Antimony implanted strained Si for nMOSFET applications

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Abstract

Incorporation of implanted antimony (Sb) in strained-silicon (s-Si) formed on relaxed-SiGe virtual substrates (10 and 30% Ge) has been studied. The implantation doses were $5 \times 10^{13} - 5 \times 10^{14}$ cm$^{-2}$ with an energy of 20 keV. The activation of dopant was performed by a rapid thermal annealing (RTA) treatment at 700 and 800 °C for 30 sec. Projected range of this implantation is about 20 nm which was also confirmed by different techniques. The layers were analyzed in terms of strain relaxation, sheet resistance, thermal stability, defect generation and dopant incorporation. X-ray diffraction (XRD), high-resolution reciprocal lattice mapping (HRRLM), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), Rutherford backscattering (RBS), four-probe measurements and Hall measurements were applied as characterization tools. This work demonstrates that the Sb incorporation in Si has improved in the presence of strain. The strain amount in s-Si does not alter after implantation or subsequent thermal treatment for dopant activation. The Sb-implanted s-Si layer on Si$_{0.70}$Ge$_{0.30}$ virtual substrate ($5 \times 10^{14}$ cm$^{-2}$ 700 °C, 30 sec RTA) demonstrated substitutional Sb concentration of $2.5 \times 10^{20}$ cm$^{-3}$ where the same dose for a Si reference sample could only show $1 \times 10^{20}$ cm$^{-3}$. The fraction of active-to-atomic concentration of Sb-implanted Si was estimated nearly to 90%. HRTEM micrographs of Sb-implanted annealed samples illustrate almost defect-free material.
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1. INTRODUCTION

Strain engineering is an important field to tailor the carrier transport in optical and electrical devices. This can be realized for Si materials by inducing tensile strain when the electron mobility is intended to be increased. The strained Si is obtained when the layer is deposited on a relaxed SiGe [1-2], or it is buried under a stressor material such as a nitride layer [3-4]. The strained Si is used for instance as channel layer in nMOSFETs, where a high electron mobility is required.

Although the issue of strain and mobility is well studied, there are still problems to handle the implantation steps in the process flow. The problem rises for the choice of appropriate dopant material with high incorporation and low thermal diffusivity to form the source/drain junctions. So far, the implanted dopants are boron for p-MOSFET and arsenic or phosphorous for n-MOSFETs. A rapid thermal annealing (RTA) treatment is followed afterwards to activate the implanted dopants [5], and the effect on implanted strained layers is also an open issue.

One of the main problems for CMOS manufacturing is the diffusion of dopants from the S/D regions. A low diffusive dopant element is mainly preferred to create steep profiles. Antimony is a candidate as a replacement for previous dopants (arsenic or phosphorous) for n-MOSFET due to its low diffusivity [6-7]. Both arsenic and phosphorous have the same size as Si. Therefore they cannot compensate any strain, but Sb as a large atom induces compressive strain which can compensate the tensile strain in Si.

This work reports on the investigation of structural and electrical properties of Sb-doped tensile strained Si produced by chemical vapor deposition and ion implantation. Sb implantation in Si structures has been considered as an optional method to deposit group IV elements. The main goal is to find an appropriate implantation energy, dose and rapid thermal annealing to maximize Sb incorporation and activation in strained Si. Strain relaxation, defect generation, and dopant incorporation are the main issues. The samples were characterized by X-ray, high-resolution reciprocal lattice mapping, transmission electron microscopy, four probe technique, Hall measurement and secondary ion mass spectrometry and Rutherford back scattering.
2. STRAINED GROUP-IV MATERIALS

2.1 Strained Silicon:

The major idea in strained Si CMOS is to change the carrier transport properties of Si by introducing strain in order to develop the performance of MOSFETs. The concept biaxial and uniaxial strain can be used in the channel or in the source and drain regions in MOSFETS to increase the carrier mobility. Biaxial tensile strain in the strained Si layer can be achieved by epitaxial growth on relaxed virtual SiGe substrate and the strain can be modified by the Ge content.

In general biaxial strain is introduced by the incorporation of relaxed Si$_{1-x}$Ge$_x$ buffer layers. The relaxed buffer layers of Si$_{1-x}$Ge$_x$ are described as virtual substrates, which create a larger crystal lattice constant than a Si substrate, and are typically used as epitaxial pattern for depositing Si layers in a status of biaxial tensile strain [3-4]. Mainly Si$_{1-x}$Ge$_x$ or strained-Si layers have been integrated either in S/D areas or in the channel region, see Figure 1a, b respectively. By biaxial strain we mean a lattice distortion in two dimensions (or plane) whereas uniaxial strain can be induced by two stressors on two sides of a crystal. Chemical vapor deposition (CVD) provides a unique possibility for the growth of strained layers for device application. One of the most beneficial outputs from this epitaxial technique is selective deposition. With this we mean deposition only on the exposed silicon areas in the oxide openings on a patterned substrate.

One of the integration issues of selective epitaxy in device is a lack of control of Ge or B amount in the SiGe layers due to the pattern dependency of epitaxy. This is very important point since Ge and B are the main elements for inducing strain in Si matrix. A novel approach has been proposed recently by Intel [3], based on applying stressor material on the CMOS structures. This was realized for pMOSFETs by an etch step followed by selective epitaxy of B-doped SiGe layer and for nMOSFETs deposition of a nitride layer was proposed. The results demonstrated an increase of hole mobility of 50% in pMOSFETs and electron mobility of 20% in nMOSFET with 45 nm gate length.
2.1.1 The influence of strain on Si band structure

Carbon, silicon and germanium belong to group IV with diamond crystal structure and they may be mixed to form alloys. The SiGe alloy has also a diamond structure but its electrical and optical properties differ from both Si and Ge. Since the Ge atoms are larger than Si, the lattice constant of SiGe becomes larger than for Si. An epitaxial growth of SiGe on Si substrate induces a compressive strain. In contrary, a relaxed SiGe can be used as a virtual substrate to grow a tensile strained-Si layer. A schematic drawing of these types of strain, compressive and tensile strain is shown in Figure 2.

