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Defect distribution of through-oxide boron-implanted silicon with and without fluorine incorporation

Amy C. Lam
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TITLE: Defect Distribution of Through-Oxide Boron-Implanted Silicon with and Without Fluorine Incorporation

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DEFECT DISTRIBUTION OF THROUGH-OXIDE 
BORON-IMPLANTED SILICON WITH AND WITHOUT 
FLUORINE INCORPORATION

by

Amy C. Lam

A Thesis
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May 13, 1992
(Date)

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Abstract

Defect distribution in through-oxide boron-implanted silicon was studied using transmission electron microscopy (TEM) imaging (both planar and cross-sectional) and high resolution TEM imaging (HRTEM). The introduction of fluorine affects the defect distribution and their nature. The fluorine was either introduced by separate implantation following boron-implant or during thermal oxidation. These samples were then compared to the control set of samples with no fluorine introduction in any processing steps. It was demonstrated that implanted fluorine is beneficial for the reduction of residual defect density upon annealing. It was suspected that fluorine suppressed the precipitation of recoil oxygen atoms and/or reduced the ejection of silicon interstitials. Thus, fluorine increased the vacancy concentration at the implanted range. However, for samples of fluorinated oxide with boron implants only, no significant reduction in residual defect density was observed upon annealing. This result indicates that fluorine was incorporated into the oxide structure and was relatively immobile even during annealing. Furthermore, oxide thickness was critical to the density of residual defects.
Chapter 1

Background

As the lateral dimensions of VLSI/ULSI devices are reduced to the submicrometer range or nanometer, shallow source and drain p-n junctions must be used to decrease short-channel effects (See Fig.1.1) [1]. Short-channeling behavior is undesirable and compromises the device performance.

In order to obtain shallow p-n junctions, ion implantation is one of the most common methods used because of its superior control of dopant concentration and junction depth, reproducibility, doping uniformity and its high throughput [2]. However, ion implantation of light ions such as boron and fluorine cause a channeling effect (i.e., the ion finds its way through the rows of atoms with fewer than normal target-atom collisions and thus rests at a greater depth in the crystal). The channeling effect is undesirable because it alters the profile of the implanted distribution from the normal gaussian shape (See Fig.1.2) [3]. The ion channeling can be minimized by tilting the wafer 7° off the major zone axis to the implantation direction. Furthermore, this effect can be suppressed by implanting heavy ions or implanting through an amorphous layer such as an oxide.

In the case of implanting heavy ions to minimize channeling, BF$_2^+$ is usually used
Figure 1.1: Schematics showing NMOS transistor scaling. In the middle figure, short channel effects occur when depletion regions overlap.
Figure 1.2: An example showing channeling of ion-implanted P in silicon. Different curves represent different ion beam direction with respect to the (110) axis.
instead of B⁺ in order to obtain a shallower implanted layer at the same accelerating energy. The implantation of BF⁺₂ molecular ions into silicon has other advantages as well, such as higher electrical activation after low-temperature annealing and lower leakage current for p-n junction [4]. However, the heavier the ion, the higher the concentration of defects that will be generated. The damage produced by molecular ions is greater than that produced by the implantation of the equivalent atomic ions. The molecules are considered to split into their component atoms upon impact with the substrate surface, with energy in proportion to their atomic masses [22]. An amorphous layer is usually produced on top of the silicon wafer before implantation. This layer protects the underlying crystalline silicon by absorbing much of the initial impact energy and reduces the channeling effect.

Oxidation of the silicon wafers is carried out prior to implantation. During dry oxidation, strain is produced at the oxidizing interface. This strain is associated with a large volume increase (120%) due to the difference in lattice constants between silicon and oxide [13]. The large molecular volume difference between the silicon and the oxide requires the creation of free volume [12]. This free volume can be compensated by the generation of point defects, which will be discussed in the next chapter.

The main advantages of through-oxide implantation are that it can be used to form shallow p-n junctions, and to reduce the damage resulted in silicon [5]. The ion stopping powers of silica and silicon are assumed to be the same [19]. Therefore, the residual range of the implanted ions in the underlying semiconductor will be the subtraction of the oxide thickness from the total projected range. The thickness of the oxide and the implantation range should be compatible enough for maximum annealing effects afterwards. If the oxide thickness is too thin, most of the damage occurs in silicon. If the oxide thickness is too thick, the implanted ion concentration will be too low (See Fig.1.3). Generally, the thickness of the oxide should be about
equal to the implantation range [6].

Through-oxide ion-implantation is the introduction of atoms into the surface oxide layer of a solid substrate by bombardment of the solid with ions in the keV energy range. The incident ion loses energy in both electronic and nuclear collisions as it slows down and comes to rest within the crystal. For electronic collisions, the moving particles excites or ejects atomic electrons; while for nuclear collisions, the energy is transmitted as translatory motion to a target atom as a whole. The former type of collision involves small energy losses per collision, negligible deflection, and negligible lattice damage. The latter type involves much larger discrete energy losses and significant angular deflection of the trajectory. This process is also the one responsible for displacing lattice atoms [20]. Thus, a distribution of vacancies, interstitial atoms, and other types of lattice disorder will result in the region around the path of the ion (See Fig.1.4) [21]. As the number of ions incident on the crystal increases, the individual disordered regions begin to overlap. At some point, an amorphous layer is formed. The relative importance of the two energy-loss mechanisms changes rapidly with the incident energy E and atomic number Z of the particle. The nuclear stopping processes predominate for low E and high Z; whereas electronic stopping processes are more important for high E and low Z. Overall, the total amount of disorder and the distribution with respect to depth depend on ion species, temperature, energy, total dose, and channeling effects.

Boron implantation at 30 keV of 3x10^{15} /cm^2 is a case of low Z, low energy and low dose. Therefore, electronic collisions predominate over the major part of the ion path, and thus the disorder lies well below the surface. Nuclear collisions take over at the end of the ion path, and displacement of atoms occur. However, the annealing of disorder takes place during room temperature implantation. This occurs because there is significant recombination of interstitials and vacancies, which are separated
Figure 1.3: Schematic representations showing the concentration profiles for boron (25keV to 3E15 /cm²) and recoil implanted oxygen. Shaded area represents the implantation damage.
Figure 1.4: Schematic representation of the disorder produced by ion-implantation. (a) Low dose; (b) Light ions-individual regions with degree of disorder increasing as ions penetrate deeper into substrate; Heavy ions-individual regions of more uniform disorder along entire ion trajectory; (c) Heavy doses - formation of amorphous layer.
by short distances [23]. Overall, no amorphous layer will be created by boron implants less than $10^{16} \text{ /cm}^2$.

