atoms.

Figure 5.2: Schematic illustration showing the formation of (a) grain boundaries and (b) twins.
and mechanical processing. Grain boundaries, stacking faults, and twins are some common types of planar defects. Grain boundaries are usually found in poly-crystalline semiconductor materials where at least two single crystalline orientations are separated by a grain boundary [Fig. 5.2(a)]. Stacking faults are irregularities in stacking sequence in the lattice. Twin defects are related to stacking faults and can also be considered as a specific type of grain boundary where both sides of the twin boundary have a mirror lattice symmetry [Fig. 5.2(b)].

Three-dimensional defects including volume or bulk defects are normally introduced during the fabrication processes. They are usually observed by electron or optical microscopy. Some examples of the volume defects are pores, cracks, local amorphous regions, voids or cavities, and precipitates. The last two kinds have already been exemplified in Chapter 3 and Chapter 4.

5.1.2 Fundamental defect luminescence

While large defect clusters can be analysed using an electron microscope or occasionallyting an optical microscope, photoluminescence (PL) is one of the convenient methods used to identify extremely small optically active defects [see Sec. 2.2.3.1 for technical details].

Most of the radiative defects that are discussed herein act as a stepping stone in the interband transition process and often lead to phonon-less radiative recombination. Figure 5.3 schematically illustrates the photoluminescence process in the presence of a defect state \( E_1 \) lying within the forbidden gap of an indirect gap semiconductor. The mechanism involves the generation of an electron-hole pair where the electron in the host lattice with an energy \( E_1 \leq E_V \) is excited by a photon beam from the valence band to an upper energy level \( E_2 \geq E_C \) in the conduction band, leaving a hole in the valence band. The energy of the photon is defined as \( h\nu \), where \( h \) is a Planck's constant and \( \nu \) is the corresponding photon frequency. The electron-hole pairs may loosely bond in the form of an exciton\(^1\). Since the lifetime of excitons in silicon is relatively long (in the order of \( \mu s \)), the excitons can diffuse and be captured by an optical centre (i.e. an optically active defect of interest) to which the energy is transferred, promoting the optical centre to an excited state. The subsequent recombination of the electron and hole can take place via the luminescent defect centre and this is accompanied by photon emission of a unique energy (signature). Such a radiative recombination process is known as spontaneous emission.

\(^1\)bound states of electrons in the conduction band and holes in the valence band due to Coulomb electrostatic interaction.
Figure 5.3: Schematic energy $E$ versus momentum $k$ diagram illustrating simplified photoluminescence processes in the presence of an optically active defect centre. An electron (filled circle) is initially excited with a photon of energy $\hbar \nu$ above energy gap $E_g$ to a higher quantum state in the conduction band and then radiatively recombines with hole (open circle) via an isolated defect level in the bandgap, emitting a photon of energy less than $E_g$.

It should also be noted that the exciton diffusion is favourable at temperatures below 30 K [6–8]. This is because the ionisation of excitons occurs at higher temperature, allowing direct band-to-band transition to dominate the radiative recombination. For this reason, the luminescence study of defects is preferable at cryogenic temperature.

5.1.3 Brief reviews on silicon photoluminescence

Photoluminescence characterisation at low temperature has revealed several luminescence peaks in silicon. A selected summary of reported photoluminescence in
silicon is provided in Table 5.1. To begin with, four intrinsic phonon-assisted peaks were identified at photon energies of 1.135 eV (1093 nm), 1.097 eV (1130 nm), 1.068 eV (1161 nm), and 1.032 eV (1202 nm). Haynes et al. have related these emissions to the transverse acoustic (TA) phonon, longitudinal acoustic (LA) phonon, longitudinal optical (LO) phonon, and transverse optical (TO) phonon, respectively [25]. Later works [21] have confirmed the association of the TA phonon (Si_{TA}) but attributed the second line (1.097 eV) to the TO phonon (Si_{TO}). The third and fourth emission lines (at 1.068 and 1.032 eV) were also reassigned to the radiative transitions involving a single TO phonon plus either an inter-valley scattering component (IV) or Brillouin zone centre phonon (O^{F}), denoted by Si_{TO+IV} and Si_{TO+OF}, respectively.

Other peaks were detected in both p- and n-type silicon wafers due mostly to the localised recombination at impurity-associated centres. Some of the relatively strong

<table>
<thead>
<tr>
<th>Photon energy (eV)</th>
<th>Common name</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>0.790</td>
<td>C</td>
<td>Emission from centre involving C and O</td>
<td>[9, 10]</td>
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<td>0.807</td>
<td>D1</td>
<td>Dislocation-related centre</td>
<td>[11, 12]</td>
</tr>
<tr>
<td>0.874</td>
<td>D2</td>
<td>Dislocation-related centre</td>
<td>[11, 12]</td>
</tr>
<tr>
<td>0.902</td>
<td>R</td>
<td>Interstitial-based {311} extended defect</td>
<td>[13, 14]</td>
</tr>
<tr>
<td>0.939</td>
<td>D3</td>
<td>Dislocation-related centre</td>
<td>[11, 12]</td>
</tr>
<tr>
<td>0.970</td>
<td>G</td>
<td>Emission from C-related centre</td>
<td>[15-17]</td>
</tr>
<tr>
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<td>D4</td>
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<td>[11, 12]</td>
</tr>
<tr>
<td>1.018</td>
<td>W or l1 or l3</td>
<td>Si interstitial cluster with trigonal symmetry or di-interstitial</td>
<td>[18, 19]</td>
</tr>
<tr>
<td>1.032</td>
<td>Si_{TO+OF}</td>
<td>Si with TO + OF phonon emission</td>
<td>[20]</td>
</tr>
<tr>
<td>1.039</td>
<td>X or l3 or l4</td>
<td>tetra-interstitial</td>
<td>[19, 22]</td>
</tr>
<tr>
<td>1.068</td>
<td>Si_{TO+IV}</td>
<td>Si with TO + IV phonon emission</td>
<td>[21]</td>
</tr>
<tr>
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<td>Y or l2 or B_{3+}</td>
<td>A cluster of two B and one Si interstitial</td>
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<tr>
<td>1.091</td>
<td>A_{STO}</td>
<td>As-bound exciton with TO emission</td>
<td>[21, 24]</td>
</tr>
<tr>
<td>1.0914</td>
<td>G_{STO}</td>
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<td>[21]</td>
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<td>[21]</td>
</tr>
<tr>
<td>1.0921</td>
<td>S_{TO}</td>
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<td>[21]</td>
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<td>1.093</td>
<td>B_{TO}</td>
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<td>[21]</td>
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<tr>
<td>1.097</td>
<td>Si_{TO}</td>
<td>Si with TO phonon emission</td>
<td>[21]</td>
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<tr>
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<td>[21, 25]</td>
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<tr>
<td>1.149</td>
<td>A_{BE}</td>
<td>Emission from exciton bound to As</td>
<td>[21, 24]</td>
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</tbody>
</table>
extrinsic luminescence peaks are worthy of mention. Sharp luminescence lines at 1.091 eV (1137 nm) and 1.149 eV (1079 nm), for instance, were observed in arsenic-doped n-type silicon and attributed to recombination of As-bound excitons [21, 24]. The integrated intensity of these lines was also found to increase with the doping density. Similar luminescence peaks were also detected in phosphorus-doped (P_{TO}) and antimony-doped (Sb_{TO}) silicon wafers with slight blue-shifts [see Table 5.1] [21]. For boron-doped p-type silicon, several peaks have been reported including the most prominent B_{TO} line at 1.093 eV (1135 nm). The line has been recognised as an emission from TO phonon-assisted boron-bound exciton recombination. This impurity-related peak also appears (with small energy shift) when gallium or aluminium atoms are substituted for boron [21].

In addition to those luminescence peaks mentioned above, light emission from defects in silicon has received considerable attention since the early 1970s due in part to the study of defect formation in processed silicon. Some of the first reports on luminescence from defects in silicon were published after electron [26], boron [27, 28], and phosphorus [28] irradiation. Important emissions include zero-phonon C-, G-, W, and Y-lines that were observed at photon energies of 0.790 eV (1570 nm) and 0.970 eV (1278 nm), 1.018 eV (1218 nm), and 1.080 eV (1147 nm) respectively. The two former lines (C and G), in particular, have been reported after a low-temperature anneal of electron-irradiated CZ-silicon [26]. The observation of both peaks are strongly dependent on measurement temperature. The G-line was initially thought to arise from a di-vacancy, while the C-line was linked to an oxygen-dependent complex previously identified in the electron paramagnetic resonance (EPR) study as Si-G15 [29] or K-centre [30] due to the similarities in annealing behaviour [31]. One should, however, be aware that such a correlation, although intuitive, is prone to mistake. This is because the defects with a non-paramagnetic property do not show up in an EPR spectrum and the identification of the interstitial atoms by the EPR technique is usually complicated. In addition to that, there is orders of magnitude difference in concentration between the detection levels for the two techniques. Successive works [15–17] have rejected the possibility of the di-vacancy as a G-centre and associated the G-line with a cluster of two carbon atoms as responsible for a Si-G11 peak [32] in an EPR spectrum. On the other hand, further studies on the origin of the C-line have confirmed the oxygen-dependency of the C-centre and also suggested that the centre is made up of at least one oxygen atom and one carbon atom [9, 10].

Likewise, the W-line or I1 has been initially observed following bombardment of crystalline silicon with electron [34, 35], boron [27, 28], and phosphorus [28]. Further
works have shown that the \( W \)-line is not known to be dependent of any doping species [27, 28, 34, 36, 37]. An appropriate thermal treatment following irradiation was found to significantly enhance the intensity of the \( W \)-line and this is especially necessary when the emission is not readily observed. Although the nature of the \( W \)-centre has been investigated over the past few decades, the exact structure of the centre is still arguable. Correlation of the results obtained from different characterisation techniques has led to a large continuing controversy over the origin of the \( W \)-line emission. Kirkpatrick \textit{et al.} performed a range of boron and phosphorus ion-implantations into various silicon substrates followed by annealing and attributed the \( W \)-line to five-vacancy clusters [28]. A theoretical study by Estreicher \textit{et al.} on the defects formed by noble gas implantation indicates that the \( W \)-centre is a neutral di-vacancy [38], while others have argued that it is a silicon-interstitial cluster with tentative structures of di-interstitial [20] or trigonal interstitial (\( I_3 \)) [18, 19, 39]. Today, it is widely accepted that the \( W \)-centre is a small interstitial complex comprising two to three silicon-interstitial atoms. The atomic model proposed by theoretical calculation is portrayed in Fig. 5.4(a). The \( W \)-line is subject to a severe thermal quenching effect. Our own PL characterisation [see inset of Fig. 4.12] and a previous temperature dependence study reveal that the \( W \)-line intensity drops drastically from \( \approx 50 \) K and disappears above a measurement temperature of about 90 K [20].

Figure 5.4(b) illustrates a model of boron-interstitial cluster (BIC) that is thought to
be responsible for the $Y$-line or I$_2$ luminescence initially observed in boron-implanted silicon followed by a 400 °C anneal [27]. The structure is similar to that of the $W$-line (tri-interstitial) defect except that two silicon interstitials (small white balls) are replaced by two boron atoms (small black balls), and therefore is named B$_2$I$_3$ [33]. We will refer back to these models later in order to understand the results in Chapter 7.

The evolution of small radiation-induced defects occurs with increasing annealing temperature, leading to the formation of larger defects that can also be characterised by electron microscopy in addition to PL. A well-known planar defect on {311} planes, for instance, has been imaged by high-resolution transmission electron microscopy (HRTEM) and reported to be a silicon-interstitial chain of a length from about 5 to 30 nm [40, 41]. The dissolution of these {311} or rod-like defects (RLDs) after extended thermal annealing has led to observations of transient enhanced diffusion (TED) of several dopants commonly used in silicon-based microelectronic devices including boron [42], phosphorus [43], and arsenic [43, 44]. Recently, the study on the transition of interstitial clusters in ion-implanted silicon has suggested a direct relationship of a sharp and intense luminescence at 0.902 eV (1375 nm) namely the $R$-line and the {311} defects [14]. However, the evolution pathway is not fully understood. The possible structure of the {311} defect precursors was tentatively proposed to be different from that of the {311} defect itself. That is, the transformation mechanism to the {311} defects involves more than just a simple Ostwald ripening process [45].