![Figure 2](image-url)

**Figure 2:** a) A schematic illustration of bulk SiGe and Si b) Inducing the strain on substrate with a larger lattice constant than the grown layer on it (compressive strain). c) Inducing the strain on substrate with a smaller lattice constant than the grown layer on it (tensile strain) [8]
The interesting benefit of generating strain in Si matrix is bandgap engineering. Si and Ge have an indirect bandgap of 1.1 and 0.66 eV respectively. Then SiGe alloy has a bandgap in range 1.1-0.66 eV which was constituted asymmetrically. The effect of compressive strain is on light and heavy hole (LH and HH) band together with spin-orbit splitting. The heavy hole band is shifted upwards and change the curvature into light-hole band. The original light-hole bands also change their character to become heavy holes. The induced strain shifts furthermore the spin-orbit splitting band (see Figure 3). The SiGe/Si system forms a quantum well at the interface due to the band off-set between the valence band of Si and SiGe layer. If we have a transport of holes along this quantum well the scattering phenomena are reduced remarkably and a two-dimensional hole gas (2DHG) is created. In the SiGe band diagram, the conduction band feature does not change at all. The SiGe/Si can be applied in pMOSFETs design as channel and the hole mobility is increased [9].

![Figure 3: a) A schematic drawing of the valence band of Si and SiGe. b) Tensile strain splits the valence band heavy hole / light hole degeneracy lift up at Γ. As a result interband scattering is reduced and a result of band deformation there is a smaller in-plane transport mass](image)

In general, the conduction band of Si consists of six-electron pockets along the [100] [010] (in- plane) and [001] (out of plane direction), these valleys have equal energy Δ₆ as shown in Figure 4a. The effective mass is the reciprocal of the curvature of the electron energy in any direction. So the effective mass related to Si conduction band is anisotropic in each ellipsoid, with the transverse mass (perpendicular to the axis) given by \( m_t = 0.19m_0 \) and longitudinal mass (parallel to the axis) given by \( m_l = 0.98m_0 \), where \( m_0 \) is the free electron mass. The growth of a Si layer on a relaxed-SiGe results in tensile strain in the Si layer. The tensile-strained Si layer experiences a change in the constant energy surfaces and a splitting of the Δ₆ level into an in-plane level Δ₄ with smaller mass, and an out of plane level Δ₂ with heavier mass. The low mass of Δ₄ electrons leads to enhancement of electron mobility in the plane which is very attractive for the channel layer of nMOSFETs.
**Figure 4:** a) A schematic view of effects of biaxial tensile strain on the Si conduction band diagram in unstrained and strained Si which is grown on relaxed Si$_{1-x}$Ge$_x$. b) Tensile strain separates conduction band degeneracy so as a result intervalley scattering is reduced and the tensile-strained Si layer experiences a downward shift of $\Delta_z$ electrons. c) In-plane effective mass is reduced [9]
3. EXPERIMENTAL DETAILS

3.1 Processing and sample matrix

Tensile-strained Si layers (70 nm thick) were grown on SiGe virtual substrates (with 20 and 30% Ge content) which were created by grading Ge content (10% Ge / 1 µm) as shown in Figure 5. N-type Si substrates with 20-40 Ω cm was used as reference sample. The samples were grown in an ASM-Epsilon 2000 RPCVD reactor with growth temperature of 650°C at 20 torr.

![Diagram of implanted Sb and strained Si channel](image)

**Figure 5**: Planar schematic of strained epitaxial grown Si on graded SiGe substrate.

Both the strained and unstrained wafers underwent the same processing order, as follows. All wafers were implanted with 20 keV Sb with a dose of $1 \times 10^{14}$, $2.8 \times 10^{14}$, and $5 \times 10^{14}$ cm$^{-2}$. The mean depth of implanted Sb was 25 nm with an estimated peak concentration in range of 1-5x10$^{20}$ cm$^{-3}$. The implanted samples were cut into pieces 1 × 1 cm$^2$ and the dopants were activated by using Rapid thermal annealing (RTA) cycle in the range of 700°C – 850 °C for 30 seconds in N$_2$ ambient.

High-resolution x-ray diffraction (HRXRD) and high resolution reciprocal lattice mapping (HRRLM) have been performed by using a Philips X’pert instrument to measure the lattice mismatch parallel and perpendicular to the surface prior and after RTA treatment. Cross-sectional transmission electron microscopy was used to study the quality of the strained layers and the types of eventual created defects due to implantation. Rutherford backscattering (RBS) was applied using channeling orientation. The Sb profile was also measured by secondary mass spectrometry (SIMS).

Four point probe measurements were performed to obtain the resistivity and to estimate the active dopant concentrations. The measured data were also compared with Hall measurement to ensure active dopant concentration.
The outcome demonstrates that strain has a significant role for incorporation and activation of Sb. If the tensile strain in the Si layer increases, higher degree of Sb is activated also a large fraction of Sb atoms was incorporated in substitutional sites already during the implantation process.