Since this is a through-oxide ion-implantation, the incident ions can lose energy to the oxygen atoms in the oxide. Those oxygen atoms pick up sufficient energy to penetrate into the substrate as recoiled oxygen atoms (See Fig 1.5). In the case of the oxide thickness being roughly equal to the projected range of a certain incident ion energy, the largest surface concentration of recoil atoms is obtained (See Table 1.1) [7]. These recoil oxygen atoms would form Si-O$_2$ complexes and precipitate out during annealing. The effect of these precipitates will be discussed in the next chapter.

Many studies have investigated the role of fluorine during oxidation and post-implantation annealing in silicon. During oxidation, fluorine acts as an oxidation enhancer. Fluorine can act catalytically at the interface, and competes with oxygen to form Si-F bonds (based on electronegativity differences) [14]. This increases the available number of silicon dangling bonds, thus the reactivity at the interface and subsequently the rate of oxidation. Fluorine can also effectively substitute for oxygen as an oxide network modifier, and thus modify the structure (i.e., open the structure to more readily allow ingress of the oxidant). This also directly relates to the change in the local stress and viscosity at the interface [17]. Thus, it influences the generation of point defects during oxidation as will be explained in greater detail in the next chapter. The positive effect of fluorine on oxidation rate will be reversed if the fluorine concentration exceeds a crucial level (i.e., a weakened structure with pinholes in the oxide is observed). In the case of 1000°C oxidation, the critical concentration is about 0.011%. Furthermore, from the SIMS results of Kim's [17], the oxide exhibits a high uniform concentration of fluorine throughout the entire thickness region, as if the fluorine atoms are tightly bonded into the oxide network and are immobile.

For fluorine implantation, the fluorine ion is a bit larger and heavier than boron
Figure 1.5: Schematic illustrating the through-oxide implantation processes. Oxygen from the silicon dioxide layer is introduced into silicon substrate as impurity.
Table 1.1: Numerically calculated values for recoil implantation of oxygen by implanting boron at various energies to 1E15/cm².
but it is still considered a light element. The lattice damage from fluorine will resemble that from boron. The calculation on the disorder from fluorine and boron implants will be presented in the next chapter. Recoil processes of oxygen atoms during implantation should also be taken into account, just like all other through-oxide implantation. Upon annealing, the residual damage observed from studies that involve fluorine implants show somewhat less damage than anticipated [22]. This suggests that fluorine reduces the residual defect distribution in silicon, and thus is beneficial to the integrated circuit device behavior. The generation of these point defects during processing and their interaction with each other or with implanted atoms is of great interest.
Chapter 2

Introduction

Crystalline defects in silicon usually have a detrimental impact on device performance. Some of the most important device/material properties that are influenced by crystalline defects include: a) leakage currents in p-n junctions; b) collector-emitter leakage currents in bipolar transistors; c) minority carrier lifetimes; d) gate-oxide quality; e) threshold voltage uniformity in MOS devices; and f) resistance to warpage by wafers during thermal process steps [9]. Some defects are present in the starting material, but still others are induced by subsequent processing. In this study, the defects present in the starting material are negligible and both interstitials and vacancies are present in their respective thermal equilibrium concentrations $C_i$ and $C_v$. Subsequent processings such as oxidation and ion implantation, are responsible for any perturbation of the point defect concentrations.

As mentioned in the previous chapter, creation of free volume is required during dry oxidation. The free volume may be supplied by a flux of vacancies from either the bulk silicon to the interface, a flux of silicon interstitials from the interface to the bulk oxide or silicon, or a viscous flow of the oxide. If the free volume is to be supplied entirely by point defect fluxes, extremely large fluxes would be needed,
which is unlikely. However, if less than 45% of the silicon at the interface is oxidized, the rest of the silicon (55%) is placed at interstitial sites. This expansion can be compensated by the viscoelastic flow of the newly formed oxide and the generation of silicon interstitials near the interface [11]. These excess silicon interstitials at this high temperature are free to move, and most of them diffuse back into the oxide for further oxidation [12]. However, a significant amount of excess interstitials are segregated near the interface in the silicon side.

The extrinsic silicon interstitials in silicon may recombine with vacancies. The bimolecular annihilation of vacancies with self-interstitials proceeds at a slow rate (there exists an energy barrier on the order of 1.4eV) [36]. When local dynamical equilibrium is reached, the mass action law yields for the actual point defect concentrations $C_i$ for self-interstitials and $C_v$ for vacancies is: [24]

$$C_i C_v = C_i^* C_v^*$$

(2.1)

where $C^*$ represents the equilibrium value. From the above equation, it can be determined that a supersaturation of self-interstitials ($C_i / C_i^*$) is coupled with a corresponding vacancy undersaturation ($V_v / V_v^*$). According to U.S.Kim, this further confirms that dry oxidation increases injection of interstitials and the depletion of vacancies by the correlation of the dopant diffusion with the point defect concentration (See Fig 2.1). The plots reveal the change of interstitial concentrations and the corresponding vacancy concentrations with oxidation time. Dry oxidation obviously induces simultaneously a self-interstitial supersaturation and a vacancy undersaturation. Therefore, it is very likely that some excess silicon interstitials grow into extrinsic faults.

During fluorinated oxidation, fluorine can act catalytically at the interface and compete with oxygen to form Si-F bonds. The uniform incorporation of fluorine can decrease the strain at the interface according to the reduced density of fluorinated
Figure 2.1: Change of $C_i/C_i^*$ and $C_v/C_v^*$ versus oxidation time in silicon at 1100°C after dry oxidation.
oxide, thereby reducing the requirement of free volume to continue oxidation. Thus, a decrease in the generation of silicon interstitials and an increase of vacancy concentration result [11]. Fig 2.2 shows a similar plot of oxidation time versus normalized concentrations of interstitials and vacancies for fluorinated oxidation [25]. Conversely, the data shows the opposite result for dry oxidation. Fluorinated oxidation thus induces a vacancy supersaturation and a corresponding self-interstitial undersaturation. The point defect concentrations at the interface are disturbed and thus the resultant defects are different.

During through-oxide ion-implantation, energetic ions lose their energy in a series of nuclear and electronic collisions before they come to rest. Only the nuclear collisions result in displaced silicon atoms and corresponding vacancies [26]. The damage from the production of interstitials and vacancies simultaneously are referred to as Frenkel defects. In general, ion-implantation leaves a vacancy-rich surface layer and a deeper region enriched in interstitials. To be more specific, the formation of a vacancy (V) excess is usually situated in a region between the surface and about 0.8 times the ion-projected range $R_p$; while the formation of an interstitial (I) excess is located in a region between $R_p$ and $2R_p$. The number of displaced atoms or the degree of damage is linearly proportional to the energy. Also, the higher the dose at constant energy, the higher the V and I surplus, the thicker the excess V layer and the deeper the excess I region [32]. For light ion-implantation, large angle scattering of the primary beam can occur. The peak in defect distribution occurs at almost the same depth as the peak in range distribution of the implanted ions [35]. In order to obtain accurate distributions of interstitials and vacancies, computer simulations have been performed to further understand the presence of residual damage after implantation [29].

