Quantification of the number of Si interstitials formed by hydrogen implantation in silicon using boron marker layers

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H implantation results in the appearance of tensile out-of-plane strain in the implanted region which evolves during further annealing. \( V_n H_m \) complexes and/or larger platelets, both co-precipitates of vacancies and \( H \) atoms, are believed to be responsible for strain generation. However, during \( \text{H}^+ \) implantation, Frenkel pairs i.e., both vacancies and interstitials are generated. Silicon self-interstitials have been rarely detected and thus their possible role in strain generation has been ignored so far. In this work, we demonstrate that Si interstitials are actually present in large measurable quantities in such implanted layers. For this, we have studied by Secondary Ions Mass Spectrometry the diffusion of boron delta layers during annealing at 350 °C, 550 °C and 850 °C after \( \text{H}^+ \) implantation at 12 keV with a fluence of \( 1 \times 10^{18} \text{H}^+/\text{cm}^2 \). The Si self-interstitial supersaturations were extracted by comparison with simulations. Frank dislocation loops, i.e., precipitates of Si atoms, were observed by Transmission Electron Microscopy growing by Ostwald ripening during 850 °C annealing. The supersaturation of Si self-interstitials in dynamical equilibrium with these loops was extracted showing consistency with the values found from the diffusion experiments. These results and more generally the role of interstitials in the strain build up are discussed.

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1. Introduction

Hydrogen implantation is used in the Smart Cut™ process for the manufacturing of Silicon on Insulator (SOI) wafers. The incorporation of hydrogen in the lattice results in a tensile out-of-plane strain [1]. This strain plays a decisive role during the process, and the understanding of its origin is mandatory for further improvement. This strain is believed to originate from the overlapping of nano-strains generated by all the implantation defects. Hence, the identification and the quantification of these defects are needed to estimate their contribution to the overall strain. During implantation, the slowing down of the ion generates interstitials and vacancies named Frenkel pairs. Hydrogen atoms can then bind with both vacancies and interstitials to form immobile complexes. Optical measurements (Infrared Spectroscopy [2] and Raman [3]) identified those complexes as \( \text{H}_2 \) for interstitials and \( V_n H_m \) (with typical values \( n < 3 \) and \( m < 8 \)) for vacancies, but the estimation on their individual densities is difficult. Transmission Electron Microscopy (TEM) shows the growth of platelets [4], i.e. co-precipitates of vacancies and hydrogen during annealing. However, for the same annealing, no precipitates of interstitials were previously detected by TEM. The motivation of this work is to understand the behaviour of silicon interstitials after hydrogen implantation and during annealing. For this, we have set-up experiments to prove the existence and quantify the number of silicon interstitials induced by implantation using two independent approaches. The first one consists in identifying the silicon interstitial supersaturation by measuring the diffusivity of boron delta layers during annealing. This relies on the fact that boron is mainly diffusing through B–I pairs and the amplitude of its diffusion is proportional to the concentration of silicon interstitial atoms. The second approach consists in imaging by TEM then quantifying the population of interstitial precipitates found after high temperature annealing. Then, the supersaturation of free silicon interstitials in dynamical equilibrium with these defects can be calculated from the Gibbs–Thomson equation which applies during the Ostwald ripening of precipitates [5]. Finally, the results provided by the two methods are compared and a scenario describing the evolution of silicon interstitials during annealing is proposed.

2. Experimental setup

A silicon (001) wafer containing three doping boron delta layers grown by MOCVD was implanted with hydrogen. The delta markers are 10 nm wide and are located at depths of 100, 500...
and 900 nm, respectively, below the sample surface. The sample was implanted by 12 keV H\(^+\) ions at a fluence of \(1 \times 10^{16}\) cm\(^{-2}\) at room temperature. According to Monte Carlo simulations, the hydrogen peak should be located beyond the first boron marker at a depth of about 170 nm. After implantation, the wafer was first annealed at 350 °C for 5 min to allow for platelet formation and to stay in the frame of the technological process. A piece of this wafer was then additionally heated at 550 °C during 60 min. Parts of this sample were annealed at 850 °C for different durations (15, 30, 60 and 90 s) using rapid thermal annealing. The objectives of the 550 °C and 850 °C annealing are to activate the exo-diffusion of hydrogen and to possibly form silicon interstitial precipitates detectable by TEM. TEM and Secondary Ions Mass Spectrometry (SIMS) were performed on each sample to follow the evolution of defects and of both the hydrogen and boron profiles. The TEM samples were prepared in cross-section by mechanical polishing and subsequent ion thinning. Statistical measurements for the analysis of the defect populations were performed on a large number of images obtained using a 200 keV JEOL2010. The imaging of platelets was performed under off-Bragg under-focus conditions, while dislocation loops were imaged under weak beam dark field (WBDF) conditions, as described in [6].

3. Results

3.1. Hydrogen evolution during annealing

After implantation, the hydrogen “peak” is located at 200 nm below the surface (Fig. 1). The profile shrinks after 350 °C annealing and its maximum amplitude decreases, a classical characteristic resulting from hydrogen precipitation [7]. Indeed, TEM observations (Fig. 2) indicate the presence of thin platelets after this first annealing. In the 550 °C annealed sample, the hydrogen concentration as detected by SIMS becomes very low and, at the same time, the thickness of the platelets is larger. This shape modification of the platelets to less flattened cavities results from the loss of hydrogen during annealing [8]. Above 850 °C and for any duration, hydrogen is no longer detected by SIMS and neither platelets, nor cavities are detected by TEM.

