Experimental Study of the Behavior of Point Defects and Dopants in Silicon using Isotope Superlattices

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## Abstract

Advancement of silicon (Si) complementary metal-oxide-semiconductor (CMOS) device performance has relied on scaling. It has progressed so much that the present accuracy requirement has reached less than 1 nm for the spatial control of source/drain regions. A typical fabrication process of source/drain regions is composed of ion implantation of dopants, followed by annealing to electrically activate the implanted species. In the previous generation of micrometer CMOS, separation distances between the source, gate, and drain were large enough to neglect the effect of defects coming from one region to the others for modeling of the entire fabrication process. However, the separation distances in today's nano-CMOS are so small that defect formation, migration, and their chemical reactions in a particular region can significantly affect the formation process of the other regions. Understanding the behavior of host Si atoms is becoming increasingly important for the precise control of both dopant diffusion and activation.

This study reports the nanoscale investigation of host Si behavior related closely to the control of the source/drain fabrication processes in advanced CMOS. In particular, 1) determination of Si self-diffusivity below 875 °C and identification of the microscopic picture of self-diffusion, 2) determination of Si displacement lengths induced by collision with ion-implanted dopants and criteria for amorphization by implantation, and 3) evaluation of time-dependent dopant and Si self-diffusion enhancement by excess Si point defects created by ion implantation (transient enhanced diffusion) were performed experimentally. Moreover, complete numerical modeling of each process has been achieved for process simulation.

Investigations of the behavior of Si atoms in the matrix of Si crystals have been extremely challenging. In this study, successful growth of isotope superlattices (SLs), composed of alternating atomic layers of different stable isotopes (<sup>28</sup>Si and <sup>30</sup>Si), has led to simultaneous observations of the behavior of dopants and Si atoms after ion implantation and annealing using the different masses of Si isotopes as markers. In Study 1), Si self-diffusion was induced by annealing of the isotope SLs, and the resulting smearing of the mass distribution was detected as changes in the phonon frequencies by Raman spectroscopy. Si self-diffusivities for 700-900 °C were determined precisely and it was found that the vacancy dominates self-diffusion in this temperature range. In Study 2), Si displacements were evaluated quantitatively by secondary ion mass spectrometry (SIMS) probing the smearing of the periodic depth profile of <sup>30</sup>Si in the isotope SLs induced by ion implantation. Further analysis involving cross-sectional transmission electron microscopy revealed that amorphization occurred when our displacement parameter exceeded  $\sim 0.5$  nm. This critical value was found to be independent of the implanted ion, energy, and dose. In Study 3), transient enhanced diffusion of boron and <sup>30</sup>Si in boron-implanted isotope SLs were observed by SIMS. Their time-dependent depth profiles were reproduced successfully by numerically solving rigorous diffusion and chemical reaction models that were developed.

Some parts of the above findings have already been implemented in commercial simulators used by semiconductor industries. The importance of understanding Si nanoscience is expected to grow along with the further advancement of Si electronics.

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# Chapter 1

# Introduction

### **1.1 CMOS Technology**

Technology of the complementary metal-oxide-semiconductor (CMOS) field effect transistors (FETs) has advanced rapidly in the past half century. The semiconductor industry is expected to experience exponential growth in the scaling-down of the CMOS devices beyond the 22 nm generation, in accordance to the long-term guiding principles known as Moore's law [ITRS07]. Such miniaturization of the silicon (Si)-based CMOS devices will enable even higher integration and performance.

MOS structure is composed mainly of the source, gate, and drain regions. By controlling the gate voltage, the carrier flow between the source and drain can be switched on and off. The region between the source and the drain is known as the channel region, and its length is called the channel length or gate length. Figure 1.1 shows cross-sectional transmission electron micrographs of micro- and nano-size MOSFET devices [Packan00, Furuyama06]. Today, 65 nm-size CMOS devices are produced. As miniaturization progresses, the number of Si atoms along the MOSFET channel becomes countable, and therefore fluctuations in transistor characteristics due to small differences in the dopant distribution and/or channel length becomes problematic. Figure 1.2 shows a trend of the product half-pitch, physical gate length, source/drain ex-



**Figure 1.1** Cross-sectional transmission electron micrographs of (a) micro-size MOSFET [Packan00] and (b) nano-size MOSFET [Furuyama06]. Source/drain extension regions in (b) are formed to control the short-channel effects.



**Figure 1.2** Scaling of the product half-pitch, physical gate length, drain extension depth, and transistor intrinsic speed [ITRS07].

tension depth, and switching speed of MOSFETs in production. According to the ITRS 2007, the physical gate length will reach 14 nm by 2012. By the same year, a switching speed of 2500 GHz is expected to be achieved. The development of an ultra-thin body fully depleted SOI and double-gate MOSFETs is expected by 2010–2011.

### 1.2 Challenges in Formation of the Source/Drain Regions in Advanced CMOS

Formation of source/drain regions is currently realized by using ion implantation of impurities: arsenic (As) for N-MOS and boron (B) for P-MOS. According to the ITRS 2007, source/drain extension regions [shown in Fig. 1.1 (b)] to attain progressively shallower junction depths for CMOS transistors are needed for control of the shortchannel effects. The extension depth is expected to be scaling down as shown in Fig. 1.2. Concomitantly, the sheet resistance-junction depth product, doping abruptness at the extension-channel junction, and extension-gate overlap should be optimized. The realization of ultra-shallow source/drain extension junction depths involves not only the development of new and enhanced methods for implanting doping species, but also the development of thermal activation processes that have an extremely small thermal budget. In the micro-size transistor era [Fig. 1.1 (a)], the interaction between the source/drain and gate regions was negligibly small since these regions were sufficiently separated from each other. Therefore, process simulators assuming thermal-equilibrium point defect concentrations are sufficient to model the formation process of the source and drain regions. In nano-size transistors [Fig. 1.1 (b)], however, the migration of defects generated, for example, at the insulator-gate interfaces to the source and drain regions can significantly affect the resulting shape of the drain and source regions. Such interactions and their chemical reactions need to be

understood and considered in order to accurately predict the behavior of dopants.

Further miniaturizations of the source and drain regions require confinement of a higher concentration of electrically active dopants in shallower regions [Plummer00]. Ion implantation has been widely used for the doping of the source/drain regions in the production of the Si-based integrated circuits for the past 20 years. In this process, dopant ions are accelerated to several keV of energy and implanted into a Si wafer. The implantation provides a very precise method to introduce a specific dose or number of dopants into Si wafer because the electrical charge of the ions allows them to be counted by a Faraday cup. The electrical measurements are very precise, therefore, a number of dopant atoms ranging between  $1 \times 10^{12}$  and  $1 \times 10^{16}$  cm<sup>-2</sup> are routinely introduced successfully during the fabrication of MOS devices. High-dose implantation minimizes the parasitic resistances associated with the source/drain regions in the CMOS devices. However, the implantation process also creates lattice damages ranging from an accumulation of point defects, dislocations, stacking faults, to amorphization. Because the maximum electrical activation of implanted dopants can be achieved only when they replace Si host lattices substitutionally and other damages are removed, it is becoming extremely important to establish experimental methods to characterize the effect of implantations on the Si host lattices. The conventional crosssectional transmission electron microscope (XTEM), double crystal X-ray diffractometry (DCXD), and Rutherford backscattering spectrometry channeling (RBS-C) allow for the estimation of the fraction of Si atoms displaced from the substitutional sites in the single-crystalline region [Lulli00]. However, characterization of the length of the displacement of recoiled Si atoms from their original positions is impossible, even in single crystal structures, and all of the above mentioned methods become useless when the implanted region becomes amorphous. The present thesis reports the development of a method to realize such an evaluation.

Electrical activation of the implanted dopants is achieved routinely by postimplantation thermal treatments. Optimization of the annealing process changes from one device to another. However, the source/drain regions must be confined in nanoscale regions, *i.e.*, annealing is performed either at high temperature (> 1000 °C) for a very short time (< 1 s), or low temperature (< 800  $^{\circ}$ C) for a longer time (a few minutes). It is also important to note that a variety of thermal treatments are performed even after completion of the source/drain regions, since gate insulators and other components must be fabricated. Therefore, understanding the dopant diffusion at a relatively low temperature is very important. One of the important factors that affect dopant diffusion is self-diffusion of Si, since dopant diffusion is always mediated by the Si point defects. While Si self-diffusion has been investigated at high temperatures (> 850 °C), the determination of self-diffusivity at low temperatures (< 850 °C) is difficult due to a very short diffusion length (a few nano-meters) for such temperatures that are difficult to be measured by existing methods. The present thesis describes successful measurements of such short diffusion lengths. Precise understanding of the Si self-diffusion under equilibrium conditions allows for accurate understanding of dopant diffusion under equilibrium conditions. The following step is understanding of dopant diffusion in imperfect lattices, e.g., dopant diffusion in the damaged region after implantation. It is well known that dopant diffusion in the very initial stage of thermal annealing (even at temperatures  $\sim 550$  °C [Cowern90]) is significantly enhanced with respect to the equilibrium condition. This phenomenon, known as transient enhanced diffusion (TED), is caused by enhancements of dopant diffusion mediated by Si self-interstitials generated by implantation significantly beyond their equilibrium concentrations. More precisely, Si clusters, such as {311} defects, that are formed by implantation and post-implantation annealing, are dissolved gradually to provide supersaturated Si self-interstitials that in turn enhance diffusion of dopants. Although such phenomena have been studied for many years, the precise behavior of the dopants and Si host atoms in shallow regions is still unknown. The present work successfully probes TED in detail and provides a model that accurately reproduces the time dependence of dopant diffusion in post-implantation annealing.

After all, complete understanding of the source/drain formation process is important for the development of the so-called technology computer aided design (TCAD) simulators. TCAD allows simulation and therefore develops a manufacturing process that leads to a certain device structure with which electrical characteristics can also be simulated. Availability of reliable TCADs leads to much improved efficiency in device development time and cost. For example, vertical junction depth simulation accuracy of within 10% is needed now. Because the expected drain extension depth is 7 nm in 2012, 10% of 7 nm corresponds to an accuracy of 0.7 nm and better. Therefore, precise modeling of the entire device fabrication processes including the behavior of dopants and Si host atoms throughout the whole fabrication processes is demanded [Uematsu07]. Such precise modeling can be achieved only after the challenges described in the present section are overcome.

### **1.3 Methods Employed in This Thesis**

The present thesis describes studies on:

- 1) Si self-diffusivities at low temperatures ( $< 850 \degree$ C),
- 2) Si displacements induced by ion implantation, and
- 3) Si self-interstitial behavior during transient enhanced diffusion.

In order to reveal the interactions between dopants and Si host atoms in the nanoscale, we employed a method of isotope engineering [Haller95, Plekhanov03]. Naturally available Si (<sup>nat</sup>Si) is composed of three stable isotopes in the fixed abundances: <sup>28</sup>Si (92.2%), <sup>29</sup>Si (4.7%), and <sup>30</sup>Si (3.1%). We took advantage of their mass differences as depth markers. Isotope engineering allows us to reveal how dopants and Si host atoms interact during CMOS device fabrication processes. The Si isotope superlattices (SLs) employed in the present work has been grown using solid-source molecular beam epitaxy (SS-MBE).

Raman spectroscopy measurements were used to reveal Si self-diffusion using Si isotope SLs. Raman spectroscopy can detect optical phonon frequencies in the isotope SLs. It is known that Raman scattering of longitudinal optical (LO) phonons in the isotope SLs depends strongly on the change of the isotopic distribution at the interfaces. From the shift of the LO phonons in Si isotope SL as a function of the annealing time, Si self-diffusivities have been determined for a given temperature. Ion implantations were used to introduce the impurities into the Si wafer. Secondary ion mass spectrometry (SIMS) was used to obtain depth profiles using  $O_2^+$  or  $Cs^+$  as the primary ions for the sputtering of surface atoms. The sputtered atoms were analyzed by a mass spectrometer to provide compositional information as a function of the sputtered depth. SIMS allows the probing of the isotope distribution in isotope SLs [Wittmaack90, Kojima03, Bracht05, Bracht07b, Shimizu08b] to probe the behavior of Si atoms. Simultaneous observations of dopant diffusion and Si self-diffusion revealed how the dopants and Si atoms interacted. Moreover, by combining XTEM observation with SIMS, it was possible to reveal the condition of Si amorphization. SIMS and XTEM characterizations of the impurities implanted into Si isotope SLs before and after post-implantation annealing enabled precise determination of the degree of mixing of Si host atoms induced by implantation, and the migration of Si point defects during post-implantation annealing.

### **1.4 Thesis Organization**

The present thesis is organized as follows.

Chapter 2 describes the growth and characterization of Si isotope SLs that are composed of alternating layers of different isotopes. SS-MBE is employed for the fabrication of isotope SLs and SIMS is used for the depth profiling of Si isotopes in the SLs. The behavior of confined optical phonon frequencies without any annealing is revealed by Raman spectroscopy. It is shown that experimentally found Raman shift positions agree very well with theoretical positions predicted for each isotope SL.

Chapter 3 describes the determination of Si self-diffusivity at low temperatures (< 875 °C) by a Raman spectroscopy technique. We have determined Si self-diffusivity at temperatures 735–875 °C based on the Raman shift of longitudinal optical phonon frequencies of diffusion annealed <sup>28</sup>Si/<sup>30</sup>Si isotope SLs. The activation enthalpy of 3.6 eV is obtained in such low temperature diffusion annealing. This value is significantly smaller than the previously reported 4.95 eV of the self-interstitial mechanism dominating the high temperature region T >> 855 °C, and is in good agreement with the theoretical prediction for the vacancy-mediated diffusion. In this chapter, we present a model containing both the self-interstitial and vacancy terms that quantitatively describes the experimentally obtained self-diffusivity between 735 and 1388 °C, with a clear cross-over of the two diffusion mechanisms occurring around 900 °C.

Chapter 4 presents quantitative determination of Si displacement induced by ion implantation. We established a new method for quantitatively evaluating the Si displacement as a function of the depth from the surface induced by As implantation into a Si wafer. A simulation based on a convolution integral was developed successfully to reproduce the experimental depth profiles of isotopes in the As-implanted <sup>28</sup>Si/<sup>30</sup>Si isotope SLs, from which the average distance of the Si displacements due to the collisions

with implanted As is obtained. In this chapter, we show that it takes an average displacement parameter of  $\sim 0.5$  nm to make the structure appear amorphous by XTEM observations.