As mentioned in the previous chapter, through-oxide implantation promotes recoil oxygen atoms in silicon. For a high dose ($10^{15}$ ions /cm$^2$) through an oxide, the
Figure 2.2: Change of $C_i/C'_i$ and $C_v/C'_v$ versus oxidation time in silicon at 1100°C after $O_2/NF_3$ oxidation.
concentration of recoil implanted oxygen at the oxide interface can be greater than $10^{21}$ oxygen atoms /cm$^3$ [5]. The departure from equilibrium due to solubility provides the driving force for precipitation. Since the oxygen is expected to be extremely mobile at the processing temperatures, it would diffuse interstitially both toward the surface and deeper into the material (where the damaged regions are) [33]. The oxygen atoms are expected to react chemically with silicon during the annealing to form stable SiO$_x$ complexes, which appear as fine defect clusters and restrict the growth of the dislocation loops [5]. These crystallized precipitates grow by taking up oxygen atoms along [110] edges [28].

These bulk defects can be responsible for creating other crystalline defects as they grow. The growth of oxygen precipitates in silicon occurs by the reaction of oxygen with silicon at the precipitate surface to form SiO$_2$. The volume change from Si to SiO$_2$ is quite large and consequently, the lattice surrounding such a precipitate is subject to large compressive stresses. This compression can be relieved in a number of ways. All of them involve the generation of other crystal defects, including: a) emission of Si self-interstitials; b) absorption of vacancies; or c) punching out of dislocation loops [30]. The production of self-interstitials to accommodate volume expansion is apparently predominant, and thus such oxygen precipitates are sources of Si self-interstitials. These emitted self-interstitials also have a propensity to form dislocation loops. These stacking faults also grow by absorbing the self-interstitials (at the bounding dislocation loop) that are continually emitted by the growing precipitates [31]. The presence of oxygen precipitates does not severely degrade device performance and yield directly, but the precipitates indirectly cause such effects by generating dislocation loops and stacking faults during their growth.

The dual purpose of annealing treatments after ion-implantation in a furnace is to restore the pre-implanted structure and to electrically activate the implanted species.
In the high temperature atmosphere, the mobilities of interstitials and vacancies are increased. They could move to annihilate each other. However, the mobility of interstitials is higher than that of the vacancies. Therefore, the interstitials can cluster to form dislocation loops. This is due to the fact that circular loops represent an energetically more favorable state than that of self-interstitials distributed randomly in the lattice with a stacking fault [28]. If the distance between two loops is less than twice the diameter of the larger loops, these two loops may coalesce by glide and climb processes to form larger loops. If the loops are farther apart than that distance, they shrink by a normal bulk diffusion process. Dislocations are formed by the growth and multiplication of the dislocation loops or generated at the interface in response to the stress. Dislocations can move to the surface and disappear by similar climb and glide processes.

In order to characterize the implantation damage, transmission electron microscopy (TEM) is a very suitable tool. Since the scale of distances between damage features is of the order of nanometers and microns, most of them are in the range of TEM resolution. Also, the defects are present in shallow layers just below the surface of the implanted crystal. These layers are accessible to TEM analysis by simply etching away the substrate wafer [34]. The image in TEM is produced by the differential scattering of electrons from an incident beam as it passes through very thin samples. The sample must be thin enough to transmit the beam, to preserve the essential information caused by differences in sample thickness, phase composition, crystal structure, and orientation.

Some common defect features seen include point defect clusters, pure dislocation loops, faulted dislocation loops, dislocation lines and precipitates. They can be categorized according to their geometry (See Table 2.1). The average size of the vacancy loops had been shown to be much smaller (5-10Å) than that of interstitial loops,
normally below the resolution limit of the strain-contrast imaging mode of the microscope [10]. Therefore, the observed dislocation loops are all interstitial in nature. It is believed that the point defect concentrations of interstitials and vacancies in silicon can influence the presence of the defects.

The objective of this thesis is to study and provide understanding on the role which fluorine plays on point defect generation during processing, and thus the distribution of residual damage after annealing. There is an emphasis of both oxidation and through-oxide implantation induce crystalline defects in silicon. The correlation between the effect of fluorine addition on the point defect generation and the point-defect cluster distribution of as-implanted samples is investigated. The residual damage seen in the annealed samples are examined to determine the role of fluorine in annealing characteristics. The results of this study is believed to be valuable to shallow junction formation for submicron devices.
<table>
<thead>
<tr>
<th>Type</th>
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<th>Examples</th>
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<td>(Intrinsic - silicon self-interstitial)</td>
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<td>(Extrinsic - dopants, oxygen, carbon, metals)</td>
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<td>Precipitates, voids</td>
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</tr>
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</table>

Table 2.1: Crystalline Defects in Silicon
Chapter 3

Experimental

3.1 Cleaning of silicon wafers

N-type (100)-oriented, 8-10 Ω-cm, 2-inch silicon FZ wafers were used. The following cleaning procedure is adopted for furnace oxidation:

1. Immerse the wafers in a solution of $4 \text{H}_2\text{SO}_4 : 1 \text{H}_2\text{O}_2$ for 5 minutes at room temperature. Thoroughly rinse 5 times with deionized (DI) water. This strips off any inorganic resist.

2. Place the wafers in a solution of $5 \text{(DI)} \text{H}_2\text{O} : 1 \text{H}_2\text{O}_2 : 1 \text{NH}_4\text{OH}$ at 75°C for 10 minutes. Rinse the wafers thoroughly in DI water 5 times. This removes any residual organic contaminants and certain metals.

3. Immerse the wafers in a solution of $4 \text{HF} : 1 \text{H}_2\text{O}$ for 1 minute at room temperature. Thoroughly rinse with DI water and check for a hydrophobic condition on the surface of the wafer. This removes any surface oxide. Once the wafers have been cleaned, they are dried completely with compressed N$_2$ gas and processed immediately.
3.2 Oxidation

In order to perform through-oxide implantation, two-third of the wafers were thermally oxidized at 1000°C in dry oxygen ambient. Oxidation was carried out using a Mini-Brute laboratory double-wall diffusion furnace. A schematic of this oxidation/diffusion furnace consisting of gas supply system is shown in Fig. 3.1. The oxidizing gas flow \( \text{O}_2 \) was maintained at 2 l/min. Purging gas \( \text{N}_2 \) with a flow rate of 20 cc/min was also used in all cases to minimize moisture and contamination penetrating into the inner process tube. The oxide thicknesses on the wafers were determined to be around 100 nm using an ellipsometer.