The above mentioned defects evolve further into more stable loops and dislocations by raising the annealing temperature up to about 900 °C. Pioneering photoluminescence studies of plastically deformed [11, 46] and ion-implanted silicon [47] have shown typically four dislocation-related luminescence peaks denoted by D1, D2, D3, and D4 at 0.807, 0.874, 0.939, and 0.997 eV, respectively. The PL intensities of these D1 to D4 bands were found to increase with the dislocation density. A very small amount of transition metal (Cu, Fe, Ni, Ag or Au) contamination ($\approx 10^{13}$ cm$^{-3}$) appears to be needed for the observation of intense D-bands, while higher level of contamination (enough to form metal precipitates) results in a quenching of the bands [48, 49]. Geometrical kinks [50] on dislocations, jogs [51], stacking faults [52], Lomer–Cottrell and Frank dislocations [51, 53] were postulated to give rise to D1 and D2 bands. Higgs et al. [54, 55] alternatively proposed from their cathodoluminescence (CL) measurements that the D1 and D2 bands originate from point defects in the vicinity of dislocation cores, in agreement with the conclusion of Sauer et al. [12], while the D3 and D4 were suggested to arise from dislocation cores.
Weronek et al., however, interpreted the D1 and D3 bands as phonon replicas of D2 and D4 bands, respectively [52]. In addition to the dispute over the origin of D-bands, the controversial effects of oxygen [50, 56] and hydrogen [56–58] on the D1 intensity have also been reported.

This chapter concentrates on the luminescence from some of the zero-, one-, and two-dimensional defects in low-doped (high resistivity) silicon produced by self-implantation to various fluences with successive thermal treatments. Optimal processing conditions for different types of defect complexes were obtained based on photoluminescence results. A coherent picture of defect-mediated luminescence is developed and presented accordingly.

5.2 Experimental procedures

A range of samples was prepared from boron-doped p-type Czochralski (CZ) silicon (100) wafers of resistivity 5-25 Ω cm by 300 keV \(^{28}\text{Si}^+\) ion implantation to fluences ranging from \(10^{10}\) to \(10^{17}\) cm\(^{-2}\) at room temperature. Over the large range of fluences, the ion flux was increased with fluence to achieve manageable times for each implantation. The samples were subsequently annealed in Ar by either rapid thermal annealing (RTA) for up to 2 minutes or in a conventional furnace for times longer than 2 minutes at a temperature between 275 and 900 °C to form certain types of optically active defects, most of which are silicon-interstitial type. Low-temperature photoluminescence was principally used for characterisation [see Sec. 2.2.3.1 for details]. TEM examination was additionally performed on selected samples to obtain structural information of the defects, provided that the size of defect clusters are larger than the TEM resolution limit. The results obtained in this study are categorised into three classes according to the post-implantation annealing temperature: room-temperature to 525 °C as a low temperature regime, 600 to 700 °C as an intermediate temperature regime, and above 850 °C as a high temperature regime.

5.3 Results

5.3.1 Low annealing temperature (up to 525 °C)

In this subsection, we concentrate on the evolution of small defect clusters driven by low-temperature isochronal annealing where the effect of the implantation fluence on luminescence is monitored by PL.
5.3.1.1 As-implanted

Low-temperature photoluminescence spectra of a virgin silicon wafer and as-implanted samples are shown in Fig. 5.5. Three intrinsic peaks are identified at 1.034 eV (Si$_{TO+O^+}$), 1.097 eV (Si$_{TO}$), and 1.137 eV (Si$_{TA}$), with the second peak much brighter than the others. A B$_{TO}$ peak appears at 1.093 eV as a shoulder of the Si$_{TO}$ for all the fluences. The overall PL intensity is found to decrease with increasing implanted fluence, whereby the Si$_{TO+O^+}$ and Si$_{TA}$ peaks are not observed at fluences larger than $10^{11}$ cm$^{-2}$. Shown in the inset is a plot of the integrated PL intensity $I_{PL}$ of the Si$_{TO}$ versus logarithm of dose, $\phi$, where the straight line representing the best fit of the data is defined by $I_{PL} = -6.36(\log \phi) + 91.4$.

![Photoluminescence spectra](image)

Figure 5.5: Photoluminescence spectra at 13 K of p-type CZ-silicon samples subjected to various fluences of 300 keV Si$^+$ ions. The inset plots integrated intensity of Si$_{TO}$ as a function of silicon dose. The (red) line is an approximate linear fit to the data, where the uncertainty in each point is estimated from several measurements of different spots on the same sample to be within 15%.
5.3.1.2 275 °C annealing

By 275 °C for 2 minutes, the 1.018 eV (1218 nm) luminescence line (namely W or I1) is predominantly observed regardless of the implantation dose (up to $10^{14}$ Si cm$^{-2}$), as shown in Fig. 5.6. The zero-phonon W-line is accompanied by lower-energy phonon replicas (i.e. a vibrational sideband) extending for more than 0.5 eV from the W-line peak. The inset of the figure plots the integrated intensities of the W-line and a combination of Si$_{TO}$ and B$_{TO}$ (from 1122 to 1140 nm) as functions of silicon fluence with respect to the left-hand axis. The plot with respect to the right-hand axis presents the intensity ratio of the W-line to the sum of Si$_{TO}$ and B$_{TO}$. It is clear that the W-line intensity increases with Si fluence and peaks by $10^{12}$ cm$^{-2}$, in contrast to the Si$_{TO}$ and B$_{TO}$. The decrease of the Si$_{TO}$ and B$_{TO}$ with increasing implantation dose follows the same trend as that of the as-implanted case. Our results are consistent with those reported earlier for PL of ion-implanted silicon [59].

![Photoluminescence spectra](image)

Figure 5.6: Photoluminescence spectra after 2-minute RTA at 275 °C of the silicon samples self-implanted to various fluences. The inset shows integrated PL intensities of W-line (W letter) and Si$_{TO}$ + B$_{TO}$ (open triangle) with 15% uncertainty versus 300 keV Si$^{+}$ dose. The intensity ratio of W to silicon peak (solid circle) is plotted in the right ordinate. The solid lines are guide for the eyes.
5.3.1.3  400 °C annealing

The PL spectra measured at 13 K of the Si-implanted samples after 400 °C annealing are illustrated in Fig. 5.7. The W-line and its phonon replicas are still present in all spectra but much weaker than those observed following a 275 °C anneal, especially in the lowest dose case ($10^{10}$ cm$^{-2}$). The intensity of the line even in the brightest case is not much stronger than that of the Si$\text{TO}$ and B$\text{TO}$, integrating from 1122 to 1140 nm. The intensity of the W-line becomes stronger with increasing dose up to about $10^{12}$ cm$^{-2}$ and then decreases, while the Si$\text{TO}$ peak decreases with increasing dose. Also shown in Fig. 5.7 is a new and rather sharp peak at 1.039 eV, namely the so-called X-line. Although the X-line is relatively weak compared with the W-line, both attain maximum intensity at the same dose range of $10^{12}$ cm$^{-2}$ [see inset of Fig. 5.7]. The rise of the broad background feature under the W-line phonon replicas should also be noted.

![Photon energy (eV)](image)

**Figure 5.7:** Typical photoluminescence spectra after 2-minute RTA at 400 °C of the silicon samples self-implanted to various fluences. The inset plots integrated intensities of the W-line (W letter), X-line (X letter), and intrinsic peak (open triangle) versus implantation dose. The solid lines are guides for the eyes.
5.3.1.4 525 °C annealing

Following 525 °C annealing, the W-line luminescence disappears from all the spectra of Fig. 5.8. The Si_TO peak appears to be very strong at the lowest dose and decreases with increasing dose similar to the as-implanted and the previously presented annealed cases. In contrast to the signal from silicon, a weak broadband, which was seen after 400 °C annealing, becomes stronger and dominates the PL spectra of the samples irradiated to the fluences of $10^{12}$ Si cm$^{-2}$ and above. The zero-phonon X-line is found superimposed on the broad luminescence background and its intensity is marginally influenced by the silicon dose (above $10^{11}$ cm$^{-2}$). The integrated intensity of the broad luminescence band is plotted with respect to the implanted fluence and compared with that of the X and Si_TO, as shown in the inset of Fig. 5.8. The features around 1375 nm (0.902 eV) are known to result from atmospheric water vapour absorption [60, 61].

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**Figure 5.8:** Photoluminescence spectra of the silicon samples self-implanted to various fluences. The inset plots integrated intensities of a silicon peak (open triangle), X (X letter), and a broad luminescence band (solid square) as functions of silicon dose. The uncertainty was estimated to be about 15% for all the cases. The solid lines are guide for the eyes.
5.3.2 Intermediate annealing temperature (600–700 °C)

The work discussed above refers primarily to the evolution of simple point defects and small clusters whose dimensions are such that they are not visible in standard TEM measurements. Under higher annealing temperature and longer annealing times, extended defects form by agglomeration of small clusters. Some of them are visible in TEM so their evolution can be monitored by both PL and TEM. In this section, the defect evolution is mainly studied by varying the annealing time while the implantation dose is kept constant at a level that allows easy identification of extended defects (so-called \{311\} defects) by TEM.

5.3.2.1 600 °C annealing

The PL spectra of self-implanted silicon samples after annealing at 600 °C for up to 90 minutes are displayed in Fig. 5.9. The results from a $5 \times 10^{13}$ cm$^{-2}$ fluence are chosen to present, for they clearly exhibit most of the important spectral features. We note that this dose is slightly higher than the optimal dose ($10^{12}$ cm$^{-2}$) for luminescence (W-line) in the low temperature annealing regime. This can be explained by the tendency for some of the small point defects and clusters to anneal out (i.e. they break up and interstitials diffuse to annihilate at free surfaces and other defects in the bulk). Indeed, it has previously been observed that below a critical dose, such annihilation dominates and extended defects do not form on annealing [45]. By 600 °C, the W- and X-lines are eliminated. Small local mode peaks instead appear on a broad background at the wavelengths of 1245 (0.996 eV), 1263 (0.982 eV), and 1277 nm (0.971 eV). Previous studies by PL and positron annihilation of the samples treated under similar conditions to those in this study have related these zero-phonon peaks to the formation of larger silicon-interstitial clusters [35, 62]. In addition, it is noteworthy that the appearance of the broadband luminescence spectrum observed following 600 °C in the wavelength range of 1147 to 1640 nm (referred as ‘Broadband$_{600}$’) is different from that which emerged after 525 °C [see also Fig. 5.8 for comparison].

The intensity ratio of the Broadband$_{600}$ to Si$_{TO}$ is plotted against the silicon fluence and presented in the inset of Fig. 5.9. The ratio is found to gradually decrease with annealing time, suggesting the rise of Si$_{TO}$ peak and/or fall of the broad luminescence band with longer thermal annealing exposure. Since this broad luminescence feature dominates the PL spectrum and the overall luminescence intensity is noted to decrease with increasing thermal annealing time, we can conclude that the intensity of the broadband feature also
Figure 5.9: Photoluminescence spectra of the silicon samples implanted with silicon to a fluence of $5 \times 10^{13}$ cm$^{-2}$ and isothermal annealed in Ar at 600 °C for various times. The integrated intensity of the local modes (from 1120 to 1146 nm) and the broad luminescence band (from 1147 to 1640 nm) measured with respect to the silicon peak ($\text{Si}_{\text{TO}}$) is plotted in the inset as a function of annealing time.

decreases with increasing annealing time. Contradicting results, where this broad peak does not decrease in intensity but rather shifts towards lower energy with annealing time (up to 810 minutes), are reported in the samples with boron concentration of about two orders of magnitude higher [63].