Chapter 5 shows Si self-interstitial behavior during transient enhanced diffusion. We investigated the contributions of neutral and charged Si self-interstitials to selfand B diffusion during transient enhanced diffusion in Si. We simultaneously observed self- and B diffusion in Si using  $^{nat}Si/^{28}Si$  isotope SLs. Calculations based on diffusion equations involving {311} defect and B–Si self-interstitial cluster models were employed to reproduce the diffusion profiles in Si-implanted (intrinsic) and B-implanted (extrinsic) Si isotope SLs followed by annealing. To investigate the diffusion processes, the time evolution of the Si self-interstitial profiles during the transient diffusion was simulated. The results directly demonstrate that excess neutral selfinterstitials dominantly enhance self-diffusion during the transient process under intrinsic conditions, while doubly positively charged self-interstitials dominate the selfdiffusion under *p*-type extrinsic conditions.

Chapter 6 concludes this thesis.

Appendix A presents the application of the Si isotope SLs as SIMS standards for shallow junction characterization. We present a Si isotope SL structure that we believe to be the most ideal SIMS standard sample for the dopant concentration depth profiling required for characterization of the shallow junction formed by ion implantation. The precisely stacked alternating layers of Si isotopes function as a depth ruler. Therefore, it enables us to calibrate the depth scale of dopant based on the positions of Si isotopes.

Appendix B presents the solution of Fick's diffusion law for the analysis of isotope profiles in the Si isotope SLs.

### Chapter 2

## **Silicon Isotope Superlattices**

We report molecular beam epitaxial growth of Si isotope superlattices (SLs) composed of alternating layers of isotopically enriched <sup>28</sup>Si and <sup>30</sup>Si. We have prepared <sup>28</sup>Si<sub>n</sub>/<sup>30</sup>Si<sub>n</sub> isotope SLs, where *n* is the number of atomic monolayers. Zone-folded optical phonon frequencies due to artificial mass periodicity in the growth direction have been observed by Raman spectroscopy. We have used a planar bond-charge model to calculate the frequencies. We find that the frequencies of the observed Raman shift closely agree with those of optical phonon modes calculated for each SL structure. A detailed analysis reveals that the degree of intermixing between adjacent layers for our condition is approximately two monolayers [Shimizu06].

### 2.1 Introduction

Semiconductor isotope superlattices (SLs) that are composed of alternating layers of different isotopes have attracted much attention recently. Optical phonons in isotope SLs have been investigated using Si [Kojima03], Ge [Fuchs93, Spitzer94, Silveira97, Morita00], GaAs, GaP, and GaSb [Göbel99] by Raman spectroscopy. For example, naturally available Si (<sup>nat</sup>Si) is composed of three stable isotopes in fixed proportion (<sup>28</sup>Si: 92.2%, <sup>29</sup>Si: 4.7%, <sup>30</sup>Si: 3.1%). Isotopically separated Si crystals have been

grown successfully [Takyu99, Itoh03]. The different mass numbers between <sup>28</sup>Si and  $^{30}$ Si is ~ 7%. We have reported the growth and characterization of Si isotope SLs  $({}^{28}\text{Si}_n/{}^{30}\text{Si}_n)$ , where n is the number of atomic monolayers (MLs), each one 0.136 nmthick) with n = 8, 12, and 24 [Fig. 2.1], based on Raman characterization of the isotope effect of optical phonons that there was very little intermixing of Si atoms between the <sup>28</sup>Si and <sup>30</sup>Si adjacent layers during our solid-source molecular beam epitaxy (SS-MBE) growth at 650 °C [Kojima03]. In this chapter, we show the growth of a series of much shorter period  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$  isotope SLs and Raman characterization, with which structural perfection of isotope SLs can be probed nondestructively. With the isotope SLs, we expected to observe characteristic phonon frequencies which appear due to confinement of longitudinal optical (LO) phonons in specific isotope layers [Fuchs93, Spitzer94, Silveira97, Göbel99, Morita00, Nakajima01, Kojima03]. Comparison of such peaks with calculations assuming an appropriate number of monolayers n, and a degree of interface intermixing l, will allow for determination of n and l in each SL. It also allows us to test the validity of the standard phonon calculation model. It should be noted that the resolution of other techniques such as secondary ion mass spectrometry is not sufficient to characterize the short-period isotope SLs. We report excellent agreement between experimental Raman peak positions and calculated ones by the planar bond-charge model [Molinàs-Mata91, Molinàs-Mata93] taking into account intermixing at interfaces between the <sup>28</sup>Si and <sup>30</sup>Si adjacent layers.

### 2.2 Growth of Silicon Isotope Superlattices

We have grown  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$  isotope SLs with n = 1, 2, 3, 4, 7, 8, and 20 by SS-MBE system equipped with an electron beam evaporator for growing  ${}^{\text{nat}}\text{Si}$  buffer layers and Knudsen cells with tantalum crucibles for growing isotopically enriched  ${}^{28}\text{Si}$  and  ${}^{30}\text{Si}$ 



**Figure 2.1** Schematic illustration of a  ${}^{28}$ Si<sub>n</sub>/ ${}^{30}$ Si<sub>n</sub> isotope SL structure grown in the [001] direction.

layers. A high resistivity ( $\rho > 2000 \ \Omega \ cm$ ), *n*-type, 2-inch, {001}-oriented <sup>nat</sup>Si was employed as a substrate. A <sup>nat</sup>Si buffer layer of 100–200 nm was grown on the substrates at 650 °C to achieve an atomically flat surface prior to the growth of isotope SL. The growth rate of Si isotopes was approximately 0.1 nm/min. The depth profiles of Si isotopes concentrations were obtained by ATOMIKA SIMS-4000, which sputtered with Cs<sup>+</sup>, 1 keV of primary ion energy, 45° of incident angle. The total thickness of SL was ~ 100 nm as shown in Fig. 2.1.

#### 2.3 Characterization of Silicon Isotope Superlattices

#### 2.3.1 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a good technique to obtain the depth profiles by sputtering the materials. In this case, ions  $(O_2^+ \text{ or } Cs^+)$  are used to bombard the sample. Collision of these ions with sample atoms causes ejection (sputtering) of the sample atoms. The sputtered atoms are mass analyzed to provide compositional



**Figure 2.2** Schematic illustration of SIMS process, where an incident ion beam sputters atoms from the surface of a sample. Some of the sputtered atoms are ionized and can be collected and mass analyzed. (Revised figure from "*Secondary ion mass spectrometry*," edited by the Surface Science Society of Japan, p. 6 (Maruzen, 1999) [in Japanese].)



**Figure 2.3** SIMS depth profiles of <sup>28</sup>Si, <sup>29</sup>Si, and <sup>30</sup>Si in the <sup>28</sup>Si(2.7 nm)/<sup>30</sup>Si(2.7 nm) isotope SL. Cs<sup>+</sup> is used as a primary ion. Sputtering energy and angle are 1 keV and 45°, respectively.

information on the sample. SIMS is used to measure the chemical concentration of the dopants. It would be useful to be able to directly probe a particular location in a submicron device and obtain a dopant profile.

Figure 2.3 shows the SIMS depth profiles of Si isotopes in the <sup>28</sup>Si/<sup>30</sup>Si isotope SL. Cs<sup>+</sup> is used as a primary ion. As expected, the oscillations of <sup>28</sup>Si and <sup>30</sup>Si are clearly observed as a function of the depth to  $\sim 80$  nm. Depletion of the <sup>29</sup>Si concentration is also confirmed. <sup>nat</sup>Si layer appears in the region deeper than  $\sim 80$  nm.

#### 2.3.2 Mixing Roughness Information-Depth Model

The model described in the following is based on the three parameters of atomic **M**ixing (*w*), surface **R**oughness (*s*), and **I**nformation-depth ( $\lambda$ ) and is named the MRI model [Hofmann94]. Let us consider the profile, as described in Fig. 2.4.

Atomic Mixing (w): The approach is based on the most simple approximation of atomic mixing to instantaneously generate a compositionally homogeneous zone of a limit depth w, by complete atomic redistribution. Such a zone is built up after a certain sputtered depth and is then assumed to be stationary, *i.e.*, constant with the sputtered depth and of the order of the mean ion range. With an additional assumption of a constant sputtering rate, the change concentration  $C_A$  of component A in matrix B with sputtered depth x is therefore given by

$$\frac{dC_A}{dx} = \frac{C_{A(x+w)}^0 - C_A}{w},$$
(2.1)

where  $C^0_{A(x+w)}$  is the original, unaltered concentration of A at a distance w in front of the instantaneous surface at x. For a sandwich layer structure B/A/B, with abrupt interfaces at  $x_1$  (B/A) and  $x_2$  (A/B), the solution of Eq. (2.1) for the leading region (for  $x_1 - w \le x \le x_2 - w$ ) is

$$C_A^l = C_A^0 \cdot \left[1 - \exp\left(-\frac{x - x_1 + w}{w}\right)\right],\tag{2.2}$$



**Figure 2.4** Concentration distribution of component *A*. We define  $x_1$  as a *leading edge*, and  $x_2$  as a *trailing edge*, respectively.  $x_1 - w \le x \le x_1$  and  $x_2 - w \le x \le x_2$  are defined as a *leading region* and a *trailing region*, respectively.

and for the trailing region ( $x \ge x_2 - w$ ),

$$C_A^t = C_A^l \cdot \exp\left(-\frac{x - x_2 + w}{w}\right),\tag{2.3}$$

where  $C_A^0 = 1$ . Upper subscripts l and t represent leading and trailing, respectively.

**Surface Roughness** (s): In the most simple case, the roughness term can be approximated by an error function like distribution. It is taken into account by superposition of a normalized Gaussian function broadening as described by

$$C_A = \frac{1}{\sqrt{2\pi}s} \int_{x-\infty}^{x+\infty} C_A^{l,t}(x') \cdot \exp\left[-\frac{(x-x')^2}{2s^2}\right] dx',$$
 (2.4)

with a standard deviation s.

**Information-Depth** ( $\lambda$ ) : In this thesis, the depth profiles were obtained by SIMS, therefore, there is no broadening due to the information depth. This parameter is used for AES or XPS profiling. In AES or XPS profiling, the information depth,  $\lambda$ , is larger



**Figure 2.5** MRI analysis result and SIMS depth profiling of <sup>30</sup>Si in the <sup>nat</sup>Si/<sup>28</sup>Si isotope SL. Atomic mixing, w = 2.6 nm, and surface roughness, s = 0.7 nm, are used for the fitting.

than the first monolayer and has to be taken into account by the usual exponential decay with the electron escape depth. For constant  $\lambda$ , a layer of thickness w contributes to the measured, normalized intensity  $I_A/I_A^0$  for the trailing region ( $x \ge x_2 - w$ ) by

$$(I_A/I_A^0)_t = C_A^t \cdot \left[1 - \exp\left(-\frac{w}{\lambda}\right)\right].$$
(2.5)

On the other hand, for the leading region  $(x_1 - w \le x \le x_2 - w)$ , an additional contribution of the original layer of A beyond the distance x + w from the surface has to be considered:

$$(I_A/I_A^0)_l = C_A^l \cdot \left[1 - \exp\left(-\frac{w}{\lambda}\right)\right] + \exp\left(-\frac{w}{\lambda}\right) \cdot C_A^0 \cdot \left[1 - \exp\left(-\frac{x_2 - x - w}{\lambda}\right)\right].$$
(2.6)

When we employed SIMS, we considered  $\lambda = 0$ .

In order to obtain the degree of the smearing, this MRI model is used. We extracted the parameter values by comparison with the isotopic profiles in as-grown Si isotope SL by SIMS and a profile that initially has a rectangular shape using the MRI model. In Fig. 2.5, we show the SIMS depth profiling of <sup>30</sup>Si in the <sup>nat</sup>Si/<sup>28</sup>Si isotope SL as an example. Using the MRI model, the SIMS result is closely reproduced when atomic mixing, w = 2.6 nm, and surface roughness, s = 0.7 nm, are employed. We determined the layer thickness from SIMS measurements and the MRI analysis. In Chapters 4 and 5, the MRI model is used.

#### 2.3.3 Planar Bond-Charge Model

We calculated phonon frequencies in the [001] growth direction of the  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$ isotope SLs by so-called planar bond-charge (PBC) model [Molinàs-Mata91, Molinàs-Mata93], which has been widely used to calculate phonon dispersion in isotope SLs [Spitzer94, Göbel99, Morita00, Kojima03]. Advantages of this model are as follows: the planar force-constant models possess the advantage of being easier to handle that the full three-dimensional calculations (a reduction from a three-dimensional problem to a one-dimensional one is performed; the resulting  $2 \times 2$  secular equations can be solved analytically). They present, however, the drawback of being obliged to fit the different dispersion curves independently, *i.e.*, independent sets of parameters are obtained for the different directions of propagation and polarization; not surprisingly, the obtained fits are excellent. In Fig. 2.6, a schematic illustration of the PBC model,  ${}^{28}\text{Si}_2/{}^{30}\text{Si}_2$  SL grown in the [001] direction is shown. The three planar force constants between the nearest *ionic* planes, between the nearest *ionic* and *bond-charge* planes, and between the nearest *bond-charge* planes described in Fig. 2.6 are f = -1506 N/m, q = 3246 N/m, and r = 61.0 N/m, respectively. Zone-folding of optical phonons due to the mass periodicity in the growth direction is calculated using the PBC model.



**Figure 2.6** Schematic illustration of the planar bond-charge model, for a  ${}^{28}\text{Si}_2/{}^{30}\text{Si}_2$  isotope SL grown in the [001] direction. *f*, *q*, and *r* represent the force constants of (*ion*) – (*ion*), (*ion*) – (*bond-charge*), and (*bond-charge*) – (*bond-charge*), respectively.