Instead of introducing fluorine by implantation, a gas mixture of \( \text{O}_2 \) and \( \text{NF}_3 \) was used during oxidation. The fluorine oxidation was performed in the Thermco Pacesetter 2 furnace. \( \text{NF}_3 \) is a gaseous fluorine source, and its gas flow was monitored directly by microflowmeter before introduction into the oxidation furnace. The oxidizing gas flow was controlled at 1 l/min \( \text{O}_2 \) plus the addition of \( \text{NF}_3 \). The \( \text{NF}_3 \) addition was 100 ppm. The fluorine oxidations were carried out at various temperatures (800°C, 900°C and 1000°C). Oxide thicknesses were determined by an ellipsometer. The thicknesses vary from 80 nm to 140 nm.

3.3 Ion-implantation

After thermal oxidation, half of the wafers with a regular grown oxide and all of the wafers with fluorinated oxide were submitted to IICO Corporation for boron implant at 30 keV with a dosage of \( 3 \times 10^{15} \) /cm². The other half of the regularly grown oxide wafers were submitted to the IICO Corporation for dual-implant (i.e., boron implant at 30 keV with a dosage of \( 1 \times 10^{15} \) /cm², followed with fluorine implant at 60 keV with a dosage of \( 2 \times 10^{15} \) /cm²). The dual implantation dosages were chosen to resemble the
Figure 3.1: Diffusion/Oxidation furnace system used.
elemental concentrations of the BF$_2$ implants. The implantation energies for boron and fluorine were selected so that the projected range is approximately the same as the oxide thickness. All implantations were performed with wafer tilted 7° off the normal of wafer surface 110 direction to minimize ion channeling (See Fig. 3.2 for corresponding flow chart).

Figure 3.2: A schematic diagram of experimental procedure.
3.4 Monte Carlo Simulation

Trim program was used to simulate ion-implantation damage in the sample according to various experimental conditions. The experimental conditions included the composition & the density of each layer in the sample, the nature of the incident ion, its corresponding energy and the lattice binding energy. Distributions of implanted ions, displacement atoms, generated vacancies and recoil atoms were calculated by Monte Carlo simulations.

3.4.1 Implanted ions distributions

The implanted ions would be boron or fluorine depending on the experimental set. The plots for these ion range were the depth in angstroms from the sample surface versus (Atoms/cm$^3$)/(Atoms/cm$^2$). The number of ions used for simulation resembled the dose of the implanted ions. For example, total of 250 ions would be used to simulate a dose of 1x10$^{15}$/cm$^2$ implanted ions experimentally. Similarly, 500 ions would be used for a dose of 2x10$^{15}$/cm$^2$ and so on. Even up to a total of 750 ions used for simulations, the raw data was not an entirely smooth curve. Therefore, each data point was averaged with the point above and below in the quattro-pro before plotting.

3.4.2 Displacement ions/ Vacancy distributions

Displacement ions corresponded to ions situated interstitially such as silicon, oxygen and the implanted ions. The interstitial data used for plotting was the contribution from silicon atoms at interstitial sites and also the recoil silicon atoms from the surface layer. The plots were the depth in angstroms from the surface of the sample versus the number per ion per Angstrom. Similarly, the vacancy distribution created
by displaced silicon atoms was plotted with the same axes. These two distributions were usually plotted on the same graph using quattro pro. There was a general trend that the vacancy distribution was buried inside that of the interstitial. The possible explanation for this excess concentration in interstitials over vacancies was that the vacancies could easily be occupied by other displaced species and the extra contribution from the recoil silicon atoms. The data of these distributions had undergone with the same smoothing procedure as those for ion range distribution due to the small number of total ions used for simulation.

3.4.3 Recoil atoms distributions

The recoil data was quite straightforward. The number of atoms from the oxide layer picked up enough energy from the incident ions and traveled into the silicon substrate before coming to rest. The recoil species depend mainly on the composition of the surface layer. Recoil oxygen distribution was applicable for all sets of samples because these were all through-oxide implantation. Recoil fluorine distribution, on the other hand, would only be applicable for the fluorinated oxide set. The plots were similar to those of interstitial and vacancy plots with the depth in angstroms from the surface of the samples versus the number per ion per Angstrom.

3.5 Planar and cross-sectional TEM specimen preparation

After implantation, each 2-inch wafer was divided into 4 halves. One quarter of the wafer would be prepared for analysis directly. Both planar and cross-sectional TEM (p-TEM and XTEM respectively) specimens were made. For XTEM specimens:
1. Samples were cut into similar rectangular pieces (See Fig. 3.3). Pieces 2 and 3 are samples of interest with good sides face-to-face while pieces 1 and 4 are dummy wafers for support.

2. All 6 pieces are glued together with M-bond. The whole system is placed in a precision holder and cured at 120°C for 2 hr.

3. The sample block is then sliced as shown with a diamond saw.

4. The sample slice is then cut into 3 mm discs using an ultrasonic disc cutter.

5. The 3 mm discs are mechanically thinned and polished down to 100 microns.

6. The sample is dimpled on both sides (fig 3.3 shows only one side is dimpled) to less than 18 microns.

7. The sample is ion beam thinned at liquid nitrogen temperature until a hole is seen.

For planar TEM specimens, a similar procedure is used. The oxides on the wafers were etched with a 4HF : 1H₂O solution and the preparation is done from the back of the wafer so as to preserve the good side for TEM analysis.

3.6 High-resolution TEM – as-implanted samples

The as-implanted samples are examined with a JEOL JEM 4000FX at Bellcore for high-resolution transmission electron microscopy (HRTEM) imaging. In the case of as-implanted samples, the residual defects are not as well developed as those in annealed samples that have been exposed to high temperatures for a period of time. The point defect clusters require atomic resolution spatially. High Resolution Transmission Electron Microscopy (HRTEM) can produce such images. The electromagnetic lens brings the diffracted beams to interference on the screen, thus forming a lattice image. In bringing the beams to interference, a perfect lens with no abberations would
Figure 3.3: Schematic drawings of cross-sectional TEM specimen preparation.
simply carry out the inverse Fourier transformation necessary to form an image of the sample projected potential. However, no lens is perfect. The performance of such lens can be characterized by its Contrast Transfer Function (CTF), which describes how, at a given lens defocus, the phase and amplitude of the transmitted information are changed as a function of the spatial frequency of the information. At the so called optimum or Scherzer defocus, the CTF consists of a passband followed by damped oscillations. The relative phases of the spatial frequencies lying within the first zero of the CTF (also known as the point-to-point resolution of the microscope) information is transmitted without significant modification, while outside the first zero the lens aberrations can decisively affect the transmitted information.