### 5.3.2.2 700 °C annealing

Figure 5.10 illustrates the PL spectra of the silicon samples, self-implanted to the fluence of $5 \times 10^{13}$ cm$^{-2}$, after a successive anneal in Ar at 700 °C for various times from 1 to 90 minutes. The spectrum observed after 1-minute RTA does not exhibit any interesting feature apart from a relatively weak $\text{Si}_{\text{TO}}$ peak, while annealing for 2 and 5 minutes yields the PL spectra similar to those observed from the samples annealed for an equivalent or
Figure 5.10: Photoluminescence spectra at 13 K showing the time evolution of optically active defect centres in silicon after self-implantation to a fluence of 5×10^{15} cm^{-2} and isothermal annealing in Ar at 700 °C for 1, 2, 5, 10, 40, 60, and 90 minutes. The solid lines are guide for the eyes.

longer period at 600 °C. By 10 minutes, the PL signature starts to evolve, leading to the formation of a new luminescence peak at about 1365 nm (0.908 eV) and a broadband extending from ≈ 1425 nm as well as a stronger SiTO intensity. The 0.908 eV peak (ascribed to be a peak in a transient state of the evolution) is replaced by a sharp PL line at 0.902 eV, namely the so-called R-line, after a 20-minute anneal. A broad spectral band centred at about 1550 nm is detected after annealing for both 10 and 20 minutes, where our repeated measurements show that the band fades with time at room temperature. For the present implantation conditions, the R-line intensity is found to peak after annealing for 40 minutes. The plot of peak intensity of the R-line as a function of annealing time indicates that further annealing results in an increase of SiTO but a decrease of the R-line intensity [see inset of Fig. 5.10].

The cross-sectional specimens were selectively prepared from the samples, whose PL
Figure 5.11: Weak-beam micrographs showing the cross-sectional microstructure of 300 keV self-implanted silicon samples to the fluence of $5 \times 10^{13}$ cm$^{-2}$ followed by an anneal at 700 °C for (a) 10 minutes, (b) 20 minutes, (c) 40 minutes, and (d) 90 minutes. The surface is marked by an arrowhead while the $\{311\}$ defect is indicated by an arrow. The scale bars represent 200 nm. [Images courtesy of J. Wong-Leung]

results are reported in Fig. 5.10, and then examined by TEM. Figure 5.11 illustrates the observed structure after 700 °C annealing for 10, 20, 40, and 90 minutes. The presence of the $\{311\}$ planar defects (often called $\{311\}$ or rod-like defects (RLDs)) is directly connected with the observation of the $R$-line, in agreement with a previous study using high energy (MeV) silicon implantation that shows that these planar defects are chains of interstitials on $\{311\}$ planes and they are responsible for the $R$-line luminescence [14]. We also note that while the $R$-line intensity is strongest by 40-minute annealing, the $\{311\}$
RLDs seem to elongate (at a non-linear rate) with annealing time. Indeed, the defects grow at a faster rate during the initial stages of annealing (within the first 40 minutes) than later. The average length of the defects as observed after annealing for 40 minutes is around 50 nm. This relationship between the \( R \)-line intensity and the \{311\} arrangement will be commented on further in Sec. 5.4.4.

5.3.3 **High annealing temperature (above 850 °C)**

In this subsection, we examine the evolution of the irradiation damage resulting from high fluence implantation and post-implantation annealing at 900 °C for 30 minutes by TEM and PL.

5.3.3.1 **900 °C annealing**

![Photoluminescence spectra at 13 K of the silicon samples initially self-implanted at 300 keV to a range of fluences from \( 10^{15} \) cm\(^{-2} \) to \( 10^{17} \) cm\(^{-2} \), followed by annealing at 900 °C for 30 minutes.](image)

Figure 5.12: Photoluminescence spectra at 13 K of the silicon samples initially self-implanted at 300 keV to a range of fluences from \( 10^{15} \) cm\(^{-2} \) to \( 10^{17} \) cm\(^{-2} \), followed by annealing at 900 °C for 30 minutes.
Dislocation loops are generally expected following a post-implantation anneal at 900 °C of a heavily damaged silicon sample. Figure 5.12 shows PL measurements of the samples subjected to various doses of 300 keV Si⁺ (from $10^{15}$ to $10^{17}$ cm$^{-2}$) and annealing at 900 °C for 30 minutes in flowing Ar. At this stage, the R-line is no longer observed. Shown in all spectra is a D1 band with a peak at 1530 nm (0.810 eV). Two other bands (presumably D2 and D3) are barely noticeable at about 1428 and 1348 nm, respectively. Whereas the energy position of the D1 closely matches the published value, the 'D2' and 'D3' appear shifted towards longer wavelength (lower photon energy) [12]. A representative TEM image illustrating the formation of dislocation loops in silicon after 300 keV Si-irradiation to the fluence of $10^{15}$ cm$^{-2}$ and a 900 °C anneal is shown in Fig. 5.13. The nominal depth of these dislocation loops is beyond the ion projected range and is indeed near the end of range (EOR) beyond the original amorphous layer depth. Based on previous studies, it is expected that the D-band luminescence originates from the dislocation region but the origin of the D-bands remains a puzzle [12, 50-55].
5.4 Discussion

5.4.1 Silicon intrinsic and $B_{TO}$ peaks

We consider first the three luminescence peaks at 1.032, 1.097 and 1.135 eV [see Fig. 5.5]. As mentioned earlier in Sec. 5.1.3, these intrinsic peaks in crystalline silicon have previously been attributed to either single or multiphonon-assisted transitions. The first in particular is the $Si_{TO+O^*}$ and involves both the transverse optical (TO) phonon of an energy approximately equal to 58 meV and the Brillouin zone centre phonon ($O^I$) of 64.5 meV [21]. The strongest peak at 1.097 eV ($Si_{TO}$) only accounts for the TO phonon, while the last and also the weakest peak is known as the $Si_{TA}$ and is attributed to a 18.3 meV transverse acoustic (TA) phonon-assisted transition [21]. The intensity of $Si_{TO}$ decreases with increasing dose, while a post-implantation anneal was shown to recover the radiation damage and regain the $Si_{TO}$. This is suggestive of damage removal with the crystalline perfection of the silicon sample related directly to the intensity of the $Si_{TO}$. These observations strongly emphasise that the detected photoluminescence spectrum is influenced by both radiative and non-radiative or quenching centres and, therefore, should be interpreted with care.

Appearing normally as a shoulder of the $Si_{TO}$ is an extrinsic peak of a boron-bound exciton TO phonon replica $B_{TO}$ at a photon energy of 1.093 eV or at a wavelength of 1135 nm. A linear relationship between the PL intensity ratio of $B_{TO}$ to $Si_{TO}$ and the boron concentration has been established [64]. That is, one can obtain the approximate concentration of boron in the substrate by measuring the relative PL intensity of the $B_{TO}$ peak. However, we note that the calibration of the $B_{TO}$ to $Si_{TO}$ ratio for boron concentration by Tajima [64] does not directly apply to our case. The difference in measurement temperature and/or excitation intensity may be responsible for this inconsistency. In Chapter 7, we shall demonstrate that the $B_{TO}$ overwhelms the $Si_{TO}$ when the background boron concentration is as high as $10^{17}$ cm$^{-3}$, and that the $B_{TO}$ is not observed in phosphorus-doped n-type silicon samples.

According to the above discussion, we can compensate the effect of the (low level) radiation damage in a simple way by factoring the intensity of the interested peak with the sum of the $Si_{TO}$ and $B_{TO}$ intensities from the same PL spectrum [59].
5.4.2 The W-line

The W-line or I1 is observed following a 2-minute anneal at 275 °C [Fig. 5.6] and becomes weaker by 400 °C [Fig. 5.7] before disappearing by 525 °C [Fig. 5.8]. Our results are in close agreement with those obtained from annealing of boron and phosphorus implanted samples [28] and are well supported by elevated temperature silicon implantation experiments [65].

As discussed earlier, the intensity of the PL response is normally reduced by radiation damage. The comparison of results from both 275 and 400°C annealing shows consistently that the W-line increases in intensity monotonically with implantation fluence up to about $10^{12}$ cm$^{-2}$, but decreases in intensity like the integrated intensity of the Si$_{TO}$ and B$_{TO}$ at larger doses. Although it is not possible to avoid generating the quenching centres during implantation, they can subsequently be removed. Cullis et al. [66] have demonstrated a perfect recrystallisation of the amorphous region (containing a high density of non-radiative centers that provides competing channels for the radiative recombination process) by pulsed ruby-laser annealing in a time scale of the order of nanoseconds that induces near-surface melting and solidification. Skolnick et al. [67] have shown in another study that the laser melting method permits an observation of intense W-line emission from a sample heavily damaged by $3 \times 10^{15}$ Si cm$^{-2}$ implantation. Similarly, Giri et al. have reported an increase of the W-line intensity after sputter etch removal of a near-surface damaged layer produced by silicon implantation to a fluence of the order of $10^{14}$ cm$^{-2}$ [39]. Their results also suggested that the W-line defects are accumulated beyond the ion range, consistent with the supposition that the W-line defect is an interstitial cluster. This opens up another possibility to enhance the W-line intensity by removing the heavily disordered near-surface region and leaving the underlying 'W-line' defect-containing region intact.

During our 'W-line' study, the possible effect of boron (a common silicon p-type dopant) on the W-line luminescence was brought to our attention by our colleagues from the University of Melbourne. Consequently, an additional set of experiments was designed and carried out to demonstrate such an effect. Initially, silicon wafers were selectively implanted by either 100 keV B$^-$ or 250 keV P$^+$ ions to the fluences of $3 \times 10^{14}$ cm$^{-2}$ and annealed at 950 °C for 30 minutes to remove the implantation damage. The implantation energies, fluences, and annealing conditions used were chosen to result in similar dopant distribution profiles to a depth of around 700 nm as predicted by a one-dimensional process simulator (ISE-TCAD) [68] [see Fig. 5.14 for comparison of the
Figure 5.14: The B and P profiles calculated using ISE-TCAD for 100 keV B⁺ or 250 keV P⁺ ions implanted to the same fluence of $3 \times 10^{14}$ cm⁻², followed by a 30-minute anneal at 950 °C. The expected Si ion ranges for energies of 100, 300, 400, and 500 keV are indicated by vertical dashed lines.

profiles]. A subsequent Si-implantation was performed at 100, 300, 400, or 500 keV to a fixed fluence of $10^{12}$ cm⁻² (with the $R_p$ indicated for each implantation energy in Fig. 5.14 by a vertical dashed line) and subsequent annealing to activate the W-line defect formation.

In this case, the majority of the W-line defects ($I_3$) is expected to form at the depth slightly beyond the respective ion projected range. Figure 5.15 plots the peak intensity of the W-line as a function of Si ion energy. The W-line intensity from both P and B implanted samples seems to increase with the Si-implantation energy, but is still lower than that of the control sample without B or P pre-implantation at any Si energy. It also appears as if both B and P influence the formation of the W-line intensity; the latter seems to have a more significant impact than the former. However, one should keep in mind that disorder (inevitable following the conventional post-implantation annealing process) can both quench luminescence and also provide sinks for silicon interstitials, which are sources for the W-line defect formation. In this particular case, the heavier P ions have a potential
to produce more lattice damage than the lighter B ions, resulting in a formation of more complex defects that strongly reduce the number of necessary point defects. As a result, it is still not clear whether the W-line intensity reduction is due to the presence of boron (and phosphorus) impurity or the implantation-induced disorder. What we do know at this stage is that in order to obtain a strong W-line luminescence, the Si-implantation should be performed such that the W-line defects are formed well away from the B- or P-doping region. We will revisit this issue again using commercially available highly boron-doped silicon wafers in Chapter 7.

5.4.3 The X-line

Our results show that the X-line or I3 resembles the W-line in several aspects. Both are sharp zero-phonon, near-bandgap emissions and not known to depend on the presence of any specific impurity [69]. In general, the X-line preferentially forms at a slightly higher implantation fluence and annealing temperature than the W-line. It is thus reasonable
to suppose that the defect cluster responsible for the X-line is larger than the W-line defect. The X emission is relatively weak and only detected after annealing of the samples implanted to fluences $\geq 10^{11}$ cm$^{-2}$ at 400 up to 525 °C. It was found to disappear by 600 °C [Fig. 5.9]. The first observation of the X-line was reported over three decades ago after a 150 keV boron implantation to the dose of $10^{13}$ cm$^{-2}$ and a 400 °C anneal for 30 minutes [28]. Several models have been put forward to describe the X-centre geometry. Previous studies linked the emission with a multi-vacancy cluster [18, 28], while recent observation on local vibrational modes (LVMs) [70] and theoretical calculations based on ab initio cluster and supercell methods [22] associated the luminescence with tetra-interstitial aggregates.