3.2. Boron diffusion during annealing

Initial boron concentrations within the delta-layers measured by SIMS are found close to \(10^{18}\) cm\(^{-3}\) (Fig. 3). At such concentrations, the dopants are on substitutional sites in the lattice. Under equilibrium conditions, the diffusion lengths corresponding to the 350 °C and 550 °C anneal can be estimated to be of about 10 Å and 10 \(^2\) Å [9], respectively. Equilibrium diffusion should then be undetectable by SIMS. However, after each annealing, boron diffusion is visible through a peak widening and a lowering of its maximum concentration. Then, this boron diffusion is the proof of the existence of large supersaturations of silicon interstitials during these annealing. Indeed, this enhancement of boron diffusion is equal to the mean supersaturation \(S\) of free Si self-interstitials during annealing:

\[
S = \frac{D_B}{D_B^{eq}} C_i/C_f
\]

where \(C_i\) and \(C_f\) are the concentrations of silicon interstitials in the implanted layer and at equilibrium, respectively. \(D_B\) is the diffusivity of boron in silicon at equilibrium concentration of silicon interstitial \(C_f\). Using a fitting procedure, we have extracted the values of the “mean boron diffusivity” during each annealing from the SIMS data. In the diffusion model, a boron atom in substitution in the lattice is immobile and can be “kicked-out” from its position by a silicon interstitial to become a mobile entity. Using this assumption, boron diffusivity \(D_B\) relies on two parameters, \(\lambda\) the mean diffusion length of the boron-interstitial pair and \(g\), the generation rate of those pairs per unit of time:

\[
D_B = \lambda^2 g
\]

According to the diffusion equations, each pair of \(\lambda\) and \(g\) predicts a different evolution of the initial boron layer. A unique solution can be deduced when fitting with the SIMS profiles measured after annealing. This extracted diffusivity is the “mean diffusivity” that occurred during the entire annealing period of time. The mean supersaturations of Si self-interstitials that can be then extracted from these values refer to the boron diffusivity at equilibrium \(D_B^{eq} = 3.79 \times 10^{-6}\) cm\(^2\) s\(^{-1}\) [9]. \(D_B^{eq}\) can be reasonably extracted from experimental measurements at 900 °C but further extrapolation to low temperatures of annealing, i.e. 350 °C and 550 °C, cannot result in more than a rough estimation of the supersaturations at such temperatures. Still, those supersaturations are very high and this means that Si self-interstitials evolve in large concentrations in the layer during annealing.

Another notable point visible in the SIMS results is that, above 550 °C, boron is trapped in large quantities in the damaged area. From the literature we know that small precipitates of interstitials and dislocations loops can trap boron atoms [10,11]. Thus, this boron secondary peak is probably the signature of these interstitial defects.

3.3. TEM analysis of dislocation loops

When annealing at temperatures below 850 °C, the layer is very strained and the contrast in the images prevents us to conclude on the presence or not of extrinsic defects. After 850 °C annealing, for any duration, H-related platelets cannot be detected anymore but TEM shows the presence of circular dislocation loops instead (Fig. 4). The inset shows two types of contrast which can arise from
these loops when seen in cross-section. Contrast analysis shows that they are extrinsic faulted dislocation loops (FDLs) [6], i.e. precipitates of Si atoms lying on the {111} planes. When the annealing time increases, their mean diameter increases whereas their density decreases (Fig. 5). The total number of interstitials trapped in the dislocation loops per surface area (i.e. the areal density of interstitials) can be obtained by multiplying the defect density by the mean surface of the loops. Although the experimental incertitude is large, we demonstrate that this value is in the $10^{13}$ to $10^{17}$ cm$^{-3}$ range and remains unchanged during annealing at 850 °C. This shows that the loops evolve following a conservative process named Ostwald ripening as described in details in [5].

4. Discussion

Here, we briefly recall how the observed growth of the dislocation loops during annealing can be related to the time and space evolution of free Si interstitial atoms in their vicinity [5]. During their growth by Ostwald ripening, the FDLs are in dynamical equilibrium with a supersaturation of free silicon interstitials. This supersaturation only depends on the mean size of the loops and on the temperature and obeys the Gibbs–Thomson relation which can be written:

$$S = \frac{C_i}{C_j} = \exp \left( \frac{E_F}{RT} \right)$$  \hspace{1cm} \text{(3)}$$

where $E_F$ is the formation energy of the defects [5]. The results are shown in Fig. 6 and compared with those extracted from B diffusivity measurements. This comparison shows that the values of supersaturations we have independently obtained following two approaches are very consistent with each other. This definitively evidences that large concentrations of silicon interstitial atoms exist and evolve during annealing of hydrogen implanted silicon.

However, the areal density of these silicon interstitial atoms bound to the loops we have measured is significantly smaller than the hydrogen fluence. Besides, the supersaturations we have deduced from both types of experiment indicates that the absolute concentrations of silicon interstitials which evolve in the implanted layer range from about $10^{15}$ to $10^{17}$ cm$^{-3}$ depending on the annealing temperature. These values, which are large if one looks at their impact on diffusion phenomena, are small when considering their possible contribution to