Although it is in principle possible to deduce information lying well outside the first zero of the CTF, in practice it is difficult to do so reliably. Until the emergence of the latest generation of HRTEMs, only the (111) and (200) planar spacings of semiconductors lay within the first zero. Fig. 3.4 compares the CTF of the best 200kV HRTEM with the latest 400kV instruments [37]. Most significant is the fact that the (220) reflections of all semiconductors lie comfortably within the first zero of the CTF, and a number of other reflections are within its reasonable proximity. The (220) reflections, which in silicon correspond to a spacing of 1.9 angstroms, are critically important, because their faithful transmission allows the imaging of individual atomic columns in semiconductors.

3.7 Transmission Electron Microscopy – annealed samples

In order to determine the annealing characteristics of the through-oxide boron-implanted silicon, the rest of the samples were cleaned according to the previous wafer cleaning
Figure 3.4: Contrast Transfer Function at 200kV (dotted) and 400kV (solid). The vertical lines represent the various planar spacing of silicon.
schedule except for the last step with hydrofluoric acid mixture. Annealings were carried out at 900°C for various time periods (30 min, 1 hr and 2 hr) in a double-wall conventional furnace in N\textsubscript{2} atmosphere. After various thermal processing procedures, samples were analyzed using transmission electron microscopy (TEM) to characterize the residual damage.

Transmission electron microscopy was employed to examine the microstructure of the defects after annealing. Bright field (BF) and weak beam dark field (WBDF) images were taken on the Philips EM400. WBDF images actually reveal the true shape of the defects for better characterization of the residual damage from processing.

### 3.8 Electron energy loss spectrometry (EELS)

So far, TEM and HRTEM utilize the transmitted electrons and elastically scattered electrons from the transmitting specimen to obtain microstructural information and crystallographic information. For through-thickness composition information, analytical electron microscopy (AEM) is applied by making use of the inelastically scattered electrons. AEM is usually performed in a scanning transmission electron microscopy (STEM). It scans a fine (\(\sim\) 10nm) electron probe across an electron transparent specimen. If the probe is held stationary on the specimen, the characteristic X-rays produced in the region interacting with the electron beam may be detected, analyzed and displayed to provide chemical composition information by a solid-state energy-dispersive spectrometer (EDS). However, EDS is not effectual for elements of atomic number less than about 10, because the X-ray fluorescence yield drops with the atomic number. Low atomic number elements such as oxygen and fluorine are better analyzed with electron energy loss spectrometry (EELS). For EELS, microanalysis is performed in the stationary probe mode by measuring the energy
distribution of transmitted electrons. Since the electrons that ionize the atoms are scattered only through very small angles in the process, almost all can be recorded. Thus, the efficiency of EELS is much greater than EDS. However, the application of EELS to materials is not yet as widespread as that of EDS since there are specific experimental limitations, principally with respect to the specimen thickness and the ease of quantification.

EELS is performed to determine the spatial profiles of fluorine and oxygen in the cross-sectional specimens. The parallel EELS on the Philips EM400 is used, with an accelerating voltage of 120kV.
Chapter 4

Results and Discussion

In order to determine the role of fluorine in conjunction with the damage defects in silicon, the samples of dual-implant of boron and fluorine were compared with the control samples of no fluorine incorporation in any processing steps. The oxide on these two sets of samples are about 1000 Å in thickness (See Table 4.1). Therefore, the results from both sets are comparable.

Instead of having fluorine incorporated in silicon during implantation, fluorine was introduced during oxidation, followed by the boron implantation of the same dose as that resembles the elemental concentration of $\text{BF}_2^+$ implantation. Since the flow of fluorine was more difficult to control during oxidation, the oxide thickness was about 780 Å which is much thinner than the other sets (See Table 4.1). Thus, the results could not be compared with the control samples unless the effect of thickness had been taken into account.

<table>
<thead>
<tr>
<th>Control Samples $\bar{x} = 1037$ Å</th>
<th>Dual-Implant Samples $\bar{x} = 778$ Å</th>
<th>Fluorinated Oxide Samples $\bar{x} = 983$ Å</th>
</tr>
</thead>
</table>

Table 4.1: Oxide thickness of different experimental sets.
4.1 Defects after implantation

Dry oxidation of silicon wafers was performed prior to implantation. Since oxidation induced silicon-interstitial generation, excess interstitial concentrations were expected near the interface. For the point defect generations from implantation, Monte Carlo simulations were done according to the corresponding conditions and oxide thicknesses. The oxide/silicon interface was shown as dotted line on the plots for clarification.

4.1.1 Control set samples

For the set of control samples, figure 4.1 shows the vacancy concentration situated mainly in the oxide region while most of the interstitials lied in the silicon substrate region. This implied boron implantation induced a net gain of silicon interstitials over a depth of 1000 Å in the silicon substrate from the interface. Little recombination of interstitials and vacancies would be expected in the silicon. From the recoil oxygen distribution in silicon of the control samples (figure 4.2), the estimated amount incorporated in silicon would be about $10^{20}$ /cm$^3$ within 50-100 Å region from the interface.

No HRTEM image was taken for the control sample because the sample was broken on the way to Bellcore. However, as proven later, the results of the control set and the fluorinated oxide set were quite similar. Therefore, the as-implanted results should refer to the fluorinated oxide set.

4.1.2 Dual-implant samples

For the dual-implant samples, Monte Carlo simulations showed that the interstitial distribution created by boron ions fall within the region of vacancy distribution
Figure 4.1: Interstitial and vacancy distributions of control samples from ion implantation.
Figure 4.2: Recoil oxygen distribution of control samples from ion implantation.
created by fluorine ions (see Fig. 4.3). Therefore, significant recombination of interstitials and vacancies in silicon substrate region was suspected due to the short distance between them. Then the vacancy distribution created by boron ions (fig. 4.4) situated mainly in the silicon substrate region, unlike the control one. Those vacancies would recombine with the oxidation-induced silicon interstitials near the interface. For the interstitials created by fluorine ions, which happen to fall within the ion range of fluorine (fig. 4.5), Si-F complexes might be formed due to the high electronegativity of fluorine. Therefore, the dual-implant samples tended to have point defect concentrations move to the thermal equilibrium. No obvious supersaturation of interstitials was expected. Similar recoil oxygen distribution was found for the dual-implant samples. The distribution was within the first 50 Å from the interface but at a higher concentration of about $4 \times 10^{22} / \text{cm}^3$ (See Fig. 4.6).