5.4.4 The R-line

The study of the R-line is interesting, both from a structural and optical point of view. Our experiments indicate that the observation of the R-line is only favoured under restricted conditions. It is not detected at annealing temperature $\leq 600$ °C irrespective of implantation dose, consistent with the study of small defect evolution that establishes a direct relationship between the R-line luminescence and the presence of interstitial-related $\{311\}$ extended defects [14]. A nearly coincident photoluminescence line at 0.903 eV (1373 nm) has previously been reported [71]. However, this luminescent peak is believed to be different from the R-line since it was observed in CZ-silicon annealed at 450 °C for 300 hours or 600 °C for 50 hours without implantation.

The results obtained from isothermal annealing at 700 °C [Fig. 5.10] also reveal that the intensity of the R-line or the formation of responsible $\{311\}$ RLDs is not only influenced by the annealing temperature but also the annealing time. The R-line luminescence emerges after 10 minutes annealing and attains its maximum after 40 minutes [see inset of Fig. 5.10]. From the structural standpoint, the XTEM images in Fig. 5.11 correspondingly show a rapid growth of $\{311\}$ RLDs in the early stages of annealing. Further annealing beyond 40 minutes does not dramatically increase the defect size. This may be explained by competition between two processes of interstitial agglomeration and $\{311\}$ defect dissolution. Although it is not conclusive from the presented micrographs, it is very likely that the density of the $\{311\}$ defects decreases as the annealing time increases due to the Ostwald ripening effect [72]. The correlation of the R-line intensity with the formation of $\{311\}$ defects allows us to suggest that optimum R-line luminescence occurs at $\{311\}$ RLDs with an effective length of around 50 nm (or marginally longer). However, the behaviour might be more complicated if, for example, the $\{311\}$ defect density is decreasing and/or
the dissolution of the \{311\} defects results in a formation of clusters that are non-radiative recombination centres.

There is some controversy concerning the evolution of defect clusters prior to the formation of the \{311\} extended defects. First, the two broad luminescence peaks observed between 1200 and 1600 nm after annealing at 600 °C [Fig. 5.9] as well as in the first few minutes of annealing at 700 °C [Fig. 5.10] have been postulated to be precursors of the \{311\} RLDs [14]. Conversely, Nakamura et al. have formed these broad peaks by Cu-implantation followed by a 30-minute anneal at 600 °C but have not observed them to evolve into the R-line defects after 700 °C. It is, however, important to note that their study does not consider either the interaction of copper with the interstitial clusters during the annealing or the effect of copper itself, which may be detrimental to the R-line luminescence.

The formation of di-interstitials [63] or an optical transition at locally strained regions around small interstitial clusters [14] have previously been associated with the broadband luminescence prior to a well-defined R-line. Furthermore, the intensity of the broadband was found to increase with the silicon fluence (from \(10^{12}\) cm\(^{-2}\) up to \(5 \times 10^{13}\) cm\(^{-2}\)) [14]. In any cases, no extended defects were observed by TEM. We argue that the former speculation (i.e. precursors of the \{311\} are di-interstitials) is very unlikely as the di-interstitials even in the most stable configuration are very mobile [73], while the latter proposal of strain surrounding larger clusters is consistent with our annealing results [see for example the inset of Fig. 5.9].

### 5.4.5 The D1, D2, D3, and D4 lines

A 30-minute anneal at 900 °C produces the D1 line for a range of silicon fluences from \(10^{15}\) to \(10^{17}\) cm\(^{-2}\). The D2 and D3 lines appear with relatively weak intensities at longer wavelengths, while the D4 is not observed regardless of silicon fluence in our case. As reviewed earlier, these lines have been reported following plastic deformation or ion-implantation of silicon, and are known as dislocation-related lines or D-bands. The broadening of the D-bands (as compared to the W and X) indicates that they may originate from defects with inhomogeneous size distribution in a highly strained region [61, 74]. The shifting of the energetic peak positions is not unexpected since several studies have noted that the photon energies and relative intensities of the D-bands are sample-dependent [47], sensitive to stress [12] and measurement temperature [46, 75]. This seems to explain the deviation of our observed D-band energetic positions from the reported
values. Despite a number of studies to date, the origin of these dislocation-related peaks is still debatable. This is mainly because of the difficulty in spatially isolating the luminescence originating from regions around dislocation cores.

5.4.6 Overview of all the defect signatures: a big picture

Figure 5.16: Schematic showing the principal luminescence lines in silicon as a function of 300 keV Si$^+$ fluence and annealing temperature. The annealing time is 2 minutes for annealing temperature below 600 °C and 30 minutes for the rest (above 600 °C).

Figure 5.16 summarises the above results in a schematic diagram. Where a stronger PL intensity is anticipated, the area (processing condition) is presented in a darker tone. Since the D-line intensity is sample dependent, it seems inappropriate to provide details on the expected PL intensity. The zero-phonon W- and X-lines are typically observed for low-dose implantation, $\lesssim 10^{13}$ cm$^{-2}$, and low annealing temperature (up to about 500 °C). These centres are believed to be simple point defect clusters comprising of three and four silicon-interstitial atoms, respectively. Intermediate Si-implantation dose ($10^{13}$–$10^{14}$ cm$^{-2}$) and annealing temperature (600–700 °C) promote the defect-defect interactions that usually lead to larger interstitial-related clusters or interstitial-based extended defects.
Isothermal annealing at 700 °C for up to 90 minutes confirms the established relationship between the $R$-line and the $\{311\}$ RLDs. We also note that the $R$-line luminescence is maximised after 40 minutes, at which the average length of the $\{311\}$ RLDs is about 50 nm. A longer anneal results in a reduction of the $R$-line intensity in correlation with a marginal increase of the $\{311\}$ defect size and a significant decrease in the $\{311\}$ defect density, as can be anticipated from a previous TEM study [72]. Further experiments with different Si-implantation fluences and TEM analyses in plan-view are necessary in order to arrive at a definite conclusion regarding the link between the structural and optical properties of the $\{311\}$ defects. Dislocation loops are observed following a high-dose implantation and annealing above 850 °C, and their appearance corresponds with the development of the dislocation-related luminescence D-bands.

From the application point of view, all these luminescence lines are attractive for their emissions in the telecommunication wavelength window (1100–1700 nm). The dislocation-related D1 has an additional advantage over the others in that luminescence remains strong to relatively high temperature. Indeed, a room-temperature silicon LED has been engineered based on the D1-line [76, 77]. However, the further development of the D1-line LED may encounter difficulties because of the lack of understanding as to the origin of D1 emission. The $W$-line, on the other hand, has been intensively studied and there is almost a consensus that the responsible centre is a cluster of silicon-interstitial atoms with trigonal symmetry. The line is sharp and has the most intense signal among the observed peaks. Such properties are attractive for a true silicon laser. Although the $W$-line appears to suffer a serious thermal quenching, which may render it from being a practical light source, fabrication of a light emitting device from this luminescence line will serve as a proof of concept and may provide a first stepping stone for a silicon laser.

5.5 Summary

This chapter provides results from a scoping study of radiation-induced defects in silicon using low-temperature photoluminescence and transmission electron microscopy. The evolution of the defects is monitored at various silicon fluences and annealing conditions, where the prominent peaks are identified and discussed with regard to published literature.
References


In this chapter, we report an approach based on energetic beam processing to obtain light emission from point defect clusters in silicon. Sub-bandgap light emitting diodes at 1218 nm were demonstrated at cryogenic temperatures. The devices show good p-n junction characteristics with an estimated external quantum efficiency in a range of $10^{-7}$ to $10^{-6}$. 
6.1 Introduction

Intrinsic silicon is a poor light emitter because of its natural indirect energy band structure. That is electron-hole recombination (particularly at room temperature) is mostly non-radiative. This is because the indirect recombination process usually involves phonons, and hence radiative emission is very inefficient (i.e. long radiative lifetime). Having said that, the demand for low cost on-chip optical interconnects has increased significantly over the past decades, attracting considerable interest and effort among researchers, material scientists, and industries in developing efficient light sources entirely based on silicon [1–6]. Various prospects for improving the efficiency of silicon light emitting devices include the use of bandgap engineering, spatial confinement, the use of optically emitting impurities, defect sites, and Raman scattering. Some important approaches are reviewed in the following section. This chapter, however, concentrates on the fabrication of sub-bandgap silicon LEDs using point defect clusters known specifically from the previous chapter as W-centres.

6.2 Road to a silicon-based light emitting device

This section addresses several important milestones in the development of silicon light emitting devices. Efforts have been made to engineer the silicon bandgap. One of the most important accomplishments was pursued by turning the indirect bandgap of silicon into a quasi-direct one by so-called Brillouin zone folding (BZF). The first theoretical model proposed in the 1970s by Gnutzmann and Clausecker [7] suggests that the silicon band structure in wavevector space (k-space) can be tailored with a superlattice structure to achieve zero-phonon or no-phonon (NP) transitions. The concept was experimentally realised later in the following decades through Si–Ge heterostructures [8, 9]. In particular, the bandgap energy can be tuned by varying the alloy composition of ultrathin (< 20 Å for each individual layer) strained layer superlattices. The studies reported the emissions near 0.76, 1.03, 1.2 1.6, and 2.3 eV, where the first two were indirect transitions. Unfortunately, the optimisation is limited by the number of strained-layers, which can be accommodated by a substrate without sacrificing structural stability [8]. No thought or comment on the fabrication of light emitting devices has yet been proposed.

Light emission may also be obtained via spatial or quantum confinement of carriers (i.e. electrons and holes). Specifically, the effect occurs when the physical size of
semiconductor material becomes smaller than the radius of the electron-hole (e-h) pair or exciton Bohr radius (∼ 4.5 nm in bulk crystalline silicon). The energy levels consequently become discrete and the bandgap energy increases, resulting in a blue shift of the band-edge luminescence peak. In addition, the probability of the carriers recombining non-radiatively also decreases with the size of semiconductor nanoparticle. This fundamental aspect of quantum mechanics has been used to partially or fully explain the mechanism of light emission for many different low-dimensional structures including quantum wells (QWs) [10], porous silicon (PS) [11–13], quantum wires (QWRs) [11, 14–16], and silicon nanocrystals (Si-NCs) or quantum dots (QDs) [17–21]. QWs are known to confine electrons and holes in one dimension (free to propagate in the other two dimensions), while QWRs and PS are considered as two-dimensional structures. QDs are claimed to have the sharpest density of states for their zero-dimensional character (i.e. electrons and holes are confined in all three dimensions).

The presence of some specific impurity atoms in a silicon host matrix may create localised impurity states, where excitons can be trapped or relax, and hence produce NP luminescence. Out of several candidates for silicon light emission are rare earth elements. Erbium (Er³⁺) has received considerable attention since its emission (around 1535 nm) is in a standard telecommunication wavelength range [22–27], although the emitted power from Er-doped silicon was arguably too weak to be used for a practical LED [28]. In fact, the development of Er doped semiconductors is restricted by the low solubility of Er in crystalline silicon (c-Si) [29]. The problem has to some extent been overcome by the co-implantation of oxygen and electrically driven Er-doped silicon devices have now been realised [26, 30], although the luminescent intensity remains lower than is needed for many applications. Apart from Er, cerium oxide [31, 32] and terbium (Tb) [33, 34] have also been recently reported for luminescence. Isoelectronic impurities such as carbon [35–39] have also been incorporated into silicon to form optically active complexes or clusters with silicon atoms, which may also be considered as defect sites. Applications have not been demonstrated until recently when silicon was implanted with carbon, annealed to initiate solid phase epitaxy (SPE), and patterned by reactive ion etching (RIE) [40].

Light emission from point defect clusters and dislocations in silicon has been revealed through photoluminescence studies, some of which were reviewed and described in Chapter 5. The collective understanding of these optically active defects has led to a few examples of silicon-based light emitting diodes [41–43].

The most successful outcome so far has been achieved using the stimulated inelastic
scattering effect of light known as Raman scattering. The first silicon Raman laser with
an emission at 1675 nm and an efficiency of about 8.5% was demonstrated by Boyraz and
Jalali. [44] The laser was limited to pulsed mode due to the two-photon absorption (TPA)
(i.e. two photons simultaneously excite an atom) that in turn leads to a saturation of free
carriers, resulting in a significant optical Raman signal loss. By engineering the waveguide
structure to incorporate a p-i-n (p-type/intrinsic/n-type) design, a continuous-wave (CW)
silicon Raman laser can be obtained [45]. Because Raman scattering is a non-linear optical
process, the Raman laser is, however, not strictly speaking a laser but rather an optical
parametric oscillator. Other solutions, which are not in the scope of this thesis, include
quantum cascade and hybrid approaches.