3.2 Epitaxy

Epitaxy is the methods of growing a crystalline layer on top of a single crystalline substrate, in which the atoms in the grown layer have the atomic arrangements of the substrate. In this way, by epitaxial growth methods, it is possible to grow nearly defect free high quality layers. There are many different techniques to create epitaxial films, for instance:

- Molecular Beam Epitaxy (MBE)
- Pulsed Laser Deposition (PLD)
- Chemical Vapor Deposition (CVD) technique
- Reduced Pressure Chemical Vapor Deposition (RPCVD) technique

In this work the layers were grown by the CVD technique. The principle of CVD technique and the growth process will be explained below [10].

3.3 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition is a chemical reactions process of transforming gaseous precursor (gaseous molecules) into a solid material in the form of thin film, or powder, on a surface of the substrate and it’s broadly used in fabrication of semiconductor devices. There are fundamental reaction steps of chemical vapor deposition which are listed below:

- The precursor molecules move into the reactor by an inert gas (typically H₂)
- Gaseous precursor molecules diffuse to the surface
- Precursor molecules adsorbed to the surface
- Precursor molecules decomposed and are incorporated into solid films
- Residual molecular byproducts recombine and desorbs into the gas phase.

In the CVD process, other processes may happen such as segregation (diffusion from the bulk to the substrate), or inter diffusion (diffusion from the surface to the bulk), which damage the quality of the film. The schematic representation of mass different reaction processes during CVD is shown in Figure 6.
There are three different growth modes depending on the chemical properties of the adatoms and growth parameters [14], which are illustrated in Figure 7a-c.

- **Layer-by-layer mode (Frank-van der Merwe mode)**: occurs at moderate temperatures and growth conditions. The growth is two-dimensional or layer by layer. (Figure 7a). This type of the growth mode has been used when the epitaxial layers in this work are deposited.

- **Volume-Weber mode**: It occurs when the nucleation and the growth is three-dimensional (Figure 7c)

- **Stanski-Kratsanov mode**: when the growth starts with a layer-by-layer mode and then a transition to nucleation mode occurs (Figure 7b).

As the adatoms start to deposit layer-by-layer for a few monolayer, islands are formed on top of these layers. The island formation occurs as the balance of forces changes through the deposition which happens once the growing layer is strained due to lattice mismatch between the layer and substrate. Ge growth on Si substrate results in b) or c) a mode, the growth mode is not strongly dependent of the temperature and pressure.
The temperature of deposition (T) is an important factor for the growth rate (G) in CVD. For a temperature smaller than the temperature limit, T₀, the growth rate obeys the Arrhenius equation in surface reaction rate-limited regime:

\[ G = Ae^{\frac{-E_a}{kT}} \]

Where k, A and Eₐ are Boltzmann constant, pre-exponential factor and activation energy for the growth, respectively. For T>T₀, the reaction is controlled by the amount of gas, arrive at the surface and the growth rate is not dependent of the temperature. This regime that is called mass transport limited region. Figure 8 illustrates an Arrhenius plot for different Si-precursors: silane (SiH₄), dichlorosilane (SiH₂Cl₂), trichlorosilane (SiHCl₃), and siltate (SiCl₄). Region A corresponds to the surface reaction rate-limited (or kinetic) regime, whereas region B is the mass transport limited region [14, 15].
Figure 8: Growth rate as a function of inverse temperature for different Si precursors. If $T < T_0$ (temperature limit), the growth rate obeys the Arrhenius equation in the surface reaction rate-limited regime (region A). While $T > T_0$, the reaction is under the control of the amount of gas, arriving at the surface and the growth rate is not dependent to the temperature. This system is called mass transport limited region (region B) [14].

The deposition temperature which was used in this work was 650 °C, which makes the growth limited by the surface reaction rate.

### 3.3.1 Chemical vapor deposition reactor

The samples were grown in an ASM epsilon 2000 single wafer RPCVD reactor which is shown in Figure 9. The reactor has three major parts: process chamber, load-locks, and wafer handling. A quartz wand arm transfer wafers from the load-locks to a silicon carbide coated graphite susceptor. This susceptor is heated by a series of halogen lamps from both the top- and bottom, which offers an exact control over the temperature in the range of 550-1200 °C. The total pressure may be varied from atmospheric to a reduce pressure of 20 Torr. To prevent oxygen contamination, the wafer handling chamber and the load-locks are constantly purged with nitrogen. The reactant gases in this system are SiH$_4$, SiH$_2$Cl$_2$ as Si source and GeH$_4$ for Ge source. HCl is used both as an etchant of the quartz chamber, and as a process gas in selective epitaxy. The reactor pressure through deposition is changing from atmospheric pressure to 10 Torr. To have a good quality epitaxy layer cleaning all wafers (it is described in section 3.4) before loading into the Epsilon reactor is needed. The wafers are purged by N$_2$ for 30 minutes in the load-lock in order to avoid the O$_2$ contamination transfer to the process chamber [16].
3.2 Wafer Cleaning

Since contaminations degrade the quality of epitaxial films very clean surface are needed, in order to have a high quality epitaxial growth. To minimize the effect of contaminations typical an ex-situ substrate cleaning process is used before the deposition. In this study wafer cleaning has been completed in three steps. The first step is using a solution of H$_2$SO$_4$ : H$_2$O$_2$ (2.5:1) at 120 °C for 5 minutes followed by cleaning in a solution containing 5% HF for 10 sec. The wafers are rinsed in N$_2$-bubbled deionized water for five minutes after each step, and at the end, the wafers are spin dried and then loaded in the load-locks. An in-situ cleaning is applied as well to eliminate native oxide on the wafer by 2 minutes bake at 1050 °C in H$_2$ for plain wafers and 5-20 minute bake at 900°C - 950 °C for patterned substrates [16].