Even though lower point defect supersaturation was predicted from the Monte Carlo simulations, the dual-implant set was exposed to a higher energy bombardment from fluorine (60 keV). Also, the as-implanted samples were not exposed to high temperatures or time for significant recombination to occur. Therefore, the TEM BF image of 100kX showed typical damage regions right below the interface (See fig. 4.7). Heavy damage was seen to a depth of 800 Å from the interface. The damage seen was believed to be the ion implantation damage consisting vacancy/oxygen clusters near the interface. The two bright fringes, that situates deeper than the major damage region, might be interpreted as the locations of implanted boron and fluorine. These ion-implanted regions were of high tendency to form point defect clusters that could be complexes of Si, B and F. However, they might well be thickness fringes. For the HRTEM images of 400kX (see fig. 4.8), the damage regions seemed to be more localized than the amorphorized-like region when it was viewed at a lower magnification. Therefore, as confirmed with the diffraction pattern, the silicon region near the
Figure 4.3: Vacancy distribution from F-implant and interstitial distribution from B-implant of dual-implant samples.
Figure 4.4: Vacancy distribution of dual-implant samples from B-implant.
Figure 4.5: Interstitial distribution by F-implant and F-ion range distribution of dual-implant samples.
Figure 4.6: Recoil oxygen distribution of dual-implant samples.
interface was still crystalline with certain amount of damage.

4.1.3 Fluorinated oxide samples

For the fluorinated oxide samples, the Monte Carlo simulations showed the peak of the interstitial distribution fell sharply at the interface. Figure 4.9 shows the vacancy concentration fell within the interstitial concentration, unlike the control one where the two maxima were quite far apart. In this case, recombination of vacancies and interstitials would still be feasible for the short distance between them. However, a considerable greater concentration of interstitials than vacancies still resulted in the silicon substrate. With the oxidation-induced silicon interstitials, an overall high concentration of excess silicon interstitials would be expected in the damaged region. The recoil oxygen distribution was about the same as that of the set of control samples. The range was only 50-100 Å from the interface and the concentration was about $2 \times 10^{20}$/cm$^3$ (See Fig. 4.10). However, no fluorine was recoiled during implantation as seen from figure 4.11. Therefore, no effect of fluorine on the defect formation in silicon was expected because fluorine was tightly bonded into the oxide structure.

In this case, the result of the control set and the fluorinated oxide set should be quite similar in nature but different in quantity of defects seen. Fig. 4.12 showed the 100kX BF image of the fluorinated oxide sample. The damage region extended to about 500Å from the interface and followed by a bright fringe beneath the region. The damage region was not as severe as seen in the case of the dual-implant set. It could be explained that the implanted ions for these two sets were boron at 30 keV which was an energy used half of the fluorine-implant. The damage band was believed to be the consequence of ion implantation and the bright band was the point defect clusters around the B doped layer. The bright band corresponded to the maximum boron concentration (approximately 250 to 500 Å from the interface)
Figure 4.7: BF image of 100kX of the as-implanted of the dual-implant samples.
Figure 4.8: BF image of 400kX of the as-implanted of the dual-implant samples.
Figure 4.9: Interstitial and vacancy distributions of fluorinated oxide samples from ion implantation.
Figure 4.10: Recoil oxygen distribution of fluorinated oxide samples from ion implantation.
Figure 4.11: Recoil fluorine distribution of fluorinated oxide samples from ion implantation.
as simulated by Monte Carlo (See figure 4.13). These clusters could be complexes of implanted B and Si. The near-interface clusters would probably the vacancy/oxygen clusters because of the high concentration recoil profile after implantation. Fig. 4.14 which was the 400kX HRTEM BF image, showed there was real minor damage due to light ion implantation. The damage did not seem to overlap each other to form any amorphous-like layer.

4.2 Defects after annealing

Nitrogen anneals were carried out in the furnace for 30 min, 60 min and 120 min periods of time. The planar and cross-sectional specimens were viewed with a the Philips EM400. The strong 220 beam was excited resulting in a two-beam condition for imaging.

4.2.1 Control set samples

Typical defects in (100) silicon for the set of control samples were shown in Fig. 4.15 (bright field images) and Fig. 4.16 (weak beam images) for planar samples. Pure interstitial prismatic dislocation loops and Frank loops with stacking faults of sizes from 100 Å to 500 Å were observed in high density all over the sample of the 30 min anneal. The pure dislocation loops, which were platelets of extra Si material, have a boundary of a complete edge dislocation with Burgers Vector a/2 (110). The Frank loops showed characteristic contrast of parallel fringes which are stacking faults with excess Si atoms incorporated on (111) planes.

The Monte Carlo simulations indicated that interstitial supersaturation resulted. The loops were formed due to the fact that they represent an energetically more favorable state than that of self-interstitials distributed randomly in the lattice. Most
Figure 4.12: BF image of 100kX of the as-implanted of the fluorinated oxide samples.
Figure 4.13: Boron ion range of control samples from implantation.
Figure 4.14: BF image of 400kX of the as-implanted of the fluorinated oxide samples.
Figure 4.15: Planar BF images of controlled samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.16: Planar WBDF images of controlled samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
of the loops were quite circular in shape but some irregularity was observed. In order to view the defects better, fig.4.17 showed the planar BF and WBDF images of 60 min anneal at a higher magnification. Both pure dislocation loops and Frank loops were seen but no dislocation lines.

As the annealing time increased, the loops coarsened and coalesced into more irregular shape but showed no significant reduction of the loop density in the sample. The immobility and the presence of the anomalous amount of defects could be explained by the effects of the recoil oxygen atoms. During annealing, oxygen diffused rapidly to damage regions, forming SiO$_x$ precipitates. The critical radius of these precipitates could be as small as 5-10Å, therefore, they might be visible within the resolution of the TEM (as no precipitates were observed). The immobility of the loops could be explained by the pinning effect of these precipitates. For the anomalous amount of dislocation loops seen of interstitial-in-nature, the emission of interstitials due to precipitation and the already present interstitial supersaturation in the controlled samples were possible explanations.