6.3 Device Fabrication and Characterisation

A combination of ion implantation, pulsed laser melting (PLM), and rapid thermal
annealing (RTA), was used to create a W-line LED containing an excess silicon self-
interstitial concentration as the optically active region. In the previous chapter, we have
shown that the W-line is usually observed in lightly radiation-damaged silicon. Heavily
damaged silicon (as a result of $\geq 10^{14}$ Si cm$^{-2}$ implantation) only yields a low W-line
intensity unless the damaged or the amorphous layer has been removed [46]. The
well-established method of PLM offers an attractive way to return the material near-
surface to a crystalline state, free of extended defects [47], while generating a highly
supersaturated solid solution of electrically active dopants which in our case serves a
purpose of fabricating an electrical contact.

6.3.1 1st Generation Device

The first-generation device was prepared on a commercially available boron-doped p-type
silicon (100) wafer with a resistivity of 5 $\Omega$ cm. Initially, the silicon wafer was implanted
with 80 keV $^{28}$Si$^+$ to a dose of $1 \times 10^{15}$ cm$^{-2}$ followed by an 80 keV $^{34}$S$^+$ implantation
to a dose of $1 \times 10^{14}$ cm$^{-2}$, all at liquid nitrogen cooled temperature (77 K) to ensure
amorphisation of the surface silicon for a subsequent rapid liquid phase epitaxial (LPE)
growth. Rutherford backscattering spectrometry and channeling (RBS-C) was used to
confirm that $\approx 160$ nm of the top silicon layer was amorphous. A spatially homogenised
308-nm single laser pulse from a XeCl$^+$ excimer laser was used to remove excess damage
close to the surface caused by implantation and reinstate the original silicon crystallinity,
while affording sulfur supersaturation [48]. The optimal laser fluence was predetermined from the LIMP heat flow simulation [see Sec. 2.1.3 for details] shown in Fig. 6.1. The ideal fluence in this particular case (a-Si thickness = 160 nm) would be around 1.4 J cm$^{-2}$, which is sufficient to melt all the way through the entire amorphous silicon (a-Si) layer, triggering a full epitaxial regrowth of single c-Si, free of any extended defects, from an underlying crystalline substrate [48]. Insufficient laser energy density (below the epitaxial regrowth threshold) was found to promote the formation of randomly oriented polycrystalline silicon (poly-Si) possibly containing extended defects due to rapid resolidification of a primary surface melt and explosive crystallisation$^1$ [51, 52]. Overpowering the pulse fluence tends to cause superheating of the sample that consequently results in an explosion of a liquid film [53, 54]. This result is usually observed by optical microscopy as a number of pores on the sample surface. In an experiment [see Fig. 6.1], the melt duration was first determined by time-resolved reflectivity (TRR) measurement to be in a range of about 100 to 115 ns. This result was subsequently used as an input in LIMP to

$^1$A thermal process of non-equilibrium phase transformation whereby the amorphous-crystalline interface rapidly propagates away from the crystal seed [49, 50].
extract the specific fluence of the laser shot, which in turn was used to estimate the melt depth [55]. All of our samples show no visible damage on the surface. The outputs from LIMP predict a corresponding laser fluence between 1.4 and 1.53 J cm\(^{-2}\) and a melt depth of 250 to 300 nm. We note also a dip at the laser fluence of 1.0 J cm\(^{-2}\) in the plot of melt duration versus laser fluence. Such a decrease in melt duration is anticipated when the melt front penetrates the amorphous-crystalline boundary and the resolidification back to the free surface leads to the formation of c-Si instead of poly-Si – the former generally has a higher thermal conductivity than the latter [56, 57].

![Graph showing PL intensity vs wavelength](image)

**Figure 6.2:** PL spectrum collected from the sample surface at \(\approx 10\) K. W and \(\text{Si}_{TO}\) indicating the luminescence from W-centres (1.018 eV) and silicon bandgap (1.097 eV), respectively.

Although sulfur is not a common n-type dopant in silicon due partly to its low solubility in silicon, the PLM process is capable of creating a supersaturated Si:S alloy. A subsequent 2-minute RTA at 275 °C was carried out and the sample was loaded into a cryostat holder. Fig. 6.2 shows a typical surface-emission PL spectrum of the sample excited by a 458-nm Ar\(^+\) laser line. Predominantly observed in the spectrum is a strong W-line luminescence peak at the wavelength of 1218 nm, which is equivalent to the photon energy of 1.081 eV, and its phonon replicas at longer wavelengths (lower photon energy). The intensity of the
line is substantially exceeding that of the intrinsic silicon bandgap luminescence ($\text{Si}_{\text{TO}}$). However, this does not represent a fair comparison in itself as the $\text{Si}_{\text{TO}}$ intensity can be affected by the ion implantation process, as demonstrated in Chapter 5. A measurement of $\text{Si}_{\text{TO}}$ from an unprocessed silicon wafer seems to allow a more realistic comparison but the difference in the pump radiation absorption between the two specimens due to the implantation-induced damage leaves the comparison arguable. This complexity prevents one from being able to determine the reliable internal quantum efficiency.

We emphasise here that the PLM is necessary for creating a shallow junction and removing heavy near-surface damage while preserving the $W$-line defects. This is considered to be a better approach than the low-dose direct implantation proposed in Chapter 5 since the surface disorder is completely annealed out and an $n^+$ layer (potentially suitable for electrical contacts) is simultaneously formed. It is expected that interstitial clusters will remain in the unmelted region below the original amorphous layer, as we indicate below.

Since the PLM process has recrystallised the damaged/amorphous layer, it is interesting and equally important (from a device fabrication perspective) to physically locate the origin of the $W$-centres that give rise to luminescence. Previous observations on the $W$-line luminescence formed by 80 keV Si-implantation and ruby laser annealing have suggested that the $W$-centres are produced at a depth beyond the amorphous layer, or to be specific, in the channeling tail of the implantation profile [58]. This speculation is supported by our etching study, in which the $W$-line intensity is close to zero in the high damage region up to the ion projected range ($R_p$). Figure 6.3 plots the $W$-line PL intensity depth profile of a 500 keV self-implanted silicon to fluences from $1 \times 10^{13}$ to $3 \times 10^{14} \text{ cm}^{-2}$. We note that a partly amorphous/heavily damaged layer in the region from the surface up to around $R_p$ is expected by fluences below $10^{14} \text{ cm}^{-2}$ with an otherwise continuous a-Si layer for the higher fluences. The results show that the peak of the profile (arrowed) appears beyond the $R_p$ and tends to move deeper into the substrate when the dose increases, as does the thickness of the highly damaged or amorphous layer. At this stage, it is clear that there is a window where the pulsed laser energy density is sufficient to melt through the heavily damaged or amorphous layer but not enough to eliminate the $W$-line defects below the melt depth (although they are exposed to temperatures above the dissolution threshold from about 500 to 1350 °C as determined by the LIMP simulation, but only for a very short period of a few nanoseconds). Other aspects of the $W$-line have already been given in Chapter 5.
Figure 6.3: Low-temperature PL measurements showing the W-line intensity as a function of etch depth. The W-line luminescence is observed following 500 keV Si-implantation and 275 °C anneal. The peak W-line luminescence is shown arrowed.

A device with ridge structure was formed by photolithography, reactive ion etching (RIE), and mechanical cleaving, with specific dimensions as illustrated in Fig. 6.4. To fabricate an electronic device, metallic contacts were deposited by thermal evaporation.
The top or front ohmic contact consists of a 5 nm thick Ti layer and a 100 nm Au layer, while the bottom or back contact is a layer of 1500-nm Al. A post-processing 2-minute RTA at 275 °C was performed to activate the W-line defect clusters as well as to improve the electrical contacts. Figure 6.5 shows the corresponding optical images for (a) the plan view and (b) cross-sectional view of the device.

**Figure 6.4:** A schematic cross-section of the first-generation LED fabricated on a bulk p-type silicon wafer (dimensions are not to scale).

**Figure 6.5:** Optical images illustrating (a) top view and (b) cross-sectional view of the device with ridge structure.

The quality of the electrical contacts was confirmed by a current-voltage (I-V) measurement. The I-V curves presented in Fig. 6.6 exhibit a good rectifying p-n junction behaviour (i.e. the current flows in one direction) regardless of the operating temperatures. However, an increase in the turn on voltage indicates a high resistance of the p-type substrate owing to the carrier freeze-out effect (majority of the boron acceptors are not
ionised at cryogenic temperatures).

![Current-voltage characteristics of the device at cryogenic (6 K), liquid nitrogen (80 K), and room (290 K) temperatures.](image)

Figure 6.6: Current-voltage characteristics of the device at cryogenic (6 K), liquid nitrogen (80 K), and room (290 K) temperatures.

EL measurements were performed at various temperatures. A typical edge emission of the fabricated device at a cryogenic temperature is shown in Fig. 6.7(a). The EL data show a strong W-line luminescence similar to that of the PL spectrum [see Fig. 6.2]. The inset of Fig. 6.7(a) illustrates the W-line output power measured at cryogenic temperature as a function of electrical current. The W-line intensity increases in proportion to the injected current up to about 4 mA and then decreases at a much larger current (not shown) possibly due to a heating effect. We estimate an external quantum efficiency (EQE) of the LED to be close to $10^{-6}$ or 0.0001% using Eq. 6.1,

$$
EQE = \frac{\Delta P}{\Delta I} \left( \frac{q \lambda}{hc} \right),
$$

(6.1)

where $P$ and $I$ denote the light emission power and the input current, respectively, $h$ is Planck's constant and is equal to $6.626 \times 10^{-34}$ J s, $c = 2.99 \times 10^8$ m s$^{-1}$ is the speed of light in vacuum, $q = 1.602 \times 10^{-19}$ C is the electronic charge, and $\lambda = 1218$ nm is the wavelength of the W-line. This low efficiency that renders the device impractical is attributed to several factors including but not limited to poor light collection associated with the lack of a
waveguide from the substrate side and the poor quality of the etched ridge and the cleaved facets.

More importantly, the $W$-line luminescence exhibits a strong temperature dependence, which in fact is a common characteristic of most optically active defects. The relative intensity of the $W$-line decreases with increasing measurement temperature and this is illustrated in Figs. 6.7 and 6.8. The $W$-line intensity is over three orders of magnitude
greater than the SiTO at 6 K, whereas at 80 K, the difference in intensity of both peaks is within an order of magnitude. The slight red shift of the W peak in Fig. 6.7(b) at higher temperature is probably due to the bandgap shrinkage. The temperature dependence plot of the W-line shown in Fig. 6.8 can be described by the following Arrhenius equation:

\[ I_w = A \cdot e^{-E_{\text{deact}}/k_B T}, \]  

(6.2)

where \( I_w \) is the W-line intensity, \( A \) is the pre-exponential factor and is temperature independent, \( k_B \) is the Boltzmann's constant, and \( T \) is the measurement temperature. By rearranging Eq. 6.2 into linear form,

\[ \ln(I_w) = -\frac{E_{\text{deact}}}{k_B T} + \ln(A), \]  

(6.3)

where the deactivation energy \( E_{\text{deact}} \) of \( \approx 70 \) meV can be determined from the slope of the fitting line. It should be noted that the W-line EL intensity drops rapidly above \( \approx 50 \) K due possibly to the competing non-radiative recombination processes (e.g. Auger recombination). This implies that a practical device operated at room temperature is not possible with this PL line under the present fabrication conditions. However, the
development of the W-line device provides a simple proof-of-concept example, which is the main purpose of this work.