For calculations of LO phonons in Si isotope SLs, we assumed that the force constants between <sup>28</sup>Si–<sup>28</sup>Si, <sup>28</sup>Si–<sup>30</sup>Si and <sup>30</sup>Si–<sup>30</sup>Si are the same because the isotope effect on the spring constant is negligibly small in the present case. The force constant parameters are the same as the ones given for bulk Si in Refs. [Molinàs-Mata91, Molinàs-Mata93]. LO phonons at  $\Gamma$ -point ( $k \sim 0$ ) in the phonon dispersion can be detected by Raman spectroscopy. It is possible to induce intermixing between <sup>28</sup>Si and <sup>30</sup>Si adjacent layers during the growth. Therefore, it is necessary to consider imperfect interfaces between the adjacent layers in the calculation. The depth profile of the <sup>30</sup>Si concentration,  $C_{30Si}(x)$ , in the <sup>28</sup>Si/<sup>30</sup>Si isotope SLs is given in terms of the depth x:

$$C_{^{30}\mathrm{Si}}(x) = C_{^{30}\mathrm{Si}}^{d} + \frac{C_{^{30}\mathrm{Si}}^{e} - C_{^{30}\mathrm{Si}}^{d}}{2} \sum_{k=1}^{p} \left[ \mathrm{erf}\left(\frac{x - \{(k-1)d_{e} + kd_{d}\}}{2l}\right) - \mathrm{erf}\left(\frac{x - (kd_{e} + kd_{d})}{2l}\right) \right].$$

$$(2.7)$$

Here,  $C^e_{30}_{Si}$  and  $C^d_{30}_{Si}$  are the concentrations of  ${}^{30}Si$  in the isotopically enriched and depleted layers, respectively, in the as-grown  ${}^{28}Si/{}^{30}Si$  isotope SL assuming perfectly

abrupt interfaces. Likewise,  $d_e$  and  $d_d$  are the thicknesses of the isotopically enriched "<sup>30</sup>Si layer" and the depleted "<sup>28</sup>Si layer," respectively. The degree of intermixing is introduced by the intermixing parameter l. p is the number of periods of the <sup>28</sup>Si/<sup>30</sup>Si layers. The isotope SL employed in the present study has  $C_{30Si}^e = 0.993$ ,  $C_{30Si}^d = 0.0008$ ,  $d_e = d_d = 2.7$  nm, and l = 2. In calculation of the phonon dispersion in the SL structures, an average mass distribution along the growth direction is important to solve the dynamical matrix. The depth profile shown in Eq. (2.7) is similar to a convolution of the ideal depth profile with a Gaussian shape. We can characterize the degree of intermixing in SLs by the PBC model assuming distribution of the concentration with Eq. (2.7).

#### 2.3.4 Raman Spectroscopy

We have characterized the Si isotope SLs by Raman spectroscopy. This technique is believed to be the best method to characterize the short-period isotope SLs because Xray diffraction analysis can be employed only for SLs that are composed of different chemical constituents. The depth resolution of SIMS is not enough to characterize the isotope SLs having the layer thickness of nano-meters.

Raman scattering measurements of the isotope SLs were performed in the backscattering geometry using Ar<sup>+</sup> 514.5 nm line. The spectral resolution was 0.7 cm<sup>-1</sup>. We used a DILOR XY single monochrometer and accumulated the signal with a charged coupled device multi-channel detection system. All samples were kept in a closed cycle cryostat at temperature of ~ 8 K. The measured Raman spectra of  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$  isotope SLs with n = 4, 8, and 20 are shown in Fig. 2.7. We can observe some small peaks of the confined LO phonons due to the artificial mass periodicity in  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$  isotope SLs, which appear clearly on the left side of the large natSi substrate LO peak 523.5 cm<sup>-1</sup>. Two LO phonon peaks, LO<sub>1</sub>( ${}^{28}\text{Si}$ ) and LO<sub>1</sub>( ${}^{30}\text{Si}$ ),



**Figure 2.7** Raman spectra of  ${}^{28}\text{Si}_n/{}^{30}\text{Si}_n$  isotope SLs with n = 4, 8, and 20, recorded in the backscattering geometry at  $T \sim 8$  K using Ar<sup>+</sup> 514.5 nm line.

in the n = 8 sample are observed. LO<sub>1</sub>(<sup>30</sup>Si) peak disappears in the n = 4 sample. Due to the mass periodicity of <sup>28</sup>Si and <sup>30</sup>Si in the growth direction, the highest energy vibrational modes are confined in <sup>28</sup>Si layers because <sup>28</sup>Si are lighter than <sup>30</sup>Si. Their frequencies are very sensitive to the periodicity and intermixing. We can theoretically calculate the frequencies <sup>28</sup>Si localized phonons as a function of the periodicity and degree of intermixing using the PBC model. A comparison between calculations and an experiment is shown in Fig. 2.8. This figure shows the wavenumbers (Raman shift) of the confined modes in SLs predicted by the calculation assuming no intermixing



**Figure 2.8** Theoretical Raman peak shifts as a function of *n* calculated by the PBC model assuming no intermixing (solid curves) and l = 2 intermixing (broken curves). Calculated curves were shifted by 7 cm<sup>-1</sup> to lower wavenumber as was done in Ref. [Kojima03]. Experimental results (filled-in circles) agree with the theory assuming l = 2.

 $(l \sim 0)$  of Si atoms between the adjacent <sup>28</sup>Si and <sup>30</sup>Si layers (solid curves) and two layers of intermixing l = 2 (broken curves). The calculated peak positions are shifted approximately 7 cm<sup>-1</sup> to lower frequencies to fit the experiment as was done in Ref. [Kojima03]. Such shift was done in the same manner for Raman characterization of Ge isotope SLs [Spitzer94], therefore the force constant parameters in the PBC model could be recalculated in order to be accurately fitted the experimental Raman peak positions of isotope SLs. We find in Fig. 2.8 excellent agreement between the experimental Raman peak positions (filled-in circles) all the way down to n = 1 SLs, and calculated ones by the PBC model with l = 2, taking into account intermixing at the interface between the <sup>28</sup>Si and <sup>30</sup>Si adjacent layers. The source of intermixing can be i) imperfect shutter open-close timing control and/or ii) anomalously fast diffusion of Si across the interface. The shutter should terminate the growth when the layer is completely filled by one type of isotope. However, such precise shutter control is not possible, so one layer of intermixing is unavoidable. Atomic scale roughing of the surface also contributes to intermixing though our atomic force microscope images show very flat growth of less than 1 ML disorder. At the growth temperature of 650 °C, the expected Si self-diffusivity is below  $10^{-23}$  cm<sup>2</sup>/s [Bracht98]. With our typical growth rate, the total growth time is approximately 20 h. With these numbers, we obtain a diffusion length  $2\sqrt{D_{Si}^{SD}t} \sim 0.01$  nm, where  $D_{Si}^{SD}$  is the Si self-diffusivity and *t* is the growth time. Therefore, a much faster diffusion mechanism is needed to explain the intermixing of 2 MLs. At this point, we see no evidence for such an unusual diffusion. Finally, we should note that the Raman measurement using Ar<sup>+</sup> 514.5 nm probes the sample area of a few microns and a depth 0.77  $\mu$ m [Parr01]. Therefore, any fluctuation of the layer thickness will contribute to the Raman peak positions and widths obtained as an average.

#### 2.4 Summary

We have successfully grown short-period <sup>28</sup>Si<sub>n</sub>/<sup>30</sup>Si<sub>n</sub> isotope SLs by SS-MBE. We have performed Raman spectroscopy analysis to observe the confined LO phonon frequencies in the SLs due to artificial mass periodicity in the growth direction as a function of layer thickness, *n*. Consequently, the Raman peak positions of each SL agree well with the theoretical calculation. We have investigated the degree of intermixing in SLs by the PBC model assuming an average mass distribution with the error function. We obtained excellent agreement with theory, using an l = 2 intermixing parameter.

## Chapter 3

# Silicon Self-Diffusivities at Low Temperatures

We have determined the Si self-diffusivity at temperatures 735–875 °C based on the Raman shift of longitudinal optical phonon frequencies of diffusion annealed <sup>28</sup>Si/<sup>30</sup>Si isotope SLs. An activation enthalpy of 3.6 eV is obtained in such low temperature diffusion annealing. This value is significantly smaller than previously reported 4.95 eV of the self-interstitial mechanism dominating the high temperature region T >> 855 °C, and closely agrees with the theoretical prediction for the vacancy-mediated diffusion. In this chapter, we present a model containing both selfinterstitial and vacancy terms that quantitatively describe the experimentally obtained self-diffusivity between 735 and 1388 °C, with a clear cross-over of the two diffusion mechanisms occurring around 900 °C [Shimizu07a].

### 3.1 Introduction

Self-diffusion investigation using Si is important because Si single crystals boast unsurpassable crystalline perfection and chemical purity, which are crucial for exclusive probing of the self-diffusion phenomena in solids. Understanding the Si self-diffusion mechanism also plays a key role in impurity diffusion, and the annealing of the implantation damage, which are needed for the development of process simulators for future Si nano-electronics. Si self-diffusion has been studied extensively for many years (*e.g.*, [Stolwijk98]). One of the major focuses of discussion is whether vacancy-dominated diffusion, which is predicted to be important theoretically [Seong96, Antonelli98, Puska98, Kumeda01, Probert03, Lento03, El-Mellouhi04, Caliste06], ever takes a visible role. Bracht *et al.* established that the experimental self-diffusivity ( $D_{Si}^{SD}$ ) between 855 and 1388 °C could be described with a single exponential as [Bracht98]

$$D_{\rm Si}^{\rm SD} = (530^{+250}_{-170}) \, \exp\left(-\frac{(4.75 \pm 0.04) \, {\rm eV}}{k_B T}\right) \, {\rm cm}^2 {\rm s}^{-1}.$$
(3.1)

Together with other studies which established activation enthalpy  $H_I = 4.95$  eV for the self-interstitial mechanism [Bracht95], it was concluded that the contribution of the vacancy mechanism is very small in diffusion at such high temperatures. Accurate determination of the self-diffusivity at low temperatures T < 850 °C, by the standard method, *e.g.*, SIMS of the depth profile of the specific Si isotopes, is difficult because the diffusion length after reasonable annealing duration in the lab (< 180 days) is still too small for the depth resolution of SIMS. The present study overcomes this challenge by detection of very small diffusion length in isotope SLs of Si by Raman spectroscopy. This method has proven useful in the past for accurate determination of the self-diffusivity in Ge [Silveira97], and characterization of Si isotope SLs [Kojima03, Shimizu06].

Si self-diffusion is expected to occur predominantly via two types of native defects [see Fig. 3.1]: self-interstitials (I) and vacancies (V) [Frank84, Tan85, Fahey89, Bracht95, Bracht98, Ural99, Bracht00, Giese00, Bracht06]. Thus, the Si selfdiffusivity  $D_{Si}^{SD}$  is expressed by

$$D_{\rm Si}^{\rm SD} = f_I \frac{C_I^{\rm eq}}{C_0} D_I + f_V \frac{C_V^{\rm eq}}{C_0} D_V.$$
(3.2)

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**Figure 3.1** Diffusion mechanisms via (a) interstitials and (b) vacancies in Si. Open circles represent Si host atoms.

Here,  $C_{I,V}^{eq}$  and  $D_{I,V}$  are the equilibrium concentrations and diffusivities of I and V, respectively.  $C_0$  is the concentration of the Si atoms.  $f_I \approx 0.73$  [Compaan58] and  $f_V = 0.5$  [Compaan56] are the correlation factors for interstitial and vacancy mechanisms in the diamond structure, respectively.

The vacancy term is not well-understood because vacancy-mediated self-diffusion has never been observed directly in its equilibrium form. The enthalpy for the vacancy-mediated diffusion  $H_V$  is given by the sum of the formation and migration enthalpies:  $H_V^f + H_V^m$ . Experimentally reported  $H_V^f$  are 2.8 ± 0.3 eV [Ranki04], 2.44 ± 0.15 eV [Lerner05], and 2.1 ± 0.7 eV [Bracht03], while large cell size (~ 256) calculations predict slightly larger values confined between 3.1 and 3.6 eV [Lento03, Probert03, El-Mellouhi04]. In parallel,  $H_V^m = 0.18-0.45$  eV [Watkins97], 1.3 eV [Ranki04], and 1.8 ± 0.5 eV [Bracht03] are found experimentally, while theory predicts 0.4 eV [El-Mellouhi04] and 0.58 eV [Kumeda01]. Because  $H_V^m = 0.45$  eV was obtained experimentally below room temperature [Watkins97], it has been suggested that  $H_V^m$  depends on the temperature. Thus, a theoretical model has been proposed that connects the between experimental values 1.3 eV (or 1.8 eV), for high temperatures and 0.4 eV (or 0.58 eV) calculated theoretically for low temperatures [Caliste06].<sup>1</sup> In this chapter, we show that experimentally obtained Si self-diffusivity can be described quantitatively by a simple double-exponential equation.

### **3.2** Experiments

A <sup>28</sup>Si<sub>n</sub>/<sup>30</sup>Si<sub>n</sub> isotope SL with n = 20 atomic layers was grown by SS-MBE [Kojima03, Shimizu06]. The starting substrate was high resistivity ( $\rho > 2000 \Omega$  cm), *n*-type, 2-inch, {001}-oriented <sup>nat</sup>Si, onto which a buffer layer of ~ 100 nm-thick <sup>nat</sup>Si was formed prior to the growth of the isotope SL, composed of alternating layers of isotopically pure <sup>28</sup>Si (99.92%) and <sup>30</sup>Si (99.3%). The degree of intermixing at the <sup>28</sup>Si and <sup>30</sup>Si interfaces is less than a couple monolayers in an as-grown isotope SL [Shimizu06]. The wafer was cut into 2×2 mm<sup>2</sup> size squares for diffusion annealing in a resistance furnace under a pure argon (99.99%) atmosphere. The temperature inside the furnace was monitored with a Pt/PtRh thermocouple to stabilize the furnace within  $\pm 2$  °C. The intrinsic carrier concentration was ~ 1×10<sup>18</sup> cm<sup>-3</sup> at the lowest diffusion annealing temperature of 735 °C, which ensured that the sample remained intrinsic and the Fermi level effect did not play a role.<sup>2</sup> The Raman measurements of the LO phonon frequencies were performed using an Ar<sup>+</sup> 514.5 nm line. The scattering light

<sup>&</sup>lt;sup>1</sup>Watkins claims that there is only one vacancy, and nothing magical happens at elevated temperatures, contrary to what has often been suggested here. The accurate measurements at cryogenic temperatures for vacancy diffusion from the early EPR and DLTS studies remain valid at elevated temperatures [Watkins08].

<sup>&</sup>lt;sup>2</sup>The carrier concentration of Si is calculated by [Morin54].
was dispersed by a single spectrometer and detected by a charge coupled device with a spectral resolution of 0.7 cm<sup>-1</sup>. All spectra were recorded through the backscattering geometry with the sample temperature T = 8 K.