Figure 9: Schematic illustration of an ASM Epsilon 2000 RPCVD reactor [16].
3.5 Ion Implantation

In present silicon technology, ion implantation is widely used instead of chemical (diffusion) doping or epitaxy as an alternative to introduce dopants. A schematic overview of an ion implantation equipment is shown in Figure 10.

![Schematic of an ion implantation equipment](image)

**Figure 10: Schematic of an ion implantation equipment.**

Ion implantation is a process, in which atoms are ionized, accelerated and then ions with certain energy are introduced into the near-surface area of a substrate. These ions are impinging into the substrate with a kinetic energy typically in the keV range. The ions will lose their kinetic energy to the substrate by two mechanisms, and will eventually come to rest (see Figure 11). The two stopping mechanisms are:

- Nuclear collisions (elastic scattering)
- Electronic collisions (inelastic scattering)

During the nuclear collisions, the ions with positive charge collide with partly screened target nuclei. These collisions with particles of similar mass lead to a substantial momentum transfer from the impinging ion to the target atoms and large angular deflections; Most of the kinetic energy is transferred to the electron system of the target by successive collisions between the ions and electrons. The depth of the implantation is dependent on the kinetic energy and the stopping power of the target. The implantation dose is controlled by the ion current and time. Since collisions with the target atoms occur randomly, the entire distance travelled range and its projection on the direction parallel to the ion beam, projected range, $R_P$ are statistical quantities, average over a large number of ions [17]:
In this work, Sb ion implantation is employed for doping of Si layers. Sb implantation with energy of 20 keV performed at room temperature in the range of $10^{13}-10^{15}$ cm$^{-2}$.

### 3.6 Rapid thermalannealing treatment

Rapid Thermal annealing (RTA) treatment is a semiconductor manufacturing processes in which a single wafer is heated to high temperatures (400-1200° C for Si) on a timescale from a few seconds to a few minutes. The reason for using RTA on implanted wafers is: To electrically activate the implanted dopants, by positioning the dopants to substitutional lattice sites and, 2) to restore the crystal damage which is inherent in the implantation process. In this work, the RTA treatment is applied in an atmospheric Mattson 100 RTP Systems using ambient such as oxygen, nitrogen and argon with a changeable pressure range up to atmospheric pressure. The wafers were heated in the range of 400 -800° C by an array of high-power quartz lamps. During the RTA process, it’s possible to monitor the ambient and temperature. The gas handling system provides a precisely defined gas pressure level in the reaction chamber. All through the RTA process, the atmosphere is analyzed by a quadrupole mass spectrometer. The optical pyrometer is used for the wafer temperature measurement [18]. In the Mattson 100 RTP System the, heating rate is between 5 – 100 °C per second and the cooling rate maximum is 50 °C per second. Available gases are argon, oxygen and nitrogen.
4. MATERIAL CHARACTERIZATION

4.1 X-ray Diffraction

X-ray Diffraction (XRD) is used as a structural and microstructural characterization technique. In a 3-dimensional crystal several sets of planes can be identified. The XRD technique, diffraction of incident x-ray beams by planes, to form a pattern. By analyzing these patterns the nature of that lattice is identified.

Peaks of scattered intensity are observed when the path length difference of beams scattered from neighboring planes is equal to an integer number of wavelengths [24]. Bragg’s law refers to the maximum intensity which is seen while the following condition is satisfied:

\[ 2d \sin(\theta) = n\lambda, \]

in which d is the distance between parallel planes, \( \lambda \) is the wavelength of the x-rays and \( \theta \) is the angle of incident beam to the surface (Figure 12).

\[ K + \Delta K = K' \]

Where \( K \) is the incoming wave vector, \( K' \) is the scattered beam wave vector; \( \Delta K \) is the difference between incident and scattered wave vectors. It is possible to create the Ewald sphere to satisfy the Bragg condition. The Ewald sphere has the radius \( K = 2\pi/\lambda \) with origin at the center. If the Ewald sphere intersects a reciprocal point, the Bragg condition is satisfied and diffraction occurs (Figure 13).
4.1.1 Scattering in single crystalline thin films

By growing single crystalline thin films on crystalline substrate, the intensity distribution over different incoming angles (θ) most often changes, since the Bragg condition is satisfied in different angles for layer and substrate because of a difference in their lattice constants. The number of existing planes for diffraction is proportional to the peak intensity which results in a lower intensity peak for the layer. By comparing the position of the layer peak relative to the substrate peak the lattice mismatch and strain can be estimated. The position of the peaks is calculated by differentiation of Bragg equation:

\[ \delta d \sin(\theta) + \delta \theta \cos(\theta) = 0 \]

As \( \sin(\theta) \) and \( \cos(\theta) \) are positive for angles less than 90 degrees a positive \( \delta \theta \) gives a negative \( \delta d \). This means that when the layer has a larger lattice constant compare to the substrate (compressive strain), its matching peak occurs at lower angles.