6.3.2 2nd Generation Device

The second-generation device was designed on a commercial silicon-on-insulator (SOI) wafer consisting of a 2200 nm thick p-type (100) silicon device layer and a 1100 nm thick buried oxide layer to provide a potential optical cavity. In general, the processing conditions are very similar to those of the bulk silicon LED except that a p⁺ layer was introduced in front of the Si–SiO₂ interface by an additional process of 650 keV ¹¹B⁺ implantation to a fluence of 2×10¹⁵ cm⁻² in order to resolve the carrier freeze-out effect observed in the first-generation device operating at cryogenic temperature [see Fig. 6.6]. A subsequent 30-minute anneal at 950 °C was performed to remove most of the implantation damage as well as to activate the boron dopants (i.e. relocate boron atoms to substitutional sites in crystalline silicon). Nonetheless, some dislocation loops on {111} planes are expected at the end of ion range [59], and these may affect W-line luminescence. In fact, the redistribution of boron dopant at this annealing condition can be influenced by transient enhanced diffusion (TED) [60–62]. However, this effect is not anticipated to pose a critical impact on the formation of the W-centres which are located at much shallower depth.

Figure 6.9 shows the PL responses from the SOI device structures after pulse laser melting with energy densities of 0.8, 1.0, 1.2 and 1.4 J cm⁻². The inset plots the W peak intensity as a function of laser fluence. The W-line is clearly observed by 0.8 J cm⁻² and maximised by 1.0 J cm⁻² before decreasing with the laser fluence. This suggests that the implantation damage is partially annealed for the fluences below 1.0 J cm⁻², at which fluence a perfect recrystallisation is expected. A dramatic reduction of the W-line intensity at higher melting fluences is understood to arise from the fact that the laser melt front has extended into the active region, removing the W-line defects. The W-line formed in the top silicon layer of an SOI wafer almost disappears by 1.4 J cm⁻², in contrast to the bulk LED where this is the optimised laser fluence (for complete melting of the surface amorphous layer). One of the possible explanations for this is the lower thermal conductivity of the buried oxide layer that hinders heat dissipation, allowing the near-surface amorphous layer to melt at lower laser pulse energy. The presence of a peak centred at about 1149 nm denoted as Y indicates that the sample contains a significant amount of (implanted) boron [63]. This Y-line was first introduced in Chapter 5, and will be discussed further in
the following chapter.

Similar processing techniques used to fabricate the first generation device were applied here to create a ridge structure on an SOI specimen. The optically active layer (with concentrated point defect clusters) is located in a crystalline region beyond the melt depth and between the sulfur-supersaturated layer and boron-doped layer. The bottom
p-type contact of the bulk LED was replaced by side contacts to benefit from the borondoped p⁺ layer. The schematic diagram of the SOI device is illustrated in Fig. 6.10.

![Graph showing I-V characteristics of the SOI LED.](image)

**Figure 6.11**: *I-V characteristics of the SOI LED measured at 7 K indicating good rectifying behaviour and reasonably low turn-on voltage due to the presence of the conductive p⁺ layer. The inset shows a plot of the W-line emission power as a function of injected current.*

The SOI LED exhibits good rectifying I-V characteristics with a turn-on voltage of about 1.5 V and low series resistance at cryogenic temperature as shown in Fig. 6.11, where the inset is the measurement of the emission power as a function of electrical current. The output power sublinearly increases with increasing input current. The carrier freeze-out effect is mitigated by an introduction of the p⁺ layer. However, unexpectedly the device EQE is about $10^{-7}$, an order of magnitude lower than that of the previous generation device. This was initially very surprising because of the several improvements to the early device. There are several possible explanations for the decrease of the efficiency. Firstly, the misalignment of the top silicon layer and the silicon substrate, coupled with a reasonably thick buried oxide layer (2.2 µm) made cleaving problematic, leading to a poor optical quality of the cleaved facets. However, compared with the previous device structure this should not have given such a great reduction in efficiency. We note that the boron implantation is an extra step performed in processing for the second generation
(SOI) device. The effect of boron on W-line luminescence has not previously been reported but a few theoretical predictions [64–66] and experimental results [67] have indicated trapping of silicon interstitials by boron atoms, some of which are immobile boron interstitial clusters (BICs) [68]. In addition to that, the results shown in Sec. 5.4.2 do not rule out this boron effect. This casts a doubt on the formation of the W-line defects in the presence of a significant boron concentration.

6.4 Summary

In this chapter, we report an approach to sub-bandgap silicon light emission from point defects that combines ion implantation, pulsed laser melting (PLM), and rapid thermal annealing (RTA) to engineer a high concentration of point defect clusters that mediate radiative recombination at a wavelength of 1218 nm (W-line or II). Two generations of W-line LEDs were demonstrated in light of the results presented in the previous chapter. The first was fabricated on a bulk silicon wafer, with an estimated external quantum efficiency of $10^{-6}$. The second generation device was constructed on an SOI wafer with an additional boron-doped layer to improve the p-n junction characteristics particularly at cryogenic temperatures. The efficiency of this device was, however, found to be about an order of magnitude lower than that of the bulk LED. In order to propose a design for a future device, it is important to be able to identify the cause of the reduced efficiency. Based on published results, we speculate that boron may potentially influence the formation of the W-centres and this accounts for our low efficiency device. To examine this speculation, the effect of boron on the formation of interstitial-related luminescence centres will be systematically investigated in the following chapter.

References


Effect of Boron on Interstitial-Related Luminescence Centres

Photoluminescence measurements have been used to investigate the optically active defect clusters formed by silicon implantation and subsequent annealing at a temperature up to 900 °C as a function of background boron concentration. The effect of the boron density in p-type silicon wafers is found to produce deleterious effects on the luminescence of several optically active interstitial-related centres including the W-, X-, and R-centres, with emissions at 1218, 1193, and 1375 nm, respectively. Importantly, it is found that for a boron concentration of $3.2 \times 10^{18}$ cm$^{-3}$, these lines are no longer observable. This chapter provides further insight into the role of boron in the initial stages of interstitial cluster formation.
7.1 Introduction

As illustrated in Chapter 5, the process of ion implantation is commonly observed to create centres in silicon that give rise to several radiative transitions including $W$-line, $X$-line, $R$-line, and dislocation-related lines. The emission intensities are found to be enhanced by appropriate thermal annealing. For example, the $W$-line is maximised by an annealing temperature of around 275 °C, the $X$-line intensity is observed by 400 up to 525 °C, whereas the $R$-line appears after 700 °C for 30 minutes. At annealing temperatures above 850 °C, the dislocation-related lines are detected. The $W$-line is so sharp and intense that it was used to demonstrate a silicon LED in the previous chapter. However, as pointed out in Chapter 6, the device efficiency is quite low when boron implantation is used to form a $p^+$ layer. Boron is one of several factors that were speculated to be responsible for this low quantum efficiency. Indeed, there was some evidence from Chapter 5 that high boron concentrations may lower the $W$-line intensity.

Evidence for boron interstitial clusters (BICs) have been reported in the literature [1, 2], in which some clusters are predicted to be optically active [3]. Luminescence from boron-implanted silicon was detected in an early study, where the emission from a boron-related cluster called the $Y$-line (or $I_2$) was observed at 1149 nm (1.080 eV) in addition to the $W$-line [4]. Although Adey et al. [3] have speculated that the $Y$-centre competes with the $W$-centre, the effect of boron on the $W$-centre has not yet been systematically studied. In contrast to the large number of publications which discuss boron and silicon interstitial clustering as well as diffusion processes at elevated annealing temperatures, very little is known about the significance of boron on these processes especially in the early stages of cluster formation during thermal treatment. Where there have previously been indications of the effect of boron on interstitial clustering, the results have been from boron-implanted samples where the boron profile has been non-uniform, making definitive conclusions impossible. In this chapter, with a view to understanding the role of boron in the initial stages of interstitial clustering, the photoluminescence (PL) results from silicon-implanted silicon wafers with over three orders of magnitude difference in background boron doping are presented.

In this chapter, we adopt the nomenclature used by many authors including Pelaz et al. in Ref. [5] and Adey et al. in Ref. [6] to describe the BIC configuration. Specifically, a BIC is denoted as $B_nI_m$, where subscript $n$ and $m$ indicate the number of boron atoms and the total number of interstitials, respectively.
7.2 Preliminary experiments

Our observation in the previous two chapters of the reduction of the $W$-line intensity and the $W$-line LED efficiency after a boron implantation has led to the following preliminary experiments, where either phosphorus or boron is co-implanted with silicon followed by reactive ion etching (RIE) to remove the highly damaged regions. An SOI wafer with a 1500 nm low boron-doped silicon layer (14–22 $\Omega$ cm) on top of a 3000 nm SiO$_2$ layer was implanted with 600 keV $B^+$ to a fluence of $3 \times 10^{14}$ cm$^{-2}$ or 80 keV $P^-$ to a fluence of $4 \times 10^{14}$ cm$^{-2}$, all at room temperature. A subsequent anneal was performed on both samples at 950 °C for 30 minutes to create a $p^+$ region near the front interface of the BOX layer or an $n^+$ region near the surface. It should be noted that some extended defects may as well form at this stage. Figure 7.1 shows the distribution of boron and phosphorus after annealing as determined by a one-dimensional process simulation module (ISE-TCAD) [7].

![Figure 7.1: The B and P profiles calculated using ISE-TCAD for 600 keV $B^+$ ions implanted to a fluence of $3 \times 10^{14}$ cm$^{-2}$ (open circle) or 80 keV $P^-$ implanted to $4 \times 10^{14}$ cm$^{-2}$ (filled square), followed by a 30-minute anneal at 950 °C. The projected ranges of 100 keV and 300 keV Si ions are also labelled.](image)

Following the annealing, the samples were implanted with either 100 keV Si$^-$ to a fluence of $10^{13}$ cm$^{-2}$ or 300 keV Si$^+$ to fluences of $7 \times 10^{12}$, $1 \times 10^{13}$, or $4 \times 10^{13}$ cm$^{-2}$, and
then annealed at 275 °C for 3 minutes. The corresponding projected ranges \( R_p \) of Si ions are shown by vertical dashed lines in Fig. 7.1, where the \( W \)-line defects are expected to concentrate slightly beyond the ranges, as discussed in Sec. 5.4.2. PL measurements and RIE were alternately performed and the results are shown in Fig. 7.2. It is clear that the \( W \)-line luminescence is relatively weak or not observed at all in the boron-implanted samples. The intensity of the \( W \)-line increases when silicon is implanted (at 100 keV) away from the boron-doped region, as can be appreciated from the profile of 100 keV Si-implantation (bottom panel of Fig. 7.2). The 300 keV energy puts Si ions close to the region with high boron concentration, resulting in a very weak, if not absent, \( W \)-line intensity. On the other hand, phosphorus does not seem to inhibit the \( W \)-line luminescence. Indeed, the P-implantation has been reported to produce \( W \)-line luminescence, similar to that of Si-implantation [8].

In order to confirm this effect of boron on the \( W \)-line luminescence, another set of samples were prepared using (100) boron-doped silicon wafers with a resistivity of \( \leq 0.05 \) \( \Omega \) cm (corresponding to a boron concentration above \( 10^{17} \) B cm\(^{-3} \)). Si-implantation was carried out to a fluence of \( 10^{15} \) cm\(^{-2} \) at -196 °C (77 K), room-temperature, and 275 °C. Pulse laser melting (PLM) with a laser fluence of 1.3 to 1.5 J cm\(^{-2} \) and rapid thermal annealing (RTA) at 275 °C was used in an attempt to remove the radiation damage as well as to activate the \( W \)-line luminescence. However, no \( W \)-signal is detected from any of these highly boron-doped samples, in agreement with the above results. Such a finding is not conclusive but has led to a systematic study in this chapter on the luminescence from interstitial-related centres in the presence of boron impurity.