#### **3.3 Vacancy Contribution**

The depth profile of the <sup>30</sup>Si concentration  $C_{30Si}(x, t, T)$  in the diffusion annealed <sup>28</sup>Si/<sup>30</sup>Si isotope SLs is given in terms of the depth x, diffusion annealing time t, and the self-diffusivity  $D_{Si}^{SD}(T)$  for a given annealing temperature:<sup>3</sup>

$$C_{30}_{Si}(x,t,T) = C_{30}^{d}_{Si} + \frac{C_{30}^{e}_{Si} - C_{30}^{d}}{2} \sum_{k=1}^{p} \left[ \operatorname{erf} \left( \frac{x - \{(k-1)d_{e} + kd_{d}\}}{2(l + \sqrt{D_{Si}^{SD}(T)t})} \right) - \operatorname{erf} \left( \frac{x - (kd_{e} + kd_{d})}{2(l + \sqrt{D_{Si}^{SD}(T)t})} \right) \right].$$
(3.3)

Here,  $C_{30\text{Si}}^e$  and  $C_{30\text{Si}}^d$  are the concentrations of  ${}^{30}\text{Si}$  in the isotopically enriched and depleted layers, respectively, in the  ${}^{28}\text{Si}/{}^{30}\text{Si}$  isotope SL prior to the diffusion annealing assuming perfectly abrupt interfaces. Likewise,  $d_e$  and  $d_d$  are the thicknesses of the isotopically enriched " ${}^{30}\text{Si}$  layer" and the depleted " ${}^{28}\text{Si}$  layer," respectively. The degree of intermixing before diffusion annealing is introduced by the intermixing parameter l. p is the number of periods of the  ${}^{28}\text{Si}/{}^{30}\text{Si}$  layers. The isotope SL employed in the present study has  $C_{30\text{Si}}^e = 0.993$ ,  $C_{30\text{Si}}^d = 0.0008$ ,  $d_e = d_d = 2.7$  nm, and l = 2.

The corresponding average mass of an atomic layer M(x, t, T) located at a depth x, before and after annealing in the Si isotope SL, is given by

$$M(x,t,T) = C'_{28\rm Si}(x,t,T)M_{28\rm Si} + C'_{30\rm Si}(x,t,T)M_{30\rm Si},$$
(3.4)

where  $M_{^{28}Si}$  and  $M_{^{30}Si}$  are the masses of  $^{28}Si$  and  $^{30}Si$  atoms, respectively.  $C'_{^{28}Si}(x, t, T)$ and  $C'_{^{30}Si}(x, t, T)$  are the normalized concentration (*i.e.*  $C'_{^{28}Si}(x, t, T) + C'_{^{30}Si}(x, t, T) =$ 

<sup>&</sup>lt;sup>3</sup>The details are described in Appendix B.

1) as introduced in Ref. [Silveira97]. Because M(x, t, T) oscillates also with the periodicity  $d_e + d_d$ , new phonon modes whose vibrations are confined in <sup>28</sup>Si and <sup>30</sup>Si layers emerge. The frequencies (wavenumbers) of such confined phonons are very sensitive to the periodicity,  $d_e$  and  $d_d$ , and the abruptness of the <sup>28</sup>Si/<sup>30</sup>Si interfaces given by l and  $\sqrt{D_{Si}^{SD}(T)t}$ . Since the interface prior to diffusion annealing is very sharp (l is only 2), the frequencies of confined phonon modes in the diffusion annealed samples are given solely by  $\sqrt{D_{Si}^{SD}(T)t}$ , since  $d_e = d_d = 2.7$  nm remain unchanged during any annealing. Thus, a measurement of vibrational frequencies of confined phonons for a variety of diffusion annealed isotope SLs allows us to precisely determine the Si self-diffusivity  $D_{Si}^{SD}(T)$  for a given temperature.

Figure 3.2 shows the Raman spectra of the  ${}^{28}Si_{20}/{}^{30}Si_{20}$  isotope SLs annealed at 815 °C for various durations t. Raman peaks of the confined LO phonons observed clearly on the left side of the large LO peak of <sup>nat</sup>Si in the as-grown sample correspond to  $LO_3(^{28}Si)$ ,  $LO_5(^{28}Si)$ , and  $LO_1(^{30}Si)$  in the order from the higher to lower Raman shifts, respectively. Here, the notations  $LO_m(^{28}Si)$  and  $LO_m(^{30}Si)$  represent the m-th confined vibrational mode in the <sup>28</sup>Si and <sup>30</sup>Si layers, respectively, as was introduced originally for confined phonons in Ge isotope SLs [Spitzer94]. Interdiffusion of isotopes at every <sup>28</sup>Si/<sup>30</sup>Si interface in the SLs occurs exactly in the same manner. Therefore, peak positions of the confined phonons shift systematically with diffusion annealing time t. For example, as t increases, the lowest Raman shift peak  $LO_1(^{30}Si)$  disappears, while the  $LO_1(^{28}Si)$  hidden in the <sup>nat</sup>Si substrate peak emerges after 12 h of annealing.  $D_{Si}^{SD}(T)$  for a given temperature is obtained by quantitative comparison with a theoretical calculation using the planar bond-charge (PBC) model [Molinàs-Mata91, Molinàs-Mata93], which allows us to precisely calculate the frequencies of confined phonons in a given Si isotope SL as we have demonstrated in Ref. [Shimizu06].



**Figure 3.2** Raman spectra of  ${}^{28}\text{Si}_{20}/{}^{30}\text{Si}_{20}$  isotope SLs annealed at 815 °C for various durations as labeled in the figure.

Figure 3.3 shows a direct comparison of the frequencies of the confined LO phonons between the experiment and calculations for the 815 °C annealed samples shown in Fig. 3.2. The filled-in circles are the experimentally determined peak positions, while the solid curves are the calculations by the PBC model using  $D_{\rm Si}^{\rm SD}(815 \,^{\circ}{\rm C}) = 6.4 \times 10^{-20} \,{\rm cm}^2/{\rm s}$ . Note that  $D_{\rm Si}^{\rm SD}(T)$  is the only adjustable parameter in the model, and the excellent agreement between the experiment and calculations as shown in Fig. 3.3 is achieved only with a single  $D_{\rm Si}^{\rm SD}(T)$  with a tolerance much less than a few percent. Figure 3.4 shows the annealing time (t) evolution of the depth profile of the  ${}^{30}{\rm Si}$  atomic fraction,  $C'_{30{\rm Si}}$  in the  ${}^{28}{\rm Si}_{20}/{}^{30}{\rm Si}_{20}$  isotope SL using the Si self-diffusivity  $D_{\rm Si}^{\rm SD}(815 \,^{\circ}{\rm C}) = 6.4 \times 10^{-20} \,{\rm cm}^2/{\rm s}$  determined for 815 °C. The sample prior to annealing has a small interdiffusion characterized by  $l \sim 2$ . The same interdiffusion of  ${}^{28}{\rm Si}$  and  ${}^{30}{\rm Si}$  isotopes at every  ${}^{28}{\rm Si}/{}^{30}{\rm Si}$  interface then takes place as



**Figure 3.3** Annealing time dependence of the Raman shifts of the localized phonons in  ${}^{28}\text{Si}_{20}/{}^{30}\text{Si}_{20}$  isotope SLs. The annealing temperature was 815 °C. Solid circles are experimental LO phonon frequencies determined from the peak positions in Fig. 3.2. Solid lines are a theoretical calculation of the confined peak frequencies using  $D_{\text{Si}}^{\text{SD}} = 6.4 \times 10^{-20} \text{ cm}^2/\text{s}.$ 

the annealing duration increases. Eventually <sup>28</sup>Si and <sup>30</sup>Si will be mixed completely for infinitely long annealing, for which the periodicity  $d_e$  and  $d_d$  disappear, and the phonon modes are characterized as those of the bulk sample having an average mass approximately of <sup>29</sup>Si.

Finally, in Fig. 3.5, the temperature dependence of  $D_{Si}^{SD}$  determined in the present study are shown by filled-in circles, together with those determined previously by SIMS of isotope heterostructures in open circles [Bracht98]. The experimental error of our  $D_{Si}^{SD}$  is the order of the filled-in circles representing the data. We stress first that the self-diffusivity determined by the present method agrees very well with the open circles determined by Bracht *et al.* in the overlapping temperature range between 850 and 900 °C. Precise determination of the self-diffusivity by the present method



**Figure 3.4** Calculated annealing time evolution of the depth profile of the <sup>30</sup>Si atomic fraction in the <sup>28</sup>Si<sub>20</sub>/<sup>30</sup>Si<sub>20</sub> isotope SLs for T = 815 °C. Experimentally determined  $D_{Si}^{SD} = 6.4 \times 10^{-20}$  cm<sup>2</sup>/s for T = 815 °C is used for this calculation.

becomes difficult above 900 °C because the periodicities  $d_e$  and  $d_d$  of the SLs disappear very quickly (within a few minutes of annealing) due to the large diffusivity at the high temperatures. Therefore, we analyze filled-in circles and open circles together to obtain an overall self-diffusivity of Si for T = 735-1388 °C. The solid curve in Fig. 3.5 is the result of such an analysis, and it is expressed by the following equation composed of a sum of two exponential terms:

$$D_{\rm Si}^{\rm SD} = 2175.4 \, \exp\left(\frac{-4.95 \, {\rm eV}}{k_B T}\right) + 0.0023 \, \exp\left(\frac{-3.6 \, {\rm eV}}{k_B T}\right) \, {\rm cm}^2 {\rm s}^{-1}. \tag{3.5}$$

Here, the first term represents the self-diffusion due to the self-interstitial mechanism I and therefore, the established value of the enthalpy  $H_I = 4.95$  eV and prefactor 2175.4 cm<sup>2</sup>s<sup>-1</sup> are assumed from the start [Bracht95]. The remaining two parameters, the enthalpy and prefactor in the second term, were obtained by fitting. The enthalpy



**Figure 3.5** Temperature dependence of the Si self-diffusivity. Results of the present study are shown by filled-in circles together with those determined previously by SIMS of isotope heterostructures in open circles [Bracht98]. The solid line is the fit described by Eq. (3.5). Contributions of the self-interstitial and vacancy mechanism are shown by the broken and dotted lines, respectively.

3.6  $^{+0.3}_{-0.1}$  eV in the second term is in agreement within the experimental error with the value  $H_V = 3.9$  eV determined previously for Si self-diffusion in vacancy-rich Si single crystals [Bracht03]. Thus, it is reasonable to conclude that the experimental results in Fig. 3.5 is the first observation of the cross-over from the self-interstitial mechanism at the high temperatures, to the vacancy mechanism at the low temperatures. To find the cross-over temperature, we separately plotted in Fig. 3.5 the first and second terms in Eq. (3.5), by broken and dotted lines, respectively. Their intersection occurs at approximately 900 °C. Seeger and Chik have obtained the same 900 °C intersection point, through very indirect experiments; Ni precipitation assuming Si vacancies are playing the dominant role [Seeger68]. Further indirect experiments, in fact, moved this cross-over temperature up to 1000 °C and above [Tan85]. The present experiment

is the first direct measurement that firmly establishes the cross-over temperature of 900 °C.

The enthalpy for the vacancy mechanism  $H_V$  is composed of  $H_V = H_V^f + H_V^m$ , where  $H_V^f$  and  $H_V^m$  are the formation and migration enthalpies of Si vacancies, respectively. The present  $H_V = 3.6 {+0.3 \ -0.1}$  eV, together with the most reliable calculation  $H_V^f = 3.1-3.6$  eV, lead to  $H_V^m < 0.8$  eV with the most probable value around  $H_V^m =$ 0.4 eV, which agrees with 0.45 eV obtained with an electron paramagnetic resonance by Watkins [Watkins97]. However, the analysis with the most direct experimental  $H_V^f = 2.8 \pm 0.3$  eV [Ranki04], yields 0.4 eV  $< H_V^m < 1.4$  eV, with the most probable value around 0.8 eV. Thus, while further experiments are needed, our analysis indicates that  $H_V^m$  is likely to be less than 1 eV, even at the annealing temperatures employed in this study.

#### 3.4 Summary

In summary, the cross-over between the self-interstitial and vacancy mechanisms was experimentally observed for the first time at 900 °C, and therefore,  $H_V = H_V^f + H_V^m =$ 3.6 eV is firmly established. This finding is of great technological importance, since the process simulations of state-of-the-art Si electronic devices require precise values of Si self-diffusivity. The present study has shown that self-diffusivity at T < 900 °C is much larger than what has been employed as a standard [Bracht98].

## Chapter 4

## Silicon Displacements Induced by Ion Implantation

We established a new method for quantitatively evaluating Si displacement as a function of the depth from the surface induced by As implantation into a Si wafer. A simulation based on a convolution integral was successfully developed to reproduce the experimental depth profiles of isotopes in the As-implanted <sup>28</sup>Si/<sup>30</sup>Si isotope SLs, from which the average distance of the Si displacements due to the collisions with implanted As is obtained. In this chapter, we show that it takes an average displacement parameter of ~ 0.5 nm to make the structure appear amorphous by transmission electron microscopy [Shimizu08a].

#### 4.1 Introduction

Arsenic (As) implantation, which is widely used for the formation of shallow junctions in Si nano-transistors, induces radiation damage that can significantly affect the redistribution of dopants during post-implantation annealing. Therefore, the relationship between the distribution of implanted As, and damage in crystalline Si, has been studied extensively [Lulli97, Lulli00, Posselt00, Son00, Tsamis05, Capello06]. While the depth profiles of impurities are routinely measured by SIMS [Clegg87], a quantitative method to directly evaluate the average distance of the Si displacements associated with the implantation does not yet exist. The ion-channeling and cross-sectional transmission electron microscopy (XTEM) can only estimate the fraction of the Si atoms displaced from the substitutional sites in the single-crystalline region [Lulli00]. Such evaluation becomes almost hopeless in the amorphous region induced by the implantation. This chapter reports a method to evaluate the average distance of the Si displacements as a function of the depth from the implanted surface, both in the amorphous and single-crystalline regions. Our statistical analysis of the perturbed Si isotope profiles measured by SIMS allows determination of the displacement with an accuracy < 1 nm, which is significantly better than direct determination by SIMS. We find that the Si displacements vary significantly even within the region that appears "uniformly amorphous" by XTEM. The critical displacement parameter ( $\sigma_c$ ), which we define as the displacement parameter at the interface of the single-crystalline and amorphous regions observed by XTEM, is ~ 0.5 nm.

#### 4.2 Experiments

A  ${}^{28}$ Si(2.7 nm)/ ${}^{30}$ Si(2.7 nm) isotope SL was grown by SS-MBE [Kojima03, Shimizu06]. A high resistivity ( $\rho > 2000 \ \Omega \ cm$ ), 2-inch, *n*-type, {001}-oriented floating zone <sup>nat</sup>Si wafer was employed as a substrate. A <sup>nat</sup>Si buffer layer of ~ 100 nm-thick was formed prior to the growth of the isotope SL that is composed of alternating layers of isotopically pure <sup>28</sup>Si (99.92%) and <sup>30</sup>Si (99.3%). <sup>75</sup>As<sup>+</sup> ions were implanted at room temperature into the SL with an energy of 25 keV corresponding to the projected range of ~ 20 nm, and with a dose of  $1 \times 10^{13}$  or  $1 \times 10^{15} \ cm^{-2}$  at a tilt angle of 7°. The depth profiles of Si isotopes and As were obtained by SIMS (ATOMIKA

SIMS-4000), using a  $Cs^+$  primary ion beam at an energy of 1 keV with a 45° incident angle. The sputtering rate was assumed to be constant. XTEM observations were performed with a TECNAI F12 electron microscope operating at 200 kV.