For cross-sectional samples, figure 4.18 and figure 4.19 showed the bright-field (BF) images and WBDF images of the control samples respectively. The depth of damage was seen to be about 1500 Å from the interface for the 30 min anneal. The depth went down to 1100 Å and even 800 Å for 60 and 120 min anneal respectively. Therefore, the increase of annealing time allowed the defects to diffuse to the interface but the reduction of defects per area was not significant. The accumulation of defects near the interface might be due to the pinning effect of recoil oxygen atoms. Furthermore, precipitation was not observed in longer annealing time, probably due to the relatively low recoil oxygen concentration. The exceptionally low defect density in the 60 min anneal sample was suspected to be the result of other sample preparation steps which allowed some defects to diffuse out of the sample.
Figure 4.17: Planar images of controlled samples of 60 min anneal; Top: BF image; Bottom: WBDF image.
Figure 4.18: Cross-sectional BF images of controlled samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.19: Cross-sectional WBDF images of controlled samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
4.2.2 Dual-implant samples

For the dual-implant samples, the defects seen were drastically different from the set of control samples. Figure 4.20 and figure 4.21 showed the BF and WBDF of the planar samples. Random dislocation lines and pure dislocation loops of sizes 100 -200 Å or irregular loops of 1000 Å were seen. A much lower defect density resulted (compared with the control). This can be explained by Monte Carlo simulation, which predicted no significant supersaturation of point defects with an assumption that fluorine ions would form Si-F complexes, and thus reduce the interstitial concentration in the sample. However, the efficiency of recombination might vary from point to point, inevitable local supersaturation of interstitials would occur. Therefore, loops and lines were observed in a low density across the sample.

The presence of fluorine increased the stacking fault energy and thus no Frank loops with stacking faults were seen. At sufficiently high stacking energy, a dislocation reaction occurs. The dislocation reaction can remove the stacking fault by sweeping a partial dislocation across the loop and reacts with the Frank partial dislocation to produce a unit slip dislocation at the outside of the loop. Tiny pure dislocation loops were seen to retain the lowest energy state as possible. The dislocation lines were formed due to the stress generated from the lattice misfit of implanted ions (B and F) or the growth and multiplication of the dislocation loops. In order to view the loops better, fig.4.22 showed the planar BF and WBDF images of the dual-implant samples of 60 min anneal at a higher magnification. No Frank loops were seen but pure dislocation loops. As the annealing time increased, significant reduction of dislocation lines were seen in 60 and 120 min anneals when compared with the 30 min anneal. The tiny dislocation loops disappeared in the longer anneals while the big irregular loops grew bigger and merged into the dislocation lines.
Figure 4.20: Planar BF images of dual-implant samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.21: Planar WBDF images of dual-implant samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.22: Planar images of dual-implant samples of 60 min anneal; Top: BF image; Bottom: WBDF image.
For the cross-sectional dual-implant samples, a significant decrease in defect concentration was seen from the set of control samples (see Figure 4.23 and 4.24, which are BF and WBDF images respectively). The depth of damage was 1300 Å for the 30 min anneal. Dislocation lines and loops could be seen in that range. As the annealing time increased, the depth of damage reduced to 1000 Å and 700 Å for 60 and 120 min anneals respectively. Most of the dislocation loops were annealed out with only long dislocation lines parallel to the interface remaining.

4.2.3 Fluorinated oxide samples

As mentioned earlier, the thickness of the samples with fluorinated oxide was much thinner than the other samples. More damage would remain in the silicon substrate. Even though fluorine oxidation was claimed to create a lower interstitial concentration, the significant amount of interstitials induced during ion implantation dominated the point defect supersaturation. As seen from figure 4.25 and figure 4.26 (BF and WBDF of the planar samples), the density of dislocation loops are high. Both pure prismatic dislocation loops and Frank loops with stacking fault are seen. The loops seemed to overlap each other and could be seen more clearly in fig. 4.27 which showed BF and WBDF images of 60 min anneal at a higher magnification. No significant reduction in defects was seen for longer annealing times. The loops, however, looked coarser and more irregular for the longer annealing time.

For the cross-sectional samples of fluorinated oxide, high concentration of defects was seen in figure 4.28 and figure 4.29. The depth of damage was 1800 Å for the 30 min anneal. The depth of damage tended to decrease as the annealing time increased. The depth were 1300 Å and 1100 Å for 60 and 120 min anneals. No precipitates were seen due to the relatively low concentration of recoil oxygen, similar to the control.
Figure 4.23: Cross-sectional BF images of dual-implant samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.24: Cross-sectional WBDF images of dual-implant samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.25: Planar BF images of fluorinated oxide samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.26: Planar WBDF images of fluorinated oxide samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.27: Planar images of fluorinated oxide samples of 60 min anneal; Top: BF image; Bottom: WBDF image.
Figure 4.28: Cross-sectional BF images of fluorinated oxide samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
Figure 4.29: Cross-sectional WBDF images of fluorinated oxide samples; Top left: 30 min anneal; Top right: 60 min anneal; Bottom: 120 min anneal.
4.3 Comparison at different annealing periods

Annealing in the furnace was carried out after thermal oxidation (with or without fluorine incorporation) and ion implantation (with or without fluorine incorporation) for time periods of 30 min, 60 min and 120 min.

4.3.1 30 min annealing

Planar TEM images are shown in figure 4.30 for 30 min annealing period. The dual-implant sample (top left) showed the most obvious reduction of defect density. This corresponds to the prediction from Monte Carlo simulations. The defects seen were mainly winding dislocation lines with tiny pure prismatic dislocation loops. No Frank loops were seen. The shape and the size of the defects were probably due to the high stacking fault energy from the presence of fluorine. On the other hand, both control sets (bottom) and the fluorinated oxide sample (top right) showed dense dislocation loops of sizes from 100 to 500 Å. Both pure prismatic dislocation loops and Frank loops with stacking faults were seen. However, the fluorinated oxide samples showed a slightly higher variation in loop size and the loops tended to overlap each other. The higher defect density of fluorinated oxide samples was probably due to the thinner oxide.

For the cross-sectional TEM images, figure 4.31 showed the defects seen for 30 min annealing. The dual-implant sample (top left) showed similar results as the planar one of the lowest defect density seen out of all the samples. Only dislocation lines and some loops were seen to a depth of 1300 Å from the interface. The highest defect density was seen for the fluorinated sample (top right) of tangled dislocation loops to a depth of 1800 Å from the interface. The control sample (bottom) showed medium amount of defects with a depth of 1500 Å from the interface.
Figure 4.30: Planar WBDF images of 30 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
Figure 4.31: Cross-sectional WBDF images of 30 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
4.3.2 60 min annealing

As the annealing time increased, reduction of defect density was seen most obviously in the dual-implant sample (top left) in figure 4.32. Fewer dislocation lines and loops were seen. The fluorinated sample (top right) showed a reduction of loops overlapping and also an increase in loop size to 700 Å. For the control sample (bottom), loop coarsening was seen with an increase of loop size to about 600 Å. The dark contrast seen on the micrograph is suspected to be a contamination spot from sample preparation.