In the case of thin layers, internal reflections of incoming waves may also create the interference inside the layer, which cause optical fringes to appear in the spectra in the region of the layer peak. The quality of the interface between layer and substrate influence the number of fringes, since defects, such as dislocation and stacking faults, cause a surface roughness which leads to a deviation from normal diffraction. As a result, a decrease of the number of fringes confirms the increase of interface defect. The other application of fringes is calculation of layer thickness (t) by measuring the distance (difference in angle) between neighboring fringes (\( \Delta \theta \)) as follow:

\[ 2 \Delta \theta \cos(\theta)t = \lambda, \]

While \( \lambda \) is the x-ray beam wavelength.
4.1.2 High Resolution X-Ray Diffraction (HRXRD)

In this work, a Philips X’pert system was used for x-ray measurements. In this system x-rays are generated when electrons from a tungsten filament strikes a Cu target at 45 keV. This generates a continuous spectrum from which \( k_x = 0.1504 \text{ nm} \) is picked up. Philips X’pert system contains several parts such as a copper target with biased tungsten filament at 45 kV which generates a continuous spectrum; also the Philips X’Pert Machine with Cu x-ray radiation from a four crystal monochromator of Ge (220) an intense mono energetic beam is formed. With this beam it is possible to perform one or two dimensional high resolution x-ray diffraction (HRXRD) scans, as shown in Figure 14. By applying a mirror and an aperture in the primary optics, an intense beam with a spot size varied between 100 \( \times \) 100 \( \mu \text{m} \) to 10 \( \times \) 10 mm \( ^2 \) can be obtained. The divergency of the diffracted beam can be decreased by placing two Ge (220) crystals in front of the detector (Figure 14). To modify the spot range of the incident beam, there is an aperture system after the monochromator which is shown in the picture below. The sample is mounted on a holder which can move in three dimensions (x, y, and z).

\[
\begin{align*}
\omega & = \text{incident angle} \\
2\theta & = \text{diffracted angle} \\
\phi & = \text{rotation angle perpendicular to plane} \\
\varphi & = \text{rotation angle perpendicular to plane}
\end{align*}
\]

\( \omega \) and \( 2\theta \) are the incident and diffracted beam angle [21].

From the other features in the spectra it is possible to obtain strain, defects, layer thickness, etc. High Resolution X-Ray Diffraction at (1 1 3) reflection is very sensitive to reveal the defect generation.

\( \omega \) and \( 2\theta \) are the incident and diffracted beam angle [21].
4.2 Different X-ray Scanning

Many varieties of x-ray measurements are possible and some of these methods are below:

4.2.1 Omega (ω) scan

The simplest way to perform x-ray diffraction is rocking curve which is called Omega (ω-2θ) scan. During ω scan, the epitaxially grown layers are scanned and the planes which satisfy the Bragg law, create peaks. For instance in our case with SiGe/Si two peaks are observed. The broader peak in Figure 15 belongs to the strained SiGe layer and the narrow peak to the right comes from Si substrate. There are some optical fringes in the spectra which are generated from the interference of x-ray beam in the epitaxial layer. The other information e.g. defect density can be extracted from the full-width-half-maximum of the layer peak in the spectra.

![Figure 15: Diffraction from mismatch systems- rocking curves [21]](image)

4.2.2 High-Resolution Reciprocal Lattice Mapping (HRRLM)

A high-resolution reciprocal lattice mapping (HRRLM) or ω/2θ scan give the crystal orientation of substrate and thin films, the thickness of the film and lattice factors. With this type of scan, ω and θ are increased by a ratio of 1:2. Through performing a number of ω/2θ scans in the range of incident angles ω±Δω with for instance (113) reflection, a two-dimensional reciprocal space map is obtained, a schematic of HRRLM is shown below. The features, such as lattice mismatch and the characteristic of the peaks which demonstrate the defect density can be derived by the position of the layer peak and the substrate peak. Additionally, the lateral and vertical lattice mismatches (f_z and f_{xy}, respectively) can be calculated from the HRRLM results [21].
Figure 16: In HRRLMs: the shape & position in the reciprocal space provide mismatch parallel and perpendicular to the growth direction [21].

\[
f_z = \frac{\Delta a_z}{a_{sub}} = \frac{a_{layer} - a_{sub}}{a_{substrate}} = \frac{\sin \theta_{sub} \cos(\omega_{sub} - \theta_{sub})}{\sin \theta_{lay} \cos(\omega_{lay} - \theta_{lay})} - 1
\]

\[
f_{x,y} = \frac{\Delta a_{x,y}}{a_{sub}} = \frac{a_{layer} - a_{sub}}{a_{substrate}} = \frac{\sin \theta_{sub} \sin(\omega_{sub} - \theta_{sub})}{\sin \theta_{lay} \sin(\omega_{lay} - \theta_{lay})} - 1
\]

Where \(a_{sub}\) and \(a_{layer}\) are substrate and layer lattice constants. The \(\omega\) and \(\theta\) angles with indexes sub and layer present the incident and diffracted angles for the layer and substrate, respectively.

The cubic lattice mismatch in bulk form: \(f = \frac{1-\nu}{1+\nu}(f_z - f_{x,y}) + f_{x,y}\)

Where \(\nu\) is so-called Poison ratio and it is 0.33 for cubic systems

Relaxation: \(R = \frac{f_{x,y}}{f}\)
4.3 Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS) is a characterization technique for determining composition and element distribution, which is based on collision among target atoms and high kinetic energy ions. These high energy ions are positively charged and they are elastically scattered from the atoms in the sample. Measuring the number and energy of these backscattered ions gives information of atomic mass, elemental concentrations and the thickness of the sample [22]. The RBS Yield spectra as a function of energy in this work is plotted in Figure 17: a) Sb-doped Si, and b) Sb doped strained-Si on graded Si$_{0.7}$Ge$_{0.3}$ virtual substrate in the result section.