#### **4.3** Determination of Silicon Displacements

Figure 4.1 (a) shows the depth profiles of <sup>28</sup>Si, <sup>30</sup>Si, and <sup>75</sup>As in the Si isotope SL implanted with As using an energy of 25 keV and a dose of  $1 \times 10^{13}$  cm<sup>-2</sup>. With such a low dose, the alternating depth profiles of <sup>28</sup>Si and <sup>30</sup>Si are almost unperturbed, even after the implantation in comparison with the profiles of <sup>28</sup>Si and <sup>30</sup>Si before the implantation [Fig. 4.2 (a)]. Note that the actual interfaces between <sup>28</sup>Si and <sup>30</sup>Si layers are abrupt (the degree of intermixing is only two atomic monolayers) [Kojima03, Shimizu06] and the smearing of the <sup>28</sup>Si and <sup>30</sup>Si profiles is due to the so-called SIMS artifact (knock-on mixing, *etc.*). On the other hand, as shown in Fig. 4.1 (b), the same energy with a factor of one hundred times higher dose of implantation of  $1 \times 10^{15}$  cm<sup>-2</sup> leads to perturbation of the <sup>28</sup>Si and <sup>30</sup>Si periodic profiles all the way to a depth of ~ 50 nm. The following simulation based on a convolution integral is employed to reproduce the perturbed depth profile of <sup>28</sup>Si and <sup>30</sup>Si to quantitatively obtain the characteristic length of Si displacements as a function of the depth (*x*) from the implanted surface.

$$C_{\text{aft-imp}}(x) = \int C_{\text{bef-imp}}(x') g(x - x') dx'.$$
(4.1)

Here,  $C_{\text{bef-imp}}(x)$  and  $C_{\text{aft-imp}}(x)$  represent the concentrations of <sup>28</sup>Si and <sup>30</sup>Si in the Si isotope SL before and after implantations, respectively. g(x) is a Gaussian function:

$$g(x) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{x^2}{2\sigma^2}\right).$$
(4.2)



**Figure 4.1** Depth profiles of <sup>28</sup>Si (open circles), <sup>30</sup>Si (filled-in circles), and <sup>75</sup>As (solid curve) measured by SIMS in the <sup>28</sup>Si(2.7 nm)/<sup>30</sup>Si(2.7 nm) isotope SLs after <sup>75</sup>As<sup>+</sup> implantation at an energy of 25 keV with doses of (a)  $1 \times 10^{13}$  cm<sup>-2</sup> and (b)  $1 \times 10^{15}$  cm<sup>-2</sup>.

In our simulation, the distribution g(x) can be expressed by a theory of random walk.<sup>1</sup>  $\sigma(x)$  is the displacement parameter as a function of the depth x, which is defined in terms of the probabilistic behavior that a host atom at a depth x is displaced by the implantation.  $\sigma(x)$  is expressed by

$$\sigma(x) = k \exp\left[-\frac{(x-c)^2}{2d^2}\right],\tag{4.3}$$

where k, c, and d are the parameters of peak amplitude, peak position, and peak width, respectively. It is known that the distribution of the displacement of atoms in solids by ion implantation can be approximated by a Gaussian function, except for the tails [Brice75]. The values of k, c, and d are determined by direct comparison with the experimentally obtained depth profiles of the implanted sample.

Figure 4.2 (a) shows the depth profiles of <sup>28</sup>Si and <sup>30</sup>Si in the Si isotope SL before implantation measured by SIMS. Figure 4.2 (b) shows the depth profiles in the implanted sample [the same ones as shown in Fig. 4.1 (b)]. We simulated the profiles in Fig. 4.2 (b) in the following manner. First, we reproduced the profiles of the as-grown sample that initially had rectangular isotopic profiles [Fig. 4.2 (a)] using the mixing roughness information-depth (MRI) model [Hofmann94]. This model includes atomic mixing (w) and surface roughness (s) for the theoretical description of the depth resolution function for SIMS profiles. The change of the concentration C, with sputtered depth x, is given by Eq. (2.1). The roughness is taken into account by superposition of a normalized Gaussian broadening as described in Eq. (2.4). From this analysis, we obtained w = 2.5 nm and s = 0.7 nm to correct for the SIMS artifact. These parameters (w and s) are used to simulate the SIMS profiles after ion implantation [Fig. 4.2 (b)], as mentioned below. Next, the convolution integral [Eqs. (4.1)–(4.3)] is applied to the

<sup>&</sup>lt;sup>1</sup>When an energetic ion penetrates a solid target, sufficient kinetic energy may be imparted to lattice atoms during nuclear collisions to cause atomic displacements. The recoiling lattice atom may itself process sufficient kinetic energy to displace many other lattice atoms. As a result, a cascade of displaced atoms may originate from a single collision between the implanted ion and a lattice atom [Williams84].



**Figure 4.2** Depth profiles measured by SIMS of <sup>28</sup>Si (open circles) and <sup>30</sup>Si (filled-in circles) in the Si isotope SLs (a) before and (b) after As implantation at an energy of 25 keV with a dose of  $1 \times 10^{15}$  cm<sup>-2</sup>. (c) Simulated profiles using the convolution integral model described in the text. (d) The depth dependence of the displacement parameter  $\sigma(x)$  of the Si atoms induced by the As implantation. (e) XTEM image of the sample implanted with the same conditions with the depth scale, the same as (a)–(d).

rectangular isotopic profiles, and then, the convoluted profiles are broadened using the MRI parameters obtained above to reproduce the profiles in Fig. 4.2 (b). We chose the appropriate set of values k = 2.7 nm, c = 13.0 nm, and d = 14.0 nm in Eq. (4.3) so that the convoluted and broadened profiles are comparable to the SIMS profiles after implantation. This allowed us to plot the distribution of the Si displacement parameter  $\sigma(x)$  as shown in Fig. 4.2 (d). The maximum displacement of 2.7 nm was induced by the implantation at 13 nm from the surface, which is shallower than 19 nm where the implanted As concentration becomes a maximum, as shown in Fig. 4.1 (b). Figure 4.2 (e) shows the XTEM image of the same implanted sample with the depth scale being the same as Figs. 4.2 (a)–(d). Due to the implantation, amorphization occurred between the surface and  $\sim$  38 nm in depth, while the deeper region (x > 38 nm), remained single-crystalline. The interface between the amorphous and single-crystalline regions is not completely flat. This can be explained by the fact that the collision event empirically occurs nonuniformly, while the obtained SIMS results show the average profiles along the depth. Note that the periodicity of <sup>28</sup>Si and <sup>30</sup>Si remains even in the amorphous layer at x = 20-38 nm. We define  $\sigma_c$  as the critical displacement parameter occurring at the interface of the amorphous and single-crystalline regions in Fig. 4.2 (e). This occurs at  $x \sim 38$  nm with a value  $\sigma_c \sim 0.5$  nm, *i.e.*, a displacement parameter of approximately three times the Si-Si bond length. The  $\sigma(x) > 0.5$  nm region appears "amorphous" by XTEM. However, even within the region x < 38 nm that appears "uniformly amorphous" by XTEM, the displacement varies significantly as shown in Fig. 4.2 (d). Thus,  $\sigma(x)$  provides the quantitative estimation of a degree of disorder in the implanted region.

To show the coherency of the analysis and significance of our findings, Fig. 4.3 shows the same analysis performed with two different As implantation conditions: i) 25 keV,  $1 \times 10^{14}$  cm<sup>-2</sup> and ii) 60 keV,  $3 \times 10^{14}$  cm<sup>-2</sup>. The solid curve in Fig. 4.3 (b)



**Figure 4.3** (a) Depth profiles measured by SIMS of <sup>28</sup>Si (open circles) and <sup>30</sup>Si (filled-in circles) in the Si isotope SLs after As implantation at an energy of 25 keV with a dose of  $1 \times 10^{14}$  cm<sup>-2</sup>, (b) the depth dependence of the displacement parameter  $\sigma(x)$  of the Si atoms induced by the As implantation, and (c) XTEM image. The same set of figures for an implantation energy of 60 keV, and a dose of  $3 \times 10^{14}$  cm<sup>-2</sup>, is shown in (d)–(f).

shows the Si displacement parameter determined by using k = 0.56 nm, c = 13.0 nm, and d = 14.0 nm to reproduce the experimental data in Fig. 4.3 (a). The XTEM in Fig. 4.3 (c) shows two single-crystalline regions, near the surface (0–3 nm) and deeper than 24 nm regions, and the amorphous region is sandwiched in between (3–24 nm). The displacement at the depths of 3 and 24 nm, where the transition between crystalline and amorphous occurs, coincides exactly with the critical displacement parameter 0.5 nm found in Fig. 4.2 (d). The structure becomes amorphous (as determined by XTEM) only when the displacement parameter exceeds the critical length of 0.5 nm. This also holds in another condition shown in Figs. 4.3 (d)–(f), where As ions are im-



**Figure 4.4** Depth profiles measured by SIMS of <sup>28</sup>Si (open circles) and <sup>30</sup>Si (filled-in circles) in the Si isotope SLs (a) before and after Sb implantation at an energy of 30 keV with a dose of  $1 \times 10^{14}$  cm<sup>-2</sup>. (b) The depth dependence of the displacement parameter  $\sigma(x)$  of the Si atoms induced by the Sb implantation. (c) XTEM image of the sample implanted with the same conditions with the depth scale, the same as (a)–(b).

planted at a higher energy, 60 keV, making the structure amorphous from the surface all the way to ~ 70 nm. We obtained k = 1.6 nm, c = 25.0 nm, d = 25.0 nm, and the displacement at ~ 70 nm shown in Fig. 4.3 (e) is 0.5 nm. Figure 4.4 shows SIMS profiles, the fitting result, and the XTEM image for antimony (Sb) implantation with 30 keV and  $1 \times 10^{14}$  cm<sup>-2</sup>. We obtained k = 1.1 nm, c = 9.5 nm, and d = 11.0 nm. The critical displacement parameter of ~ 0.5 nm was also obtained.

#### 4.4 Summary

We demonstrated direct observation of the Si displacement induced by As and Sb implantation using Si isotope SLs. A simulation based on the convolution integral was successfully developed to reproduce the experimental SIMS depth profiles of Si isotopes in the ion-implanted sample. We showed that it takes an average displacement parameter of ~ 0.5 nm to make the structure appear amorphous by XTEM. Incorporation of  $\sigma(x)$  into the next generation CMOS process simulator may prove to be useful in the improvement of the simulation reliability.

## Chapter 5

# Silicon Self-Interstitial Behavior during Transient Enhanced Diffusion

We investigated the contributions of neutral and charged Si self-interstitials to selfand B diffusion during transient enhanced diffusion in Si. We simultaneously observed self- and B diffusion in Si using  $^{nat}Si/^{28}Si$  isotope SLs. Calculations based on diffusion equations involving {311} defect and B-Si self-interstitial cluster models were employed to reproduce the diffusion profiles in Si-implanted (intrinsic) and B-implanted (extrinsic) Si isotope SLs followed by annealing. To investigate the diffusion processes, the time evolution of the Si self-interstitial profiles during the transient diffusion was simulated. In this chapter, we show that excess neutral self-interstitials dominantly enhanced self-diffusion during the transient process under intrinsic conditions, while doubly positively charged self-interstitials dominated the self-diffusion under *p*-type extrinsic conditions [Shimizu09].

#### 5.1 Introduction

Boron (B) implantation and post-annealing processes are widely used for the formation of p-type shallow junctions in Si electronic devices. For precise modeling of the behavior of B during the formation processes, thorough understanding of the diffusion mechanisms involving the charge states of native point defects and transient enhanced diffusion (TED) is required. Regarding TED, {311} self-interstitial clusters produced by B implantation and annealing are the sources of supersaturated Si selfinterstitial (I), which enhances B diffusion. In addition, B forms electrically inactive and immobile clusters even at concentrations far below the solubility limit under the supersaturation of I caused by ion implantation. TED of B in Si has been extensively investigated in experiments [Cowern90, Eaglesham94, Rafferty96, Stolk97, Jain02] and the reliable modeling of B diffusion in Si involving TED and B clustering has been published [Uematsu97a, Uematsu98a, Uematsu98b]. Regarding the I contribution involving its charge states, first-principles calculations under thermal-equilibrium conditions have been recently reported [Windl99, Windl08]. Under such conditions, recent studies revealed the contributions of the neutral, singly, and doubly positive I  $(I^0, I^+, \text{ and } I^{2+})$  and showed that  $I^{2+}$  dominates the self-diffusion under p-type doping conditions from simultaneous observations of dopants and Si atoms using Si isotope multilayers [Bracht07a, Bracht07b]. In order to develop a diffusion model involving I toward more precise process simulators, investigations of the behavior of the charge states of I are required, especially in the initial diffusion process, where TED occurs and the diffusion takes place under non-equilibrium native defect conditions. This chapter reports the contributions of neutral and charged I to self- and B diffusion during TED. Simultaneous observations of Si self- and B diffusion in Si isotope SLs were performed to understand how B and Si atoms, having charge states, interact. Based on the experimental diffusion profiles, we simulated the time evolution of  $I^0$ ,  $I^+$ , and  $I^{2+}$  during TED in Si- or B-implanted Si isotope SLs. We showed that the  $I^{2+}$  dominates self-diffusion in B-implanted SLs, *i.e.*, under *p*-type extrinsic conditions. In Si-implanted samples, *i.e.*, without the Fermi level effect,  $I^0$  dominantly enhances the self-diffusion during the transient process.

#### 5.2 Experiments

For both intrinsic and *p*-type conditions, a <sup>nat</sup>Si(10 nm)/<sup>28</sup>Si(10 nm) isotope SL was grown by SS-MBE [Kojima03, Shimizu06]. A high resistivity ( $\rho > 2000 \ \Omega$  cm), 2inch, *n*-type, {001}-oriented floating zone <sup>nat</sup>Si wafer was employed as a substrate. A <sup>nat</sup>Si buffer layer of ~ 100 nm-thick was grown prior to the growth of the isotope SL that is composed of alternating layers of <sup>nat</sup>Si and isotopically pure <sup>28</sup>Si. For the intrinsic conditions, <sup>28</sup>Si<sup>+</sup> ions were implanted at room temperature into the SL at an energy of 30 keV and a dose of  $3 \times 10^{14}$  cm<sup>-2</sup>. For simultaneous observations of B and Si, <sup>11</sup>B<sup>+</sup> ions were implanted with 12 keV and  $3 \times 10^{14}$  cm<sup>-2</sup>. The SL wafer was cut into  $5 \times 5$  mm<sup>2</sup> size squares for diffusion annealing at 850 °C (within  $\pm 2$  °C) in a resistance furnace in a pure argon (99.99%) atmosphere. The depth profiles of <sup>30</sup>Si and <sup>11</sup>B were obtained by SIMS.