Similar trends of defect distribution were seen in the cross-sectional samples shown in figure 4.33. The dual-implant sample (top left) showed the least defect density; its maxima occurred at a depth of 1000 Å from the interface. Again, the fluorinated sample (top right) showed the highest defect density within a depth of 1300 Å while the control sample (bottom) showed a medium defect density at a depth of 1100 Å.

4.3.3 120 min annealing

Similar results were observed for 120 min annealing (see figure 4.34). The dual-implant sample (top left) showed fewer dislocation lines and loops than any other samples. Coarsening of the loops was seen for both the fluorinated oxide sample (top right) and the control sample (bottom) with loop size varying from 400 to 800 Å. No significant reduction of defects was seen for the latter two.

Figure 4.35 showed the defect distribution in the cross-sectional samples for 120 min annealing. Only dislocation lines which ran parallel to the interface were seen in the dual-implant sample (top left) to a depth of 700 Å from the interface. The fluorinated oxide sample and control sample showed similar distribution of defects with a depth of 1100 Å and 800 Å respectively. Longer annealing time periods would probably allow defects to diffuse towards the surface and disappear.
Figure 4.32: Planar WBDF images of 60 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
Figure 4.33: Cross-sectional WBDF images of 60 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
Figure 4.34: Planar WBDF images of 120 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
Figure 4.35: Cross-sectional WBDF images of 120 min anneal; Top left: dual-implant sample; Top right: fluorinated oxide sample; Bottom: control sample.
4.4 EELS results

Conventionally, SIMS (Secondary Ion Mass Spectroscopy) has been used to determine the elemental profiles of similar samples. However, it is convenient to use EELS (Electron Energy Loss Spectrometry) in TEM for microanalysis. The spatial resolution of the microscope provides the possibility of correlating microstructure and quantitation. If the oxygen and fluorine profiles were obtained, the correlation between these atoms/ions and the defects would give us the insight on the behavior of the defects. In our studies, the percentage of the implanted ions and recoil atoms are low. Therefore, EELS was attempted to see if it would work for these types of problems, i.e., quantitation of typically one part per thousand in reasonably thick (100-150nm) samples.

EELS was performed only on the 60 min annealed dual-implant sample. The silicon concentration was measured using LLS (Linear least-squares) background estimation \([38]\) of the silicon L23-edge \((99eV)\). Since the oxygen K-edge at 532eV was not obvious in the normal spectrum, the first difference mode was used for acquisition (see figure 4.36) which virtually eliminates detector artifacts, suppresses the large background and enhances small peaks. In this way, the ratio of silicon to oxygen was obtained. The acquisition time for the oxygen spectra was 800 seconds and the current in the probe was 0.6 nA. The probe size is estimated to be approximately 3nm in diameter. Spectra were acquired in 100Å intervals past the interface until the oxygen concentration reached the native oxide level. These results are shown in figure 4.37.

The contribution of the native oxide grown on the silicon side perpendicular to the interface, i.e., the preparation surface, must be considered. It was calculated to be \(9.50e19 \pm 2.60\) atoms/cc at several points on the silicon side of the sample and is thus assumed to be of constant thickness everywhere on the silicon side. This
Figure 4.36: 1st difference mode spectra showing the oxygen edges (532 eV) for two different concentrations of the profile shown in Figure 4.37.
Figure 4.37: Profile of oxygen concentration in atomic percent calculated using EELS. Ordinate errors are +/- three standard deviations. The silicon/silica interface is assumed to be at 0 nm.
Figure 4.38: Profile of oxygen concentration in atoms per cubic centimeter. The native oxygen contribution is removed from points within the silicon. Ordinate errors are +/- three standard deviations.
number is subtracted from the oxygen concentration detected in the elemental silicon region and the results shown in Figure 4.38. The concentration of oxygen detected in the thin specimen may not be representative of corresponding regions within whole specimens. This could be due to loss from the IBT milling stage, out-diffusion of oxygen, and electron knock-on during analysis.

These results prove the useability of EELS for this type of analysis. The EM400 microscope used to obtain this data limited the quality of the data attainable with the technique. Fluorine and boron were detected in this study but no attempt was made to quantify their distribution due to these limitations. Smaller probe sizes and higher resolutions available with field-emission instruments make these and similar experiments feasible. Also, with a computerized line-scan analysis, i.e., the use of spectrum imaging [39], more reliable profiles could be obtained. This technique would allow analysis of thousands of points, minimize specimen dosage, minimize probe placement errors, automate analysis, and provide data in an image format.
Chapter 5

Conclusions

The incorporation of fluorine showed a significant effect on residual defect distribution in silicon caused by ion implantation. The dual-implant sample showed the least defect density for all annealing time periods. It is suspected that significant recombination of vacancies and interstitials occurred since Monte Carlo simulation shows the vacancy concentration generated from the fluorine-implant overlapped with the interstitial concentration from the boron-implant. It is also assumed that the Si-F complexes were formed to reduce the interstitial supersaturation. Furthermore, the nature, the shape and the size of the defects in respect to the annealing time are related to the overall increase of stacking fault energy due to the presence of fluorine.

The incorporation of fluorine through oxidation was quite unsuccessful because the fluorine atoms were tightly bonded to the oxide and no recoils were detected in the silicon. However, the Monte Carlo simulations predicted the interstitial and vacancy concentrations situated at about the same place from the results of ion-implantation. Therefore, significant recombination could occur and reduction of the supersaturation of interstitials would lead to a decrease in defect generation. The resultant high density of defects was mainly due to the exceptionally thin oxide formed on the
silicon substrate. Therefore, there was no observation of the reduction of defects due to the fluorine oxidation.

It is suggested that thinner TEM samples and better equipment should be used for EELS studies to determine fluorine and oxygen profiles. Determination of the kinetics of the overall stacking fault energy due to the presence of fluorine should be performed. Also, experiments should be designed to fully understand whether Si-F complexes were formed to reduce the interstitial supersaturation. Furthermore, a better designed experiment should be used to reveal the role of fluorine when it is incorporated during oxidation.
References


[29] Trim program obtained from T.S. Ravi at Bellcore


Vita

Amy Lam was born in Hong Kong on January 29, 1968. She is the only child of Mr. & Mrs. K.Y. Lam. Her parents had decided it is for her best to further her studies in the States for a higher degree. She spent her first four years at Rutgers University and obtained the B.S. degree in Ceramic Engineering in June 1990. During the summer intern with Bellcore in her junior year, she realized how much she was interested in microscopy. Therefore, she came to Lehigh University, because of its fantastic reputation in microscopy, for an advanced degree in Materials Science and Engineering. She has worked under the supervision of Professor R.J. Jaccodine and fulfilled the requirement for her Master's in May 1992. She has recently received the EMSA Presidential Scholar Award and will be attending the EMSA meeting in Boston in August.
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