### 7.3 Experimental procedures

Our experiments were performed on three commercially available CZ-grown boron-doped p-type (100) silicon wafers with different resistivities of 14 \( \Omega \) cm, 0.18 \( \Omega \) cm, and 0.018 \( \Omega \) cm. These values correspond to boron doping concentrations of \( 9.4\times10^{14} \) cm\(^{-3} \), \( 1.1\times10^{17} \) cm\(^{-3} \), and \( 3.2\times10^{18} \) cm\(^{-3} \), respectively, as determined by capacitance-voltage (CV) and four-point-probe measurements on unprocessed wafers. Two n-type phosphorus-doped (100) silicon wafers with resistivities of 2.92 \( \Omega \) cm (corresponding to a concentration of \( 1.6\times10^{15} \) P cm\(^{-3} \)) and 0.85 \( \Omega \) cm (\( 5.5\times10^{15} \) P cm\(^{-3} \)) were also used to prepare control samples. The distribution of the dopant is uniform throughout the sample in contrast to the boron or phosphorus implanted and annealed profiles. The samples are also free from
Figure 7.2: The W-line PL intensity as a function of depth in the SOI samples co-implanted with 100 keV or 300 keV Si ions to various fluences from $7 \times 10^{12}$ to $4 \times 10^{13}$ cm$^{-2}$ and either 600 keV, $3 \times 10^{14}$ cm$^{-2}$ B$^+$ (open circle) or 80 keV, $4 \times 10^{14}$ cm$^{-2}$ P$^-$ (filled square). The filled triangles note the W-line intensity from samples implanted with Si only. The vertical dashed lines indicate the $R_p$ of Si ions as determined by SRIM program.
the complicating effects of end-of-range (EOR) defects created by boron implantation.

All the wafers were irradiated at room temperature with 300 keV Si\(^+\) ions to various fluences of up to \(3 \times 10^{15}\) cm\(^{-2}\) and an average flux of around \(5 \times 10^{11}\) cm\(^{-2}\) s\(^{-1}\). It should be noted that the amorphisation threshold in silicon is around \(10^{14}\) Si cm\(^{-2}\). During the implant, the samples were tilted by 7° from normal incidence of the ion beam to minimise channeling. Following the implantation, an RTA was performed in an Ar ambient at temperatures of 275 °C, 400 °C, or 525 °C for 2 minutes, or otherwise an anneal was carried out at temperatures of 700 °C for 40 minutes or 900 °C for 30 minutes in a conventional furnace tube. Photoluminescence was thereafter carried out on all the specimens in a cryostat chamber cooled to 13 K, where they were optically excited by a 532-nm line from a solid state laser with an excitation power of \(\approx 15\) mW. The PL spectra were collected and analysed by a SpectraPro-2500i triple grating monochromator equipped with a temperature-controlled InGaAs infrared photodetector [see Sec. 2.2.3.1 for details].

### 7.4 Results and discussion

Figure 7.3 illustrates the PL spectra recorded in the wavelength range of 1100 to 1600 nm at 13 K for \(10^{12}\) cm\(^{-2}\) silicon-implanted samples with the three different boron doping concentrations after a 2-minute RTA at 275 °C. Clearly shown in the PL spectra from both (L) low (9.4\(\times\)10\(^{14}\) B cm\(^{-3}\)) and (M) intermediate (1.1\(\times\)10\(^{17}\) B cm\(^{-3}\)) boron concentration specimens is a strong \(W\)-line peak at 1218 nm (1.018 eV) and its phonon replicas at longer wavelengths (lower photon energies). For the lowest boron concentration, the \(W\)-line luminescence is observed to be brightest, with relatively weak silicon band-edge luminescence (Si\(_{TO}\)) at 1129 nm (1.098 eV). When the background boron concentration is about two orders of magnitude higher, the \(W\)-line intensity drops significantly and the two new luminescence peaks at 1135 nm (B\(_{TO}\)) and 1148 nm (Y or l2) are clearly observed. The B\(_{TO}\) peak (readily observed in the intermediate boron concentration sample) is the transverse optical (TO) phonon of the boron-bound exciton transition [9] and the shoulder at \(\approx 1130\) nm (in the spectrum (M)) is presumed to be Si\(_{TO}\). This is also true for all other silicon doses, which are plotted in the inset of this figure. The inset also shows that the \(W\)-line intensity in boron-doped silicon increases with dose up to \(10^{12}\) cm\(^{-2}\), consistent with previous studies [10]. This optimal fluence condition also appears to be independent of the background boron concentration. A different optimal condition is established for phosphorus-doped samples, in which the \(W\)-line intensity does not decrease when
Figure 7.3: PL spectra from p-type silicon wafers with different boron concentrations (L = low concentration $= 9.4 \times 10^{14}$ cm$^{-2}$, M = intermediate concentration $= 1.1 \times 10^{17}$ cm$^{-2}$, and H = high concentration $= 3.2 \times 10^{18}$ cm$^{-2}$) after 300 keV Si implantation to a dose of $10^{12}$ cm$^{-2}$ and a subsequent RTA at 275 ºC for 2 minutes. Scaling factor is given for each spectrum. Si$_{TO}$, B$_{TO}$, and Y denote the luminescence peaks from the free exciton radiative recombination associated with the TO phonon or silicon band-edge intrinsic emission, the TO phonon replica of the boron-bound exciton, and BICs, respectively. The inset shows the PL intensity of the W-line in phosphorus-doped (dot-centred triangle and star) and boron-doped (filled square and open circle) samples for different silicon fluences, where the lines are guides for the eyes.

the implantation dose is reduced from $10^{12}$ to $10^{11}$ cm$^{-2}$ but from $10^{11}$ to $10^{10}$ cm$^{-2}$. Surprisingly, it also seems that slightly increasing the phosphorus concentration results in a stronger W-line. For higher Si fluences, the W-line is quenched as the probability of non-radiative recombination channels becomes more likely with an increasing concentration of irradiation damage, as explained in Chapter 5 and Ref. [10]. The W-line luminescence is not observed in the spectrum (H) of the high boron concentration ($3.2 \times 10^{18}$ B cm$^{-3}$) wafer irrespective of Si fluence.

Now let's turn our attention to the Y-line, which has previously been observed from a boron-implanted silicon sample [4]. Further experiments using boron isotopes have attributed the luminescence Y-centre to a BIC with trigonal symmetry [11]. Theoretical calculations of this centre have identified in accordance with the experimental results that
it is a $\text{B}_2\text{I}_3^+$ cluster. As mentioned earlier in Chapter 5, this tri-interstitial cluster contains two boron atoms and one silicon interstitial [Fig. 5.4(b)] and is similar in structure to the one proposed for the $W$-line defect [Fig. 5.4](a) except that boron replaces two of the silicon interstitials [3].

![Photon energy vs. PL intensity graph](image)

**Figure 7.4:** PL spectra with scaling factors of boron-doped p-type silicon wafers implanted with 300 keV $\text{Si}^+$ to a dose of $10^{12}$ cm$^{-2}$ and subsequently annealed at 400 °C for 2 minutes. The inset is a high resolution PL spectrum showing a weak $Y$-line luminescence and a TO phonon-assisted peak observed in a wafer with the highest boron concentration (lowest resistivity).

After a 2-minute RTA at 400 °C, the $W$-line and its replicas are still observed to dominate the spectrum of the low boron concentration (L) wafer as shown in figure 7.4. In addition to the $W$-line and $\text{Si}_{\text{TO}}$, a relatively weak $X$ peak is clearly seen at 1193 nm. Similar to the samples annealed at 275 °C, the $W$-line intensity is observed to drop with increasing boron concentration. On the other hand, the $Y$-line intensity initially increases to a maximum for boron concentration of about $1.1 \times 10^{17}$ cm$^{-3}$. The sharpness of the $Y$-line indicates that it is relatively unperturbed and electronically isolated from the boron doping band. For the highest boron concentration of $3.2 \times 10^{18}$ cm$^{-3}$, the $Y$-line with a lower intensity (compared to that from the intermediate boron concentration) can be observed in the PL spectrum of the wafer. A corresponding higher resolution PL of (H)
is shown in the inset. The broad peak at around 1175 nm is presumed to arise from a TO phonon-assisted transition, indicating the bandgap shrinkage in highly boron-doped silicon [12]. This is also consistent with the optical absorption study of heavily doped silicon, in which the bandgap of silicon decreases as the doping level increases above about $3 \times 10^{18}$ B cm$^{-3}$ [13].

![Photon energy (eV)](image)

**Figure 7.5:** PL spectra of the samples containing $1.1 \times 10^{17}$ B cm$^{-3}$ implanted with 300 keV Si$^+$ to various fluences and annealed at 400 °C.

The results from annealing of the samples with intermediate boron concentration ($1.1 \times 10^{17}$ B cm$^{-3}$) at 400 °C are noteworthy. Figure 7.5 shows the PL spectra of those silicon samples self-implanted to fluences ranging from $10^{10}$ to $10^{14}$ cm$^{-2}$. Overall, it is clear that all the PL spectra are similar in shape but the peak intensities vary with silicon dose. The $W$-line intensity is observed to be relatively weak, especially for implantation fluences at and below $10^{11}$ cm$^{-2}$, where the line seems to be overwhelmed by another broad luminescence band. Similarly, the $X$-line cannot be clearly identified for the samples with low silicon fluence, in contrast to the $Y$-line, which appears to be strong for a fluence as low as $10^{10}$ cm$^{-2}$. This may be explained by the fact that the atomic structure of the
Y-centre is expected to be comprised of only one silicon interstitial atom (and two boron atoms), while the W- and X-centres are multi-silicon-interstitial clusters.

Figure 7.6: PL spectra for boron-doped p-type silicon wafers implanted with 300 keV Si⁺ to a dose of 10^{13} cm⁻² followed by an anneal at 525 °C for 2 minutes. The inset plots (a) the X-line intensity and (b) the intensity of the broad luminescence band as a function of silicon dose for the samples with low (filled square) and intermediate (open circle) boron concentration.

Figure 7.6 shows the PL spectra measured at 13 K from the different p-type silicon wafers after Si-irradiation and thermal annealing at 525 °C for 2 minutes in Ar. For the low boron concentration case (spectrum L), the W and Y peaks are annealed out by 525 °C as can be expected from the results of Chapter 5 and previous published work [14], but the more thermally stable X peak remains at 1193 nm (1.040 eV) with its transverse acoustic (TA) phonon replica on an intense broad luminescence band. This broadband luminescence is the brightest feature observed for this spectrum, extending from approximately 1220 nm to over 1600 nm. As indicated in Chapter 5, a similar broad spectral band was observed and has previously been attributed to strain surrounding interstitial defect clusters after silicon implantation and annealing at 600 °C for 4 hours [15]. The features appearing around 1375 nm are known to result from atmospheric
water vapour absorption [16, 17].

The \( B_{\text{TO}} \) peak intensity becomes strongest for the intermediate boron concentration sample. Like the \( W \)-line, the intensities of the \( X \)-line and this broadband, if observable, decrease with increasing boron concentration regardless of Si fluence [see insets of Fig. 7.6]. Therefore, we believe that the observed broadband may arise from localised strain in the early stages of extended defect formation and/or the presence of large clusters involving silicon interstitials [17, 18]. The sample with the highest boron doping concentration \( (3.2 \times 10^{18} \text{ cm}^{-3}) \) has no interesting features apart from a very weak TO phonon-assisted band.

![Image of a graph showing PL spectra for boron-doped p-type silicon wafers implanted with 300 keV Si\(^+\) to a dose of \( 5 \times 10^{15} \text{ cm}^{-2} \) followed by an anneal at 700 °C for 40 minutes. (L), (M), and (H) denote the low, intermediate, and high boron concentration, respectively.](image)

Figure 7.7: PL spectra for boron-doped p-type silicon wafers implanted with 300 keV Si\(^+\) to a dose of \( 5 \times 10^{15} \text{ cm}^{-2} \) followed by an anneal at 700 °C for 40 minutes. (L), (M), and (H) denote the low, intermediate, and high boron concentration, respectively.

Our observations of the boron doping effect on defect luminescence need to be interpreted with care. Two possible contributing factors are: (i) competition between formation of optically active silicon-interstitial clusters and BICs and (ii) a process in which the silicon-interstitial clusters are formed but the presence of BICs promotes a
non-radiative recombination pathway that acts to quench the luminescence from the W- and X-centers. Silicon interstitials are known to interact strongly with boron as in the transient enhanced diffusion (TED) process [19]. It is, therefore, rational to expect that more interstitials initially bound in small clusters become trapped in boron clusters with increasing boron concentration. Phosphorus, on the other hand, is not known to provide an efficient trap for silicon interstitials [20]. This explains the observation shown in the inset of Fig. 7.3 in which the W-line formed by $10^{11}$ Si cm$^{-2}$ is brightest in the case of low phosphorus-doped silicon but a $10^{12}$ Si cm$^{-2}$ dose provides the brightest W-line in the case of the low boron-doped sample. The effect is ambiguous at higher silicon fluences when the radiation damage dominates the optical processes. This behaviour is also consistent with an earlier study on B–Si interstitial interactions, where it was demonstrated by transmission electron microscopy (TEM) that a high concentration of boron ($\gtrsim 10^{19}$ cm$^{-3}$) was sufficient to prevent the formation of {311} rod-like defects (RLDs) [21]. An additional study has discovered that the {311} RLDs also act as interstitial sources during the TED process [22]. These results clearly show that the silicon interstitials can become tightly bound in boron-rich clusters which prevent silicon-interstitial related {311} RLDs from forming as well as suppressing the migration of silicon interstitials [2]. The presence of {311} defects has been directly connected to the R-line luminescence, as mentioned earlier in Chapter 5.