#### 5.3 Diffusion Model

B diffusion in Si is primarily governed by a kick-out mechanism and B diffuses mainly via interstitial B or BI pairs, rather than B-vacancy (V) pairs [Gossmann97]. In addition, the V contribution to Si self-diffusion is negligibly small during TED because the I is supersaturated over 10<sup>4</sup> [Uematsu97b, Uematsu98a]. Therefore, we considered only the contribution of I in this study.

The B diffusion mechanism includes substitutional B ( $B_s$ ), interstitial B ( $B_i$ ), and *I*. Regarding the charge state of  $B_i$ , B isoconcentration diffusion experiments revealed that the B diffusivity is proportional to the B concentration [Miyake85], which shows that the charge difference between  $B_s^-$  and  $B_i$  is one. Therefore, we considered only  $B_i^0$ 

for the B diffusion. Regarding the charge states of I, B doping in Si increases the equilibrium concentration of positively charged I due to the Fermi level effect [Bracht07b]. In order to simulate the diffusion profiles, we basically used a diffusion model involving  $I^0$  and  $I^+$  as reported in the past [Uematsu97b, Uematsu98a, Uematsu98b]. The recent studies of simultaneous observations of self- and dopant diffusion in Si showed that the  $I^{2+}$  contribution to self-diffusion is also important for p-type Si [Bracht07a, Bracht07b]. Therefore, we introduced the contribution of  $I^{2+}$ , and thereby the parameters were slightly changed, where more reliable values were extracted by the fitting of B in-diffusion profiles, as has been done in Ref. [Uematsu97b].

The diffusion reactions involving  $B_s^-$ ,  $B_i^0$ ,  $I^0$ ,  $I^+$ , and  $I^{2+}$  can be described as:

$$\mathbf{B}_{i}^{0} \rightleftharpoons \mathbf{B}_{s}^{-} + \mathbf{I}^{0} + \mathbf{h}, \tag{5.1}$$

$$\mathbf{B}_{i}^{0} \rightleftharpoons \mathbf{B}_{s}^{-} + I^{+}, \tag{5.2}$$

$$\mathbf{B}_{i}^{0} + h \rightleftharpoons \mathbf{B}_{s}^{-} + I^{2+}, \tag{5.3}$$

$${}^{30}I^0 \rightleftharpoons {}^{30}\mathrm{Si}_s + I^0, \tag{5.4}$$

$${}^{30}I^+ \rightleftharpoons {}^{30}\mathrm{Si}_s + I^+,$$
 (5.5)

$${}^{30}I^{2+} \rightleftharpoons {}^{30}\mathrm{Si}_s + I^{2+}, \tag{5.6}$$

where *h* represents a hole.  $I^i$  and  ${}^{30}I^i$  denote the *I* of  ${}^{28}$ Si (matrix) and  ${}^{30}$ Si with the charge states of *i* (*i* = 0, +1, and +2), respectively.  ${}^{30}$ Si<sub>s</sub> represents a substitutional  ${}^{30}$ Si. These diffusion reactions, together with a kinetic equation to describe the time evolution of the self-interstitial cluster, allow the TED to be simulated by the following partial differential equations:

$$\frac{\partial C_{\mathbf{B}_s}}{\partial t} = G_1 + G_2 + G_3 - G_8, \tag{5.7}$$

$$\frac{\partial C_{\mathbf{B}_i}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\mathbf{B}_i} \frac{\partial C_{\mathbf{B}_i}}{\partial x} \right) - G_1 - G_2 - G_3, \tag{5.8}$$

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$$\frac{\partial C_{I^0}}{\partial t} = \frac{\partial}{\partial x} \left( D_{I^0} \frac{\partial C_{I^0}}{\partial x} \right) + G_1 - G_4 + G_5 - G_8, \tag{5.9}$$

$$\frac{\partial C_{I^+}}{\partial t} = \frac{\partial}{\partial x} \left( D_{I^+} \frac{\partial C_{I^+}}{\partial x} - D_{I^+} \frac{C_{I^+}}{p} \frac{\partial p}{\partial x} \right) + G_2 + G_6, \tag{5.10}$$

$$\frac{\partial C_{I^{2+}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{I^{2+}} \frac{\partial C_{I^{2+}}}{\partial x} - 2D_{I^{2+}} \frac{C_{I^{2+}}}{p} \frac{\partial p}{\partial x} \right) + G_3 + G_7, \tag{5.11}$$

$$\frac{\partial C_c}{\partial t} = G_4,\tag{5.12}$$

$$\frac{\partial C_{^{30}\mathrm{Si}_s}}{\partial t} = G_5 + G_6 + G_7,\tag{5.13}$$

$$\frac{\partial C_{30I^0}}{\partial t} = \frac{\partial}{\partial x} \left( D_{30I^0} \frac{\partial C_{30I^0}}{\partial x} \right) - G_5, \tag{5.14}$$

$$\frac{\partial C_{30_{I^+}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{30_{I^+}} \frac{\partial C_{30_{I^+}}}{\partial x} - D_{30_{I^+}} \frac{C_{30_{I^+}}}{p} \frac{\partial p}{\partial x} \right) - G_6, \tag{5.15}$$

$$\frac{\partial C_{30I^{2+}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{30I^{2+}} \frac{\partial C_{30I^{2+}}}{\partial x} - 2D_{30I^{2+}} \frac{C_{30I^{2+}}}{p} \frac{\partial p}{\partial x} \right) - G_7, \tag{5.16}$$

$$\frac{\partial C_{\mathbf{B}_{cl}}}{\partial t} = G_8,\tag{5.17}$$

where  $C_x$  ( $x = B_s$ ,  $B_i$ ,  ${}^{30}Si_s$ ,  $I^0$ ,  $I^+$ ,  $I^{2+}$ ,  ${}^{30}I^0$ ,  ${}^{30}I^+$ , and  ${}^{30}I^{2+}$ ) is the concentration of x, and  $D_x$  is the diffusivity of x.  $C_c$  represents the concentration of I trapped in the clusters, and  $C_{B_{cl}}$  is the B concentration in the BI clusters. p represents the hole concentration.  $G_1$ - $G_8$  represent the generation terms:

$$G_1 = k_{1f} C_{\mathbf{B}_i} - k_{1b} C_{\mathbf{B}_s} C_{I^0} p, (5.18)$$

$$G_2 = k_{2f} C_{\mathbf{B}_i} - k_{2b} C_{\mathbf{B}_s} C_{I^+}, \tag{5.19}$$

$$G_3 = k_{3f} C_{\mathbf{B}_i} p - k_{3b} C_{\mathbf{B}_s} C_{I^{2+}}, (5.20)$$

$$G_4 = k_{4f} C_c C_{I^0} - k_{4b} C_c, (5.21)$$

$$G_5 = k_{5f} C_{30I^0} - k_{5b} C_{30\mathrm{Si}_s} C_{I^0}, \tag{5.22}$$

$$G_6 = k_{6f} C_{30I^+} - k_{6b} C_{30}_{\mathrm{Si}_s} C_{I^+}, \tag{5.23}$$

$$G_7 = k_{7f} C_{^{30}I^{2+}} - k_{7b} C_{^{30}\text{Si}_s} C_{I^{2+}},$$
(5.24)

$$G_8 = -k_d C_{\mathbf{B}_{cl}},\tag{5.25}$$

where  $k_j$  (j = 1-7) is the rate constant with f and b denoting forward and backward

directions. For the initial profile of I in the  $\{311\}$  clusters,  $C_c$ , a "+1" model was used, where the implanted profiles are multiplied by a factor of 1.0 [Giles91]. In order to describe TED, we used the following model of the time evolution of {311} clusters during TED [Uematsu98a], which is involved in Eqs. (5.9) and (5.12). TED consists of two time regimes; the evolution is initially governed by Ostwald ripening of  $\{311\}$  clusters and then by the dissolution of  $\{311\}$  clusters. The essential parameters for the cluster evolution are the pseudo-equilibrium I concentration,  $C_I^*$ , the time dependence rate for cluster growth,  $k_{4f} = -at + b$ , and the dissolution rate,  $k_{4b}$ .<sup>1</sup> For the B clustering model, we used an analytical formula to estimate the initial profiles of clustered B, assuming the B clusters are formed during the very early stages of annealing [Uematsu98b]. For this simulation, we introduced  $k_d$ , which is defined as the rate constant of the dissolution of the B cluster involved in Eqs. (5.7), (5.9), and (5.17). The following parameter values at 850 °C were used for the simulation:  $C_I^* = 1.8 \times 10^{14} \text{ cm}^{-3}$ ,  $a = 5.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-2}$ ,  $b = 2.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ,  $k_{4b} = 1.3 imes 10^{-2} \ {
m s}^{-1}$ , and  $k_d = 6.7 imes 10^{-4} \ {
m s}^{-1}$ . Regarding the contribution of the charged I,  $D_{I^0}C_{I^0}^{\rm eq}/C_0 = 1.4 \times 10^{-19} \ {\rm cm}^2 \ {\rm s}^{-1}, \ D_{I^+}C_{I^+}^{\rm eq}/C_0 = 2.6 \times 10^{-20} \ {\rm cm}^2 \ {\rm s}^{-1},$ and  $D_{I^{2+}}C_{I^{2+}}^{eq}/C_0 = 2.7 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$  were used, where  $C_0$  represents the Si atom concentration,  $5.0 \times 10^{22}$  cm<sup>-3</sup>. These contributions of  $I^0$ ,  $I^+$ , and  $I^{2+}$  are in good agreement with those reported in the past [Bracht07b] and the sum of them is consistent with the results of the total contribution of I to self-diffusion [Bracht95]. In addition, for the total equilibrium concentration of I, we used the values from Ref. [Bracht95]. We simulated the diffused B profiles using B diffusivity under thermalequilibrium conditions [Naganawa08]. To simulate the simultaneous diffusion of B and Si, Eqs. (5.7)–(5.17) were solved numerically by the partial differential equation

<sup>&</sup>lt;sup>1</sup>The lower limit of  $k_{4f}$  is  $k_{4b}/C_I^*$ , and therefore,  $k_{4f} = -at + b$  dose not become smaller than zero [Uematsu97a].

solver ZOMBIE [Jüngling85]. In addition, we investigated the excess I under intrinsic conditions using Si-implanted SLs. In this case, there are no diffusion reactions described in Eqs. (5.1)–(5.3). Therefore,  $G_1$ – $G_3$  and  $G_8$  should be considered zero, and Eqs. (5.9)–(5.16) were solved numerically.

#### 5.4 Contribution of Self-Interstitials

#### 5.4.1 I<sup>0</sup> Contribution under Intrinsic Conditions

In order to investigate the behavior of the excess I during TED without the Fermi level effect, we performed Si self-implantation into the <sup>nat</sup>Si/<sup>28</sup>Si isotope SL. Figure 5.1 shows the depth profiles of  ${}^{30}$ Si in the  ${}^{28}$ Si<sup>+</sup>-implanted (30 keV,  $3 \times 10^{14}$  cm<sup>-2</sup>) Si isotope SLs followed by annealing at 850 °C for 1 and 4 h. The implanted <sup>28</sup>Si profiles were obtained by TRIM calculations [Ziegler85]. Here, <sup>nat</sup>Si layers have a natural abundance with 3.1% of <sup>30</sup>Si, whereas <sup>28</sup>Si layers are depleted of <sup>30</sup>Si. With such an implantation condition, the periodic depth profile of <sup>30</sup>Si is almost unperturbed after the implantation, in comparison with the profile of <sup>30</sup>Si before the implantation. Note that the actual interfaces between <sup>nat</sup>Si and <sup>28</sup>Si layers are abrupt (the degree of intermixing is only two atomic layers) [Kojima03, Shimizu06] and the smearing of the <sup>nat</sup>Si and <sup>28</sup>Si profiles is due to the SIMS artifact (knock-on mixing, *etc.*). This is the reason the SIMS concentration of  ${}^{30}$ Si in the  ${}^{28}$ Si layer was above  $\sim 10^{20}$  cm $^{-3}$ , even in as-grown SLs as shown in Fig. 5.1, although the concentration of <sup>30</sup>Si in the enriched  $^{28}$ Si layer was below 0.1%, which corresponds to the concentration of  $5 \times 10^{19}$  cm<sup>-3</sup>. In order to obtain a degree of smearing, we introduced the mixing roughness informationdepth (MRI) model that includes the parameters of atomic mixing and surface roughness for the theoretical description of the depth resolution function for SIMS profiles [Hofmann94]. We extracted the parameter values by comparison with the isotopic pro-



**Figure 5.1** SIMS depth profiles of <sup>30</sup>Si (upper profiles) in the <sup>nat</sup>Si/<sup>28</sup>Si isotope SLs implanted with <sup>28</sup>Si<sup>+</sup> at an energy of 30 keV, and a dose of  $3 \times 10^{14}$  cm<sup>-2</sup>. The upper broken line and solid lines represent the experimental profiles of as-grown and after annealing at 850 °C for 1 and 4 h, respectively. The implanted <sup>28</sup>Si<sup>+</sup> profile (lower profile) is calculated by TRIM.

files in as-grown Si isotope SL by SIMS, and a profile that initially has a rectangular shape using the MRI model. Using the MRI parameters, we simulated the diffusion profiles by SIMS as follows; diffusion calculations were started with the rectangular profiles, and then, the MRI analysis was applied to the calculated diffusion profiles to be compared with the SIMS profiles. In Fig. 5.1, the enhancement of Si self-diffusion is observed at a deeper region (> 40 nm) during the first 1 h annealing, compared with that of the diffusion near the surface, which will be explained later.

We simulated the Si isotope profiles in Fig. 5.1 based on the diffusion models described in the previous section and investigated the time evolution of I during this process. The simulated concentration profiles of I during 0–1 h annealing are drawn in Fig. 5.2. Under the intrinsic conditions, the contribution of  $I^0$  is larger than those of



**Figure 5.2** Simulated self-interstitial ( $I^0$ ,  $I^+$ , and  $I^{2+}$ ) profiles (lower lines) in Si-implanted (30 keV,  $3 \times 10^{14}$  cm<sup>-2</sup>) Si isotope SLs during annealing at 850 °C for 1 s, 60 s, and 1 h. The upper broken line and open circles represent the SIMS profiles before and after annealing at 850 °C for 1 h, respectively. The upper solid curve represents the simulation result.