Figure 17: a) RBS spectra of Sb-doped a) Si layer, and b) strained-Si/graded SiGe virtual substrate.
4.4 Four point probe measurements

Four point probe measurements technique is an industry standard method to measure the surface resistivity in which one couple of probes pass the current through the sample, and two other probes measure the voltage potential. Surface resistivity, $\rho$ for a sample with area and length of $A$ and $l$, is defined as $\rho = R\frac{A}{l}$(\(\Omega\cdot\text{cm}\)) which means the amount of a material surface’s intrinsic resistance to the current flow that is not dependant on the physical dimensions of the material [28]. A schematic of the four point probe technique is shown in Figure 18 and the four point probe measurement results are plotted in the result section.

![Figure 18: The schematic view of four point probe measurements technique [23]](image)

In this work, the implanted Sb profile is not uniform and an etching process was applied in order to measure the resistivity profile by using four point probe measurement. The etchant solution was following:

$$\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2 \quad 5 \text{ min} \text{ followed by a HF-dip etches Si } \sim 1 \text{ nm}$$

The active dopant concentration was determined by reading from the published resistivity measurement curve for n-typed doped Si.
4.5 The Hall Effect

The Hall effect measurement represents the current flow from high potential to low potential through a conducting sample such as a metal or a semiconductor, while it is exposed to a magnetic field \( B \). The moving charge carriers, such as electrons and holes will feel Lorentz force, \( F \) according to the formula: \( F = q(E + V \times B) \) where \( q \), \( E \), \( V \) and \( B \) are charge, electric field, charge velocity and the exerted magnetic field, respectively (see Figure 19).

![Figure 19: Schematic of the Hall Effect with four ohmic contacts in a long, thin bar of semiconductor. The direction of \( B \) as the magnetic field is along the z-axis and the sample has a fixed thickness [24].](image)

Electrical characteristics of the material can be determined by the Hall effect measurement.

By measuring Hall coefficient, \( R_H \):

\[
R_H = \frac{E}{J \times B}
\]

where \( E \), \( J \) and \( B \) are established electric field, current density and the magnetic field, respectively, the Density of carriers in this n-type semiconductor can be calculated by:

\[
R_H = -(ne)^{-1}
\]

And the hall mobility is calculated from:

\[
\mu_H = \sigma R_H
\]

by performing Hall effect measurements the density of carriers and the mobility can be determined [30]. In this work, contacts of TiW/Al were sputtered in a Van der Pauw configuration on samples. A magnetic field of 0.5 Tesla has been applied.
4.6 Transmission electron microscopy

Transmission electron microscopy (TEM) as a structural and microstructural characterization technique is applied to observe the different structural features of a sample. In this thesis work, TEM has been used for structural characterization of the crystal and defect studies (types of defects) in the strained layers. TEM is based on a highly coherent and monoenergetic incoming electron beam which is generated by an electron gun by either thermionic, or field emission. Throughout the electromagnetic lenses, the incoming high energy electrons (energy of 120 keV in our case) interact with electron-transparent narrow sample, and the transmitted and diffracted (deflected) electrons are transformed into images used for strain simulation [25]. We have to consider that preparing the specimen is very critical for a successful TEM imaging. Three types of TEM imaging are mentioned here [25]:

- Bright field (BF), provides mass thickness contrast
- Dark field image (DF), provides information about stacking faults, planar defects, or particle size
- Diffraction pattern, provides the crystal structure of the solids

4.8 Secondary Ion Mass Spectrometry (SIMS)

Secondary Ion Mass Spectrometry (SIMS) as a chemical characterization technique is used for surface composition and dopant diffusion profile analysis. SIMS is an ion-based method of material characterization [26].

![Figure 20: Schematic of Secondary Ion Mass Spectrometry (SIMS) [26]](image)

A SIMS instrument is based on incident ions, called primary ions, which are directed to an area of the sample surface (see Figure 20). Hence both electrically neutral and ionized species are
ejected (sputtered) from the surface. Afterward the secondary ions are extracted from the sputtering area by being accelerated in an electrical field between the sample and an extraction lens, which form a secondary ion beam. This beam is then directed into a mass spectrometer which sorts the ions by their mass and energy. Finally these ions are counted in an ion detector such as an electron multiplier, a Faraday cup or a channel plate. The count rates of secondary ion species provide details about the composition of the sample in the sputtered area. Meanwhile, by performing SIMS, depth profiles can be measured because through the measurement, the sample is gradually eroded [27]. In this work dopant diffusion profile in strained, relaxed, and Sb implanted $\text{Si}_{1-x}\text{Ge}_x$ layers have been studied by performing SIMS.
5. RESULTS

Doping of semiconductor materials is performed by using either ion implantation, diffusion, or epitaxy. The solid solubility limit of dopants is usually a hurdle to extend the doping profile to very high levels in semiconductors. For n-type doping of Si-based materials, Sb, As and P elements are used where active dopant concentration in the range of \(10^{20}\) to \(10^{21}\) cm\(^{-3}\) is needed. Unfortunately, epitaxial growth of doped layers have demonstrated a large segregation of these dopants. The segregation of dopants in Si relates to two reasons: chemical and strain effect. The chemical part is related to lower formation energy for dopant-dopant pairs than dopant-Si. The strain effect is due to the size difference of the dopant atom compared to Si. In this thesis, we investigate the use of implantation to introduce Sb dopants in strained Si layers as an alternative to the more commonly used n-type dopants P and As. The three main objectives are following:

a) Shallow S/D junctions with low diffusion of dopants during the device processing

b) High active doping concentration

c) Preserving the strain after implantation and after the thermal treatments for dopant activation.