In the current study, we annealed Si-implanted samples containing different boron content at 700 °C to favour R-line ({311} defects) emission as in Chapter 5. A comparison of the PL spectra presented in Fig. 7.7 is consistent with the suppression of the R-line or {311} defect formation in the presence of appreciable boron due to boron-interstitial clustering. Such behaviour is also consistent with predictions from recent modelling studies that self-interstitials can be bound in immobile silicon-rich BICs in the initial stages of annealing [5, 23]. Such clusters release silicon interstitials at later annealing stages, resulting in small stable BICs or precipitates with high boron-to-silicon ratio ($B_nI_m$, $n = 3$ or 4 and $m = 0$ or 1). The W-centre in our case is formed in the early annealing stages with low annealing temperature and has been postulated to be one of the building blocks of these RLDs during higher temperature annealing [24]. Thus, it is not surprising to observe in this work that the W-line is completely suppressed with a boron concentration of $3.2 \times 10^{18}$ cm$^{-3}$, which is slightly lower than the concentration required to inhibit the formation of the RLDs in the higher annealing temperature regime. The absence of the R-line at a boron concentration below $10^{19}$ cm$^{-3}$ seems to be inconsistent with the presence
of the \{311\} defects reported in a previous TEM study [21]. The inconsistency may be attributable, in addition to the variation in experimental conditions, to the complexity of the optical processes that involve radiative and non-radiative components. The efficiency of luminescent centres in the presence of enhanced absorption within radiation-induced damage regions is also anticipated to influence the observation. Indeed, we have suggested in Chapter 5 a relationship between the R-line intensity and both the size and density of the \{311\} RLDs. Alternatively, it may be that, if boron is incorporated into \{311\} interstitial clusters, they are rendered non-radiative.

![Figure 7.8: PL spectra for boron-doped p-type silicon wafers implanted with 300 keV Si\(^+\) to a dose of 3\(\times\)10\(^{15}\) cm\(^{-2}\) followed by an anneal at 900 °C for 30 minutes.](image)

Figure 7.8 shows the PL spectrum for silicon samples with different background boron levels implanted with 300 keV Si\(^+\) to a fluence of 3\(\times\)10\(^{15}\) cm\(^{-2}\), and annealed at 900 °C for 30 minutes to form the dislocation-related D1 line. As demonstrated earlier with low boron-doped p-type silicon in Chapter 5, the D1 line is usually observed following a high silicon dose and a high temperature annealing. In this case, an increasing boron concentration is observed to reduce the D1 intensity, similar to other lines that originate
from interstitial-related centres. This result does not contradict the prediction that the D1 and D2 centres arise from point defects that are trapped within the dislocation cores or between the dislocations [25–27]. Here, the effect of boron trapping in dislocation regions seems to render the centres non-radiative in a similar way to other interstitial-related defects. Nevertheless, the situation may be more complex if, for example, the luminescence process from the dislocation-related centres is not due only to the trapping of point defects and/or is perturbed by boron decoration on dislocation loops.

Given the evidence outlined above, we believe that competition between the formation of optically active silicon-interstitial clusters and BICs is the main reason behind the dramatic reduction in the W-line intensity and the intensity of other interstitial-related luminescence centres with increasing boron concentration. Indeed, it is highly possible that the formation of the small interstitial-related defect clusters giving rise to the W-line, X-line, and broad luminescence band is suppressed by the presence of boron in a similar manner as occurred to the \{311\} RLDs. The nature of the boron-related centres and operative radiative/non-radiative de-excitation pathways are not well understood. In the samples with the lower boron concentrations, the suppression of the W-line is accompanied by an increase in the Y-line intensity. However, at the highest boron concentration, the Y-line intensity is also suppressed. In fact, all interstitial-related luminescence is suppressed across the entire spectrum in the high boron concentration case. This observation, however, does not eliminate the possibility that there may also be other quenching mechanisms at play.

### 7.5 Summary

In conclusion, we have shown that boron generally has a detrimental effect on the PL intensity of several interstitial-related luminescence centres including W- and X-centres. For the sample containing the highest boron concentration studied here, the luminescence from these centres is completely suppressed. This is attributed predominantly to the active participation of silicon interstitials in the formation of BICs. A high boron concentration, therefore, results in a higher concentration of silicon interstitials locked up in BICs and thus unavailable for the formation of optically active (purely-silicon) interstitial clusters. A similar observation whereby boron inhibits the formation of the \{311\} RLDs in a higher Si fluence and higher annealing temperature regime was discussed, as was the effect of boron on D-band luminescence.
References


Summary
8.1 Concluding Remarks

In exploring novel methods based on ion implantation for producing efficient light emission from silicon, this thesis has examined defects and their interactions with other defects and impurities from various aspects, covering structural to optical properties. We have shown in Chapter 3 that H-implantation and a successive thermal anneal can be used to form an array of cavities, whose size distribution can be tightly controlled. Such cavities are strong sinks for Au impurities introduced to the near-surface region by implantation. This results in a buried band of Au precipitates with a reasonably narrow size distribution in silicon. However, the same process is not capable of producing a band of cavities in SiO₂. Subsequent wet oxidation of the Au precipitate-containing silicon structure was found to segregate the Au particles behind the oxidising interface. By forming the Au precipitates within the top silicon layer of a silicon-on-insulator (SOI) wafer, the Au nanoparticles are incorporated in SiO₂ (after oxidation) at a depth corresponding to the original front interface of the buried oxide layer. The relocation of the Au precipitates and the increase in their size as observed in the final structure suggest that they have undergone a severe structural transformation and Ostwald ripening during the oxidation.

The evolution of the Au precipitates in an oxidising ambient is further examined in Chapter 4 to provide more insight into the behaviour of Au precipitates during oxidation of silicon. Sequential oxidation experiments have revealed several intriguing phenomena including Au-enhanced oxidation, dissolution and reprecipitation of Au precipitates initially formed at the cavities or at the surface, and preferential wetting of Au on the oxide interfaces. Based on previous experimental observations and theoretical models, our results can be explained by diffusion and interactions of oxidation-injected silicon interstitials. The photoluminescence (PL) measurements of these samples indicated several defect-related luminescence peaks, where the most intense line at 1218 nm is detected at cryogenic temperature.

The observation of defect-related luminescence in Chapter 4 has steered our focus towards the optically active (defect) luminescence centres. In Chapter 5, we performed a scoping study of Si-implanted and annealed silicon samples using low-temperature PL to map out the luminescence signatures. Low-dose implantation and low-temperature annealing was found to produce small point defect clusters that give rise to the so-called W⁻ and X-lines in PL spectra. The luminescence signals evolve with increasing Si doses and annealing conditions. Formation of extended defects ([311] rod-like defects (RLDs))
as observed by TEM results in strong luminescence at intermediate implantation doses and annealing temperatures (and times). For the highest dose (≥ 10^{15} \text{ cm}^{-2}) and highest annealing temperature (900 °C), dislocation-related luminescence bands are observed.

In Chapter 6, we explored an optical device application based on strong 'W-line' luminescence reported in Chapter 5. We presented results on a novel approach to sub-bandgap silicon light emission from point defects. A combination of ion implantation, pulsed laser melting (PLM), and rapid thermal annealing (RTA) has been used to engineer a high concentration of point defect clusters that mediate radiative recombination at a wavelength of 1218 nm. Working sub-bandgap light emitting diodes (LEDs) were fabricated but exhibited a relatively low quantum efficiency. Several factors were proposed to be responsible for such a poor diode performance. The main one is ascribed to be the effect from boron dopant atoms, which were specially implanted to improve the p-n junction characteristics at low temperature.

Chapter 7 examined the effect of boron in detail. Experiments using p-type silicon wafers with various boron concentrations, as well as n-type phosphorus-doped wafers, have allowed us to suggest that the boron has a deleterious effect on the silicon interstitial-related luminescence by forming boron-interstitial clusters (BICs) in competition with the optically active silicon-interstitial clusters. These results are fundamentally important for the design and development of any interstitial-based silicon optoelectronic devices.

### 8.2 Future Directions

Based on the observations outlined in this thesis, further study could be continued in both areas studied: (i) nanoparticles embedded in SiO₂ and (ii) defect-mediated silicon light emission. Suggestions for further work are provided in the following subsections.

#### 8.2.1 Nanoparticles in SiO₂

Our results have shown that Au particles can be encapsulated within an SiO₂ layer following a wet oxidation. The structural evolution (i.e. change in size and shape) of Au nanoparticles in silicon as oxidation progresses has been studied by RBS and TEM. We have further shown that inhibiting (or removing) silicon-interstitials from the oxidation process can reduce the size distribution of Au in SiO₂. For applications, this needs to be optimised and we suggest a series of optimisation experiments to produce (hopefully) a very narrow size distribution of Au in SiO₂. Nevertheless, the main application of these Au
precipitates (e.g. plasmonic devices) requires optical characterisation. Optical absorption measurements and modelling based on Gan's theory [1], for instance, are recommended to be carried out. In our case, the analysis and interpretation of the absorption spectra should necessarily take into account the constructive and destructive interference resulting from reflection at the internal surface. Such experiments are essential for demonstrating applications.

Other impurity species may be used instead of Au to obtain a desired nanoparticle properties. For example, the formation of direct bandgap ZnO nanocrystals in a dielectric SiO$_2$ matrix is expected to give rise to a direct optical transition at an energy of around 3.35 eV [2]. According to quantum confinement theory, the emission wavelength can be tuned by tailoring the size of ZnO nanocrystals. Hence, a series of experiments including direct implantation of ZnO into silicon and SiO$_2$ or trapping of Zn at a cavity band in silicon and subsequently oxidising to obtain ZnO nanoparticles in SiO$_2$, would be illuminating.

### 8.2.2 Defect-mediated silicon light emission

![Diagram of a lateral p-i-n silicon LED](image)

**Figure 8.1:** Schematic illustration of a lateral p-i-n silicon LED fabricated on an SOI wafer. Dotted arrows indicate the light emitting directions.

The reduction of silicon interstitial-related luminescence intensity in the presence of boron is believed to be due to the competing formation of optically active silicon-interstitial clusters and BICs. This information is important for the development of interstitial-based silicon devices. Indeed, the next generation of a W-line Si LED should be designed in such a way that the boron-doped p$^+$ layer is completely separated from
the active layer. Figure 8.1 illustrates a simple lateral p-i-n silicon LED inspired by the
design of a photodiode reported in Ref. [3]. With this lateral structure, any B- and P-
implantation-induced residual damage or dislocation loops that potentially reduce the W-
line luminescence intensity will also be isolated from the active region. Indeed, there are
several other prospects that need further work, with the severe thermal quenching being
one of the most critical challenges. The solution to this requires a deep understanding
of the luminescent defects and their energy levels as a function of temperature. Exciton
generation and recombination behaviour at the optically active centres needs to be
controlled and ultimately overcome if a room temperature W-line device is to be realised.

Fundamental studies on interstitial clustering and evolution into extended defects
on annealing can also be carried out in parallel. The effects of dopants, other
impurities, and defects on the formation of silicon-interstitial based defects and their
luminescent properties needs to be examined. Here, the dopants may be incorporated
at a supersaturated level using high energy ion implantation and solid phase epitaxial
re-growth (SPEG) [4], thus keeping the end-of-range dislocation loops (and hence their
effects) well away from the near-surface region, where a high optically active defect
concentration can be introduced, may be one approach. These results should not only
benefit the understanding of interstitial-based defects and their luminescent properties,
but the impact they have, may lead to new designs of interstitial-mediated optoelectronic
silicon-based devices operating at room temperature.

References