 $I^+$  and  $I^{2+}$ . The  $I^0$  concentration has a value of  $C_I^* \sim 10^{14}$  cm<sup>-3</sup> at the initial stage (t = 1 s) with a flat profile in the bulk, whereas the value is going down to the  $C_I^{eq}$  toward the surface, which enhances the Si self-diffusion at the deeper region (> 40 nm), where the excess I is produced by the <sup>28</sup>Si<sup>+</sup> self-implantation. Although such an I supersaturation gradient between the implanted region and the surface by the measurement using B marker layers has been reported [Lampin03, Lamrani04], the present work reports the direct observation of the enhanced Si self-diffusion using Si isotope SLs. We also observed the I supersaturation gradient for annealing at 800 °C (not shown in the figures). At 60 s in Fig. 5.2, the excess  $I^0$  is decreased to  $10^{-3}$  compared with a value at 1 s. As diffusion annealing time increases, the  $I^0$  concentration approaches  $C_I^{eq}$ . As shown in Fig. 5.1, a slower self-diffusion was observed between 1 and 4 h, compared with that during 0–1 h, and our simulation shows that  $C_I$  is close to  $C_I^{eq}$  for longer annealing times, hence, the Si self-diffusion is in the thermal equilibrium. In conclusion, the excess  $I^0$  mainly enhances the Si self-diffusion during TED at the initial stage in the area deeper than the implanted region.

#### **5.4.2** *I*<sup>2+</sup> Contribution under Extrinsic Conditions

In order to investigate the *I* behavior under *p*-type conditions, we implanted <sup>11</sup>B<sup>+</sup> ions into the Si isotope SL. Figure 5.3 shows the depth profiles of <sup>30</sup>Si and <sup>11</sup>B in the <sup>nat</sup>Si/<sup>28</sup>Si isotope SLs implanted with B (12 keV,  $3 \times 10^{14}$  cm<sup>-2</sup>) followed by annealing at 850 °C for 1 h. The solid curves in Fig. 5.3 are the simulation results that accurately reproduce our experiments. While the depth oscillation of <sup>30</sup>Si is unperturbed before annealing, the annealing broadens its profile with a much larger diffusivity than the thermal-equilibrium self-diffusivity of Si at 850 °C, which we have precisely determined using similar isotope SLs [Shimizu07a]. Furthermore, the <sup>30</sup>Si profile is especially broadened in the region 50–80 nm in depth, from which we quantitatively



**Figure 5.3** SIMS and simulated depth profiles of <sup>30</sup>Si (upper profiles) and <sup>11</sup>B (lower profiles) in the <sup>nat</sup>Si/<sup>28</sup>Si isotope SLs implanted with <sup>11</sup>B<sup>+</sup> at an energy of 12 keV, and a dose of  $3 \times 10^{14}$  cm<sup>-2</sup>. The upper profiles represent the Si profiles before (broken line), and after annealing at 850 °C for 1 h (open circles), and the lower profiles are the corresponding B profiles. The solid curves are the simulation results.

estimate the degree of excess I. Note that this depth region 50–80 nm is away from the approximately 40 nm region, where the B concentration is the highest. Thus, the enhanced diffusion of <sup>30</sup>Si is not predominantly governed by the Fermi level effect. Although it has been shown that the excess I induces the anomalous diffusion of implanted B [Cowern90, Eaglesham94, Stolk97, Jain02], this is a direct observation of the enhanced Si self-diffusion in a B-implanted Si.

In Fig. 5.4, the simulated concentration profiles of I at 850 °C for 5 s and 1 h are drawn with the corresponding B profiles. From the simulation, TED of B is observed within 1 h of annealing. Regarding the I concentrations during TED,  $I^{2+}$  dominates in the 0–70 nm region at the initial stage (t < 5 s), whereas  $I^0$  is still higher in the region deeper than 70 nm from the surface. Our simulation reveals high concentrations of both  $I^{2+}$  and  $I^0$ , which broaden the <sup>30</sup>Si profile in the shallower and deeper region at the very initial stage, respectively. As the annealing time increases, the excess  $I^0$ ,  $I^+$ , and  $I^{2+}$  decrease as compared with the values at 5 s. Then, the Fermi level effect becomes more significant with time because the B<sub>s</sub> concentration increases by the dissolution of the B clusters. Therefore, the concentration of  $I^{2+}$  becomes relatively dominant, especially near the surface, compared with those of  $I^0$  and  $I^+$ , that is, the  $I^{2+}$  dominantly enhances Si self-diffusion in the high concentration B region.

Furthermore, we simulated the profiles after 4 h annealing. Figures 5.5 (a) and 5.5 (b) show the depth profiles of <sup>30</sup>Si and <sup>11</sup>B after the annealing at 850 °C for 4 h, respectively. These SIMS profiles are well reproduced by the simulation using the same set of parameters for 1 h. In Fig. 5.5 (c), the simulated *I* profiles are shown, where the concentrations of  $I^0$ ,  $I^+$ , and  $I^{2+}$  are almost in thermal equilibrium. The Fermi level effect is still dominant for 1–4 h annealing and TED was not observed for annealing longer than 1 h because the excess *I* diffuses away from the B region into the Si bulk within 1 h of annealing. However, the concentrations of *I* are still



**Figure 5.4** Simulated self-interstitial ( $I^0$ ,  $I^+$ , and  $I^{2+}$ ) profiles (lower lines) in B-implanted (12 keV,  $3 \times 10^{14} \text{ cm}^{-2}$ ) Si isotope SLs after annealing at 850 °C for 5 s and 1 h. The solid, broken, and dotted lines represent the profiles of  $I^0$ ,  $I^+$ , and  $I^{2+}$ , respectively. In the upper region, the corresponding B profiles are shown.



**Figure 5.5** (a) SIMS and simulated depth profiles of  ${}^{30}$ Si in the  ${}^{nat}$ Si/ ${}^{28}$ Si isotope SLs implanted with  ${}^{11}B^+$  at an energy of 12 keV, and a dose of  $3 \times 10^{14}$  cm<sup>-2</sup>. The broken line and open circles represent the SIMS profiles before and after annealing at 850 °C for 4 h, respectively. (b) The corresponding B profiles in the Si isotope SLs. (c) Simulated self-interstitial ( $I^0$ ,  $I^+$ , and  $I^{2+}$ ) profiles in the B-implanted Si isotope SLs after annealing at 850 °C for 4 h. The solid, broken, and dotted lines represent the profiles of  $I^0$ ,  $I^+$ , and  $I^{2+}$ , respectively.

above the equilibrium values, even after 4 h. This is quite a contrast to the I in the Si-implanted samples, where the concentrations of I go down to the equilibrium states for 1 h as shown in Fig. 5.2. The I supersaturation in the B-implanted samples can be explained by the flux ratios between I and  $B_i$ . Supersaturation develops when  $D_I C_I^{eq} / D_{B_i} C_{B_i}^{eq} < 1$ , which indicates that I diffuses out slower than  $B_i^0$  diffuses in, to become  $B_s^-$  [Uematsu97a]. This flux balance generates an I supersaturation in the deep region [Uematsu97a, Bracht07a, Bracht07b] as shown in Fig. 5.5 (c).

#### 5.5 Summary

We presented the contribution of I to the self- and B diffusion in Si during TED. Simultaneous observations of the diffusion in Si- or B-implanted <sup>nat</sup>Si/<sup>28</sup>Si isotope SLs were performed and the behavior of neutral and charged I was investigated. Calculations based on the diffusion equations involving {311} defect and BI cluster models were employed to reproduce the diffusion profiles of Si isotopes. We simulated the time evolution of the I profiles during the transient process to investigate the diffusion processes of Si isotopes in the ion-implanted SLs. The results directly demonstrated that the excess  $I^0$  dominantly enhances self-diffusion during TED under intrinsic conditions, and that  $I^{2+}$  dominates the self-diffusion under extrinsic conditions. These simultaneous observations of the self- and B diffusion in Si isotope SLs involving the time evolution of the  $I^0$ ,  $I^+$ , and  $I^{2+}$  reveal the interactions between B and Si atoms during TED. The details of diffusion interactions between charged B and I into the next generation CMOS process simulators will be useful in the improvement of simulation reliability.

# Chapter 6 Conclusion

The present thesis reported nanoscale investigations of the host Si behavior related closely to the control of the source/drain fabrication processes in advanced CMOS. In particular, 1) determination of Si self-diffusivity below 900 °C and identification of the microscopic picture of self-diffusion, 2) determination of Si displacement lengths induced by collision with ion-implanted dopants and criteria for amorphization by implantation, and 3) evaluation of time-dependent Si self- and dopant diffusion enhancement by excess Si point defects created by ion implantation (transient enhanced diffusion) were performed experimentally. Moreover, complete numerical modeling of each process has been achieved for process simulation. Each conclusion is described as follows.

In Study 1), we determined Si self-diffusivity at temperatures 735–875 °C based on a Raman shift of longitudinal optical phonon frequencies of diffusion annealed  $^{28}$ Si/ $^{30}$ Si isotope SLs. The activation enthalpy of 3.6 eV is obtained at such low temperature diffusion annealing. This value is significantly smaller than the previously reported 4.95 eV of the self-interstitial mechanism dominating the high temperature region T >> 855 °C, and closely agrees with the theoretical prediction for vacancymediated diffusion. We showed a model containing both self-interstitial and vacancy terms that quantitatively describes the experimentally obtained self-diffusivity between 735 and 1388  $^{\circ}$ C, with a clear cross-over of the two diffusion mechanisms occurring around 900  $^{\circ}$ C.

In Study 2), we established a new method for quantitatively evaluating the Si displacement as a function of the depth from the surface induced by As implantation into a Si wafer. A simulation based on a convolution integral was successfully developed to reproduce the experimental depth profiles of isotopes in the As-implanted  $^{28}$ Si/ $^{30}$ Si isotope SLs, from which the average distances of the Si displacements due to the collisions with implanted As were obtained. We showed that it took an average displacement parameter of ~ 0.5 nm to make the structure appear amorphous.

In Study 3), we investigated the contributions of neutral and charged Si selfinterstitials to self- and B diffusion during transient enhanced diffusion in Si. We simultaneously observed self- and B diffusion in Si using <sup>nat</sup>Si/<sup>28</sup>Si isotope SLs. Calculations based on diffusion equations involving {311} defect and B-Si self-interstitial cluster models were employed to reproduce the diffusion profiles in Si-implanted (intrinsic) and B-implanted (extrinsic) Si isotope SLs followed by annealing. To investigate the diffusion processes, the time evolution of the Si self-interstitial profiles during the transient diffusion was simulated. The results directly demonstrated that excess neutral self-interstitials dominantly enhance self-diffusion during the transient process under intrinsic conditions, while doubly positively charged self-interstitials dominate the self-diffusion under *p*-type extrinsic conditions.

Our findings in part have already been applied to CMOS commercial process simulators that are widely employed in semiconductor industries. The importance of understanding of Si nanoscience is expected to grow along with the further advancement of Si electronics.

## Appendix A

# A Standard Sample for Secondary Ion Mass Spectrometry

In Chapter 2, we presented growth and characterization of Si isotope SLs that are composed of alternating layers of different isotopes. This structure is believed to be the most ideal SIMS standard sample for dopant concentration depth profiling required for characterization of the shallow junction formed by ion implantation, because the precisely stacked alternating layers of Si isotopes function as a depth ruler. Therefore, it enables us to calibrate the depth scale of dopant, based on the positions of Si isotopes. The aim of this appendix is to briefly describe SIMS standards [Shimizu08b].

#### A.1 Introduction

B and As implantation are widely used for the formation of shallow junctions in Si transistors. The depth profiles of dopants are routinely obtained by a SIMS technique [Clegg87, Eto05]. The determination of dopant distributions in shallow junctions of source/drain region in CMOS devices becomes critical, especially near the surface region because the precise profiles of dopants are not well understood in such a transient region. The profile shape strongly depends on the energy and incident angle of

a primary ion due to the atomic mixing. It has been reported that an accurate profile shape of dopant is obtained by the reduction of the primary ion energy during SIMS measurement [Dowsett03]. Furthermore, changing incident angles, backside-SIMS measurements, and mathematical deconvolution techniques have been studied extensively in order to obtain a real profile shape [Hongo04, Vandervorst04, Yang06]. Another problem is that the sputtering rate variation distorts the depth scale calibrated by the sputtering time and the crater depth because the sputtering rate is assumed to be constant during SIMS measurements. In the past, a multi-delta-layer sample, such as B delta-doped Si, was employed to evaluate the sputtering rate variations. The study revealed that variation was caused near the surface region [Magee98, Schueler00, Homma03, Tomita03, Tomita04]. However, the problem of the change in sputtering rate between the matrix Si and delta-doped B region disqualifies such B-delta-layer samples to be the ideal SIMS standards. This prompted Wittmaack and Poker to utilize alternating layers of Si isotopes that guaranteed a constant sputtering rate throughout the doped region [Wittmaack90]. Naturally available Si is composed of three stable isotopes in fixed proportions (<sup>28</sup>Si: 92.2%, <sup>29</sup>Si: 4.7%, <sup>30</sup>Si: 3.1%), *i.e.*, isotopic separation followed by alternating depositions leads to formation of a Si single crystal with alternating mass variations. Although Wittmaack and Poker employed ion beam deposition to form alternating Si isotope layers, which most likely lead to poor crystalline quality, their proof-of-concept experiments to apply Si isotopes as SIMS depth markers were very successful [Wittmaack90]. Our isotope SL has been prepared by SS-MBE and guarantees the crystallinity is as good as that of commercial Si wafers [Kojima03, Shimizu06]. Therefore, it allows for shallow SIMS depth profiling with a constant sputtering rate. Our much short periodicity of isotope SLs than those reported in Ref. [Wittmaack90] enables shallow SIMS depth profiling. Implantation of dopants into the Si isotope SLs, followed by SIMS analysis, enables
simultaneous observations of the dopant and alternating Si isotope marker depth profiles. Therefore, the isotope depth marker enables us to calibrate the depth scale of the dopant profiles. Furthermore, the sample is useful for the calibration of the atomic mixing because our Si isotope SL has an interface abruptness better than two atomic monolayers. The smearing of the SIMS profile between adjacent Si isotope layers originates from the SIMS atomic mixing, rather than from sample itself. Thus, this appendix presents a short-period Si isotope SL structure that we believe to be the most ideal SIMS standard sample for dopant concentration depth profiling required for the characterization of the shallow junction formed by ion implantation.