5.1 Secondary ion mass spectrometry

The implantation profile of Si reference and strained-Si/relaxed-Si\(_{0.70}\)Ge\(_{0.30}\) sample (\(5\times10^{14}\) cm\(^{-2}\) and 20 keV) are shown in SIMS measurement in Figure 21. Both samples are RTA treated at 700 °C. The dashed line in the figure presents the simulated data obtained from TRIM simulation program for the same energy and dose in Si. The doping peaks are located 20 nm below the surface with Sb concentration of \(3\times10^{20}\) cm\(^{-3}\) and \(2.5\times10^{20}\) cm\(^{-3}\). The simulated curve by TRIM agrees well with the experimental curve for Si. The slightly higher Sb content in the Si reference compared with the strained-Si sample is unknown but it can be speculated that there have been a slight variation of the implantation dose or the strain effect. In general, this implanted dose results in an amorphous Si region according to previous reports [27] but our RBS results show that the RTA treatment will improve the layer quality and high quality crystalline phase is obtained.

It is emphasized here that the measured data present the atomic concentration and can be significant different from the substitutional or active dopant concentration. We discuss more about the active dopant concentrations in these films later in this work.
5.2 Transmission electron microscopy

More investigations were performed by HRTEM to investigate the quality of the strained-Si layer. Figure 22a and 22b illustrates the cross-sectional view of 700 °C RTA treated Sb-implanted s-Si/relaxed- Si_{0.70}Ge_{0.30} sample. The thickness of strained-Si was 70 nm and the implantation dose was 5x10^{14} cm^{-2} creating a 25-nm thick Sb-doped Si layer. The atomic arrays in the high-resolution image in Figure 22b are well-defined and no trace of defects in forms of missing planes (or stacking faults), precipitates (or clusters) and dislocations are observed. There is a contrast in s-Si close to the SiGe interface in both Figures 22a and 22b. This can be related to strain variation induced by introducing Sb atoms. The high layer quality of s-Si with such a high Sb dose indicates that the strain has increased the solid solubility in Si and Sb incorporation has been improved.
Figure 22a and b: Cross-sectional TEM from Sb-implanted s-Si/Si$_{0.70}$Ge$_{0.30}$ ($5 \times 10^{14}$ cm$^{-2}$ RTA at 700 °C) layer. The dash line shows the interface between s-Si and relaxed SiGe layer.

5.3 X-ray measurements

The strain measurements in the layers were performed by HRXRD. The rocking curves were also simulated in order to access of the graded SiGe, the layer quality of strained-Si and the strain amount in the samples. The obtained values were used also as feedback to the epitaxy. The software requires a meshing for the layer thickness and the profiles are stepwise simulated. Figure 23 shows strained-Si/ Si$_{0.70}$Ge$_{0.30}$ RTA treated at 700 °C.
Figure 23: A HRXRD rocking curve (blue) and simulated curve (red) of graded-SiGe/Sb-implanted-strained-Si. The graded SiGe profile has a ten subdivisions feature in the simulation graded-Ge content.

Furthermore, these rocking curves provided strain in the vertical direction. Figure 24 illustrates three x-ray curves for the strained-Si/ Si$_{0.70}$Ge$_{0.30}$ samples consisting of unprocessed and RTA treated at 700 and 800 °C. The strain amount of the untreated sample is slightly higher than the annealed sample but the general feature of the curves i.e. full-width-half-maximum has not increased. There is a part of the strained-Si which is amorphous after implantation for unimplanted sample. This amorphous part does not contribute to x-ray diffraction and therefore it is not visible here in the rocking curve. The amount of strain in the vertical direction in this sample is estimated to 8000 ppm.

\[
\text{Si}_{0.70}\text{Ge}_{0.30}\text{- layer with Sb: } 5\times10^{14}\text{ cm}^{-2}
\]

Figure 24: Strained-Si peak has shifted for RTA treatment at 700 and 800° C.

Figures 25a-d illustrate HRRLMs around [113] reflection from four Si$_{0.70}$Ge$_{0.30}$ samples as follows: a) implanted by an Sb-dose of $5\times10^{14}$ cm$^{-2}$ and RTA treated at 700 °C, b) the previous
sample but annealed instead at 800 °C, c) as-grown sample which is RTA-treated at 800 °C, and d) sample in a) but RTA at 800 °C. The graded SiGe layer constitutes a peak which is not aligned with the Si substrate in $K_{\perp}$. The tensile s-Si layers are located on the upper side of the substrate peak with low intensity. The reason for the low intensity is due to diffraction from a thin layer and/or the low layer quality of these layers.

![HRRLMs around (113) reflection from s-Si layers.](image)

*Figure 25a-d: HRRLMs around (113) reflection from s-Si layers.*

The location and the shape of the strained-Si layer in the maps provide the mismatch and the strain relaxation of the strained Si layer. There is a shift of the strained-Si layer towards the substrate peak seen in Figure 25b to 25d with an increasing magnitude when the s-Si peak locates closest to Si peak. A relaxation value of 12% is measured in Figure 24d. This strain reduction from Figure 25a to 25d is due to the thermal treatment of the samples.
5.4 Electrical characterization

In order to study the relationship between the strain and Sb incorporation four-point probe measurements were performed to correlate the electrical and strain data. The obtained resistivity values were converted from the sheet resistance to active dopant concentration by reading from the published curves [28]. The layer thickness for these samples was considered to be 25 nm and the distributed dopant profile was considered constant. The resistivity and the Sb concentrations are listed in Table 1. The mobility of Si has been used for the conversion of the data in Table 1.
Table 1: Sheet resistance and estimated active concentration of Sb-implanted samples

<table>
<thead>
<tr>
<th>Material/substrate</th>
<th>Implantation Dose</th>
<th>RTA (ºC)</th>
<th>ρ (Ω-cm)</th>
<th>Active Concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Si(Ref)</td>
<td>1×10¹⁴ as-grown</td>
<td>700</td>
<td>0.0014</td>
<td>4×10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.0011</td>
<td>7×10¹⁷</td>
</tr>
<tr>
<td></td>
<td>5×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00058</td>
<td>1.3×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00054</td>
<td>1.7×10²⁰</td>
</tr>
<tr>
<td></td>
<td>2.8×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00057</td>
<td>1.4×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00053</td>
<td>1.8×10²⁰</td>
</tr>
<tr>
<td>2) s-Si/Si₀.₇Ge₀.₃</td>
<td>1×10¹⁴ as-grown</td>
<td>700</td>
<td>0.0010</td>
<td>7×10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00085</td>
<td>9×10¹⁹</td>
</tr>
<tr>
<td></td>
<td>2.8×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00061</td>
<td>1.3×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00056</td>
<td>1.4×10²⁰</td>
</tr>
<tr>
<td></td>
<td>5×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00048</td>
<td>2×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00044</td>
<td>2×10²⁰</td>
</tr>
<tr>
<td>3) s-Si/Si₀.₅Ge₀.₃₂</td>
<td>1×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00141</td>
<td>4×10¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00086</td>
<td>9×10¹⁹</td>
</tr>
<tr>
<td></td>
<td>2.8×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00080</td>
<td>1×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.00067</td>
<td>1.2×10²⁰</td>
</tr>
<tr>
<td></td>
<td>5×10¹⁴ as-grown</td>
<td>700</td>
<td>0.00037</td>
<td>4×10²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 26a and b illustrate the measured resistivity of the Si layers vs implantation dose for two RTA treatments. The untreated samples showed a large resistivity values due to the presence of an amorphous layer on the top and RTA is necessary to improve the layer quality. The resistivity decreased with increasing implantation dose, as more Sb atoms occupy substitutional sites in the Si (see Figure 26a). The strained-Si/relaxed- Si$_{0.70}$Ge$_{0.30}$ (RTA at 700 °C) demonstrates lower resistivity compared to the sample with 20% and the Si reference sample. To obtain low resistivity in the Si reference higher annealing temperature is required. Moreover, for layers annealed at higher temperature, a formation of Sb clusters (precipitates) may occur. A slightly higher resistivity for 800 °C annealed Si reference could indicate this. More analysis is necessary to confirm this statement.
Figure 26a and b: The resistivity vs implanted dose for annealed samples at 700 and 800 °C.
In the Four-point probe measurements shown in table1 and Fig.26, the Sb concentration was considered to have a constant profile, which provides a mean value for the active concentration. A more accurate measurement has been performed by differential four-point probe measurement. Since the implanted layer is 25 nm a slow etch rate was applied to remove material from the surface between consecutitive measurements. Previous results have demonstrated that a H$_2$SO$_4$+H$_2$O$_2$ solution followed by a HF-dip etches the Si surface with a rather constant rate of 1 - 1.5 nm for 5 min. This chemical solution is used in surface cleaning and it oxidizes the Si surface. In our experiments, a mean value for the etch rate of 1.2 nm for 5 min etching has been obtained. The results are shown in Figure 27.

![Figure 27: The resistivity values of the etched- Si layers vs depth.](image)

As mentioned above, the resistivity values can be converted to active dopant concentration. In order to have more accurate values for the active dopant concentration, Hall measurements have been also performed. More details about these measurements are explained in section 4.5 of this thesis.

Two samples from the differential four-point measurements have been chosen (s-Si/ Si$_{0.70}$Ge$_{0.30}$ RTA at 700 ºC) and metalized for Hall measurement (by sputtering TiW/Al contacts). The applied magnetic field was 0.5 Tesla and the measurements were done at room temperature. The obtained data for active dopant concentrations together with SIMS profile are shown in Figure 28. The estimated active dopant concentration for the strained-Si was 2×10$^{20}$ cm$^{-3}$ which, in comparison with our SIMS value, 2.5×10$^{20}$ cm$^{-3}$ indicates a value of ~ 80% activation.
**Figure 28:** SIMS data and active Sb concentration of Sb-implanted s-Si/Si$_{0.7}$Ge$_{0.3}$ ($5\times10^{14}$ cm$^{-2}$ RTA at 700 °C) layers.
6. CONCLUSIONS

The results in this work demonstrate that Sb is an excellent dopant with high incorporation level for implantation in strained Si for nMOSFET applications. Sb-implanted strained Si samples had a high quality and no extended defects were observed after RTA treatment (700-800 °C) showing low strain relaxation. The strained Si samples became amorphous after implantation but recovered fast after 700 °C annealing treatment. The strain was preserved after implantation and annealing treatment in the Si matrix. Activation levels close to 80% were observed in the Sb implanted strained-Si layers RTA treated at 700 C. The maximum active dopant concentration in this study was estimated to 2.5x10^{20} cm^{-3} for the strained-Si/ Si_{0.70}Ge_{0.30}. 
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