#### A.2 Shallow Junction Characterization

Figure 2.3 shows the SIMS depth profiles of <sup>28</sup>Si, <sup>29</sup>Si, and <sup>30</sup>Si in the 15-period <sup>28</sup>Si/<sup>30</sup>Si isotope SL (d = 2.7 nm). The primary ion condition was Cs<sup>+</sup> 1 keV at 45°. As expected, the oscillations of <sup>28</sup>Si and <sup>30</sup>Si are clearly observed as a function of the depth to ~ 80 nm. Depletion of the <sup>29</sup>Si concentration is also confirmed. <sup>nat</sup>Si layer appears in the region deeper than ~ 80 nm. Note that every <sup>28</sup>Si/<sup>30</sup>Si interface has the abruptness of the order 0.3 nm (interdiffusion corresponding to less than two atomic monolayers) [Shimizu06]. The average thicknesses of Si isotope layers are determined independently by Raman spectroscopy. When we increased the primary ion energies ranging from 1 to 5 keV, the amplitudes of the SIMS intensity oscillations of the <sup>28</sup>Si and <sup>30</sup>Si profiles became smaller due to the atomic mixing. Therefore, the rounding (smearing) of the <sup>28</sup>Si and <sup>30</sup>Si profiles in Fig. 2.3 allows us to quantitatively analyze the degree of unwanted atomic mixing during SIMS measurements (SIMS artifacts). The depth profiles of <sup>28</sup>Si and <sup>30</sup>Si alternate with the periodicity 2d = 5.4 nm in accordance with our design, and they serve as ideal depth scales.



**Figure A.1** SIMS depth profiles of <sup>30</sup>Si in the primary ions of Cs<sup>+</sup> at energies of (a) 1 keV and (b) 5 keV. w = 2.5 nm and s = 0.7 nm in (a), w = 4.4 nm and s = 1.3 nm in (b) are used to obtain good agreements with SIMS results, respectively.

Figure A.1 shows SIMS depth profiles of <sup>30</sup>Si in the primary ions of Cs<sup>+</sup> at energies of 1 and 5 keV. In order to fit with SIMS results, we used the MRI parameters, w =2.5 nm and s = 0.7 nm for 1 keV of Cs<sup>+</sup> sputtering, w = 4.4 nm and s = 1.3 nm for 5 keV. As expected, higher sputtering energies give strong mixing during the SIMS measurements. Such SIMS mixing parameters are deduced from B-delta doped Si at various SIMS conditions so far (*e.g.*, [Hayashi03, Takano03]). These parameters are constant up to the end of the isotope oscillations, showing that the SIMS mixing doesn't depend on the depth up to ~ 80 nm at least. Our values are more reliable because we use a homogeneous material. Si isotope SLs are the best samples for the investigations of the degree of mixing during the SIMS sputtering.

Lastly, Fig. 4.1 (b) shows the depth profiles of <sup>28</sup>Si, <sup>30</sup>Si, and <sup>75</sup>As in the SL im-

planted by As ions at an energy of 25 keV with a dose of  $1 \times 10^{15}$  cm<sup>-2</sup>. Now a part of the profiles is perturbed by the large number of implanted As, and therefore, the <sup>28</sup>Si and <sup>30</sup>Si periodicities from the surface to 50 nm are heavily altered. When we implanted As ions at much lower dose conditions, the perturbation of the <sup>28</sup>Si and <sup>30</sup>Si profiles became smaller due to little atomic mixing during the As implantation. Here, we stress that the remaining alternating profiles of <sup>28</sup>Si and <sup>30</sup>Si continue to serve as the excellent and complete depth scales for implanted As and the altered profiles from the surface to 50 nm allows precise calculations on how much in length Si atoms are displaced as a function of the depth. Evaluation of the Si mixing by As implantation using this isotope structure is reported elsewhere [Shimizu07b, Shimizu08a].

# Appendix B

### **Diffusion Theory**

This aim of this appendix is to give a solution of diffusion equation. Solutions of diffusion equations, giving the concentration as a function of time and position, can be obtained by various means once the boundary and initial conditions have been specified.

#### **B.1** Solution of Fick's Diffusion Law

In Chapter 3, we showed Eq. (3.3). Fick's second diffusion law [Fick1855]

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2},\tag{B.1}$$

This equation is deduced from the Fick's diffusion law. We solve the partial differential equation (PDE) in this appendix. In general, the equation is solved using the Laplace transformation (*e.g.*, [Mehrer07]). The Fourier transformation is a mathematical procedure, which is useful for various problems in mathematical physics. Application of the Fourier transformation to the diffusion equation removes the time variable, leaving an ordinary differential equation (ODE), the solution of which yields the transform of concentration field. This is then interpreted to give an expression for the concentration in terms of space variables and time, satisfying the initial and boundary conditions.

Here, we deal only with an application to the one-dimensional diffusion equation.

Let us suppose that the concentration has an initial distribution at t = 0 which is given by:  $-\infty < x < \infty$ ,  $0 < t < \infty$ , initial condition  $C(x,0) = \phi(x)$ . A Fourier transform  $\tilde{C}(\xi,t)$  of a known function C(x,t) for positive/negative values of x is defined as

$$\tilde{C}(\xi,t) = \int_{-\infty}^{\infty} C(x,t)e^{-j\xi x}dx.$$
(B.2)

The reverse transformation is defined as

$$C(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{C}(\xi,t) e^{j\xi x} d\xi.$$
 (B.3)

As an application of the Fourier transform, we consider diffusion ranging  $-\infty < x < \infty$ , when the initial conditions  $C(x, 0) = \phi(x)$ . On multiplying both sides of Fick's second law [Eq. (B.1)] by  $e^{-j\xi x}$  and integrating, we obtain

$$\int_{-\infty}^{\infty} \frac{\partial C(x,t)}{\partial t} e^{-j\xi x} dx = \int_{-\infty}^{\infty} D \frac{\partial^2 C(x,t)}{\partial x^2} e^{-j\xi x} dx.$$
 (B.4)

By interchanging the orders of differentiation and integration, the left-hand term is then

$$\int_{-\infty}^{\infty} \frac{\partial C(x,t)}{\partial t} e^{-j\xi x} dx = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} C(x,t) e^{-j\xi x} dx$$

$$= \frac{\partial \tilde{C}(x,t)}{\partial t}.$$
(B.5)

Integrating the right-hand term of Eq. (B.4) is then

$$\int_{-\infty}^{\infty} D \frac{\partial^2 C(x,t)}{\partial x^2} e^{-j\xi x} dx = D \int_{-\infty}^{\infty} \frac{\partial^2 C(x,t)}{\partial x^2} e^{-j\xi x} dx$$
$$= D(j\xi)^2 \int_{-\infty}^{\infty} C(x,t) e^{-j\xi x} dx \qquad (B.6)$$
$$= -D\xi^2 \tilde{C}(\xi,t).$$

Thus Fick's second equation transforms to

$$\frac{\partial \tilde{C}(\xi,t)}{\partial t} = -D\xi^2 \tilde{C}(\xi,t).$$
(B.7)

The Fourier transformation reduces Fick's second law from a PDE to an ODE Eq. (B.7). When an initial profile is given  $C(x, 0) = \phi(x)$ , and the Fourier transformation of  $\phi(x)$  is written by  $\Phi(\xi)$ , Eq. (B.7) can be solved. Then we obtain

$$\tilde{C}(\xi,t) = \Phi(\xi)e^{-D\xi^2 t}.$$
(B.8)

We apply the reverse Fourier transformation to Eq. (B.8), then we obtain C(x, t). The process is as follows;

$$C(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi(\xi) e^{-D\xi^{2}t} e^{j\xi x} d\xi$$
  

$$= \phi(x) * \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-D\xi^{2}t} e^{jx\xi} d\xi$$
  

$$= \phi(x) * \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-D\xi^{2}t} (\cos x\xi + j \sin x\xi) d\xi$$
  

$$= \phi(x) * \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-D\xi^{2}t} \cos x\xi d\xi$$
  

$$= \phi(x) * \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^{2}}{4Dt}}$$
  

$$= \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} \phi(z) e^{-\frac{(x-z)^{2}}{4Dt}} dz.$$
  
(B.9)

During the calculation, we employed

$$\int_{-\infty}^{\infty} e^{-ay^2} \cos 2aby \, dy = \sqrt{\frac{\pi}{a}} e^{-ab^2},\tag{B.10}$$

$$f(x) * g(x) = \int_{-\infty}^{\infty} f(z)g(x-z) dz.$$
 (B.11)

We used Eq. (B.9) for our diffusion study.

#### **B.2** Isotope Profile in a Silicon Isotope Superlattice

Let us suppose that the concentration has an initial distribution at t = 0, C(x, 0), in a Si isotope SL as illustrated in Fig. B.1. The initial profile is given by

$$C(x,0) = \begin{cases} C_H & (k-1)d_H + kd_L < x \le kd_H + kd_L & (1 \le k \le m), \\ C_L & \text{otherwise}, \end{cases}$$
(B.12)



Figure B.1 Si isotope profile in a Si isotope SL. See the details in the text.

where  $C_H$  and  $C_L$  represent the high and low concentrations of the isotope (<sup>28</sup>Si or <sup>30</sup>Si), respectively.  $d_H$  and  $d_L$  represent the thicknesses of the concentrations of the  $C_H$  and  $C_L$ , respectively, in a Si isotope SL. m represents the number of periodicity. If we consider a <sup>30</sup>Si profile in a [<sup>28</sup>Si( $d_H$ )/<sup>30</sup>Si( $d_L$ )]<sub>m</sub> isotope SL (having the top layer of <sup>28</sup>Si),  $C_H$  and  $C_L$  correspond to the concentration of <sup>30</sup>Si. Under this initial condition, we solve Eq. (B.9). We pay attention to the integral area as follows;

$$C(x,t) = \frac{1}{2\sqrt{\pi Dt}} \left( C_L \int_{-\infty}^{d_L} e^{-\frac{(x-z)^2}{4Dt}} dz + C_H \int_{d_L}^{d_H+d_L} e^{-\frac{(x-z)^2}{4Dt}} dz + \cdots \right)$$
  
$$\cdots + C_L \int_{(m-1)d_H+(m-1)d_L}^{(m-1)d_H+md_L} e^{-\frac{(x-z)^2}{4Dt}} dz + C_H \int_{(m-1)d_H+md_L}^{md_H+md_L} e^{-\frac{(x-z)^2}{4Dt}} dz$$
  
$$+ C_L \int_{md_H+md_L}^{\infty} e^{-\frac{(x-z)^2}{4Dt}} dz \right).$$
  
(B.13)

Here, we used the variable substitution:

$$\eta = \frac{x - z}{2\sqrt{Dt}},\tag{B.14}$$

$$d\eta = -\frac{dz}{2\sqrt{Dt}}.$$
 (B.15)

In addition, it is convenient to introduce the error function. Eq. (B.16) is the so-called error function

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta,$$
 (B.16)

which is a standard mathematical function. Using Eqs. (B.14)–(B.16), Eq. (B.13) may be split and rearranged as

$$\begin{split} C(x,t) \\ &= -\frac{C_L}{\sqrt{\pi}} \int_{\infty}^{\frac{x-d_L}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \frac{C_H}{\sqrt{\pi}} \int_{\frac{x-d_H}{2\sqrt{Dt}}}^{\frac{x-(d_H+d_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \cdots \\ &\cdots - \frac{C_L}{\sqrt{\pi}} \int_{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}}^{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \frac{C_H}{\sqrt{\pi}} \int_{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}}^{\frac{x-(md_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \\ &- \frac{C_L}{\sqrt{\pi}} \int_{\frac{x-(md_H+md_L)}{2\sqrt{Dt}}}^{-\infty} e^{-\eta^2} d\eta \\ &= \frac{C_L}{\sqrt{\pi}} \left[ \int_{0}^{\infty} e^{-\eta^2} d\eta - \int_{0}^{\frac{x-d_L}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \right] + \frac{C_H}{\sqrt{\pi}} \left[ \int_{0}^{\frac{x-d_L}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \int_{0}^{\frac{x-(d_H+d_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \right] + \cdots \\ &\cdots + \frac{C_L}{\sqrt{\pi}} \left[ \int_{0}^{\frac{x-((m-1)d_H+(m-1)d_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \int_{0}^{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \right] \\ &+ \frac{C_H}{\sqrt{\pi}} \left[ \int_{0}^{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \int_{0}^{\frac{x-((m+1)d_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \right] \\ &+ \frac{C_L}{\sqrt{\pi}} \left[ \int_{0}^{\frac{x-((m-1)d_H+md_L)}{2\sqrt{Dt}}} e^{-\eta^2} d\eta - \int_{0}^{-\infty} e^{-\eta^2} d\eta \right] \end{split}$$

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$$= \frac{C_L}{2} \left[ \operatorname{erf}\left(\infty\right) - \operatorname{erf}\left(\frac{x - d_L}{2\sqrt{Dt}}\right) \right] + \frac{C_H}{2} \left[ \operatorname{erf}\left(\frac{x - d_L}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x - (d_H + d_L)}{2\sqrt{Dt}}\right) \right] + \cdots + \frac{C_L}{2} \left[ \operatorname{erf}\left(\frac{x - \{(m-1)d_H + (m-1)d_L\}}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x - \{(m-1)d_H + md_L\}}{2\sqrt{Dt}}\right) \right] + \frac{C_H}{2} \left[ \operatorname{erf}\left(\frac{x - \{(m-1)d_H + md_L\}}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x - (md_H + md_L)}{2\sqrt{Dt}}\right) \right] + \frac{C_L}{2} \left[ \operatorname{erf}\left(\frac{x - (md_H + md_L)}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(-\infty\right) \right] \\ = C_L + \frac{C_H - C_L}{2} \sum_{k=1}^m \left[ \operatorname{erf}\left(\frac{x - \{(k-1)d_H + kd_L\}}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x - (kd_H + kd_L)}{2\sqrt{Dt}}\right) \right]. \tag{B.17}$$

In this work, we introduced a mixing parameter l [Shimizu06], therefore, we replaced  $2\sqrt{Dt}$  with  $2(l + \sqrt{Dt})$ ;

$$C(x,t) = C_L + \frac{C_H - C_L}{2} \sum_{k=1}^m \left[ \operatorname{erf} \left( \frac{x - \{(k-1)d_H + kd_L\}}{2(l + \sqrt{Dt})} \right) - \operatorname{erf} \left( \frac{x - (kd_H + kd_L)}{2(l + \sqrt{Dt})} \right) \right],$$
(B.18)

which could lead to Eq. (3.3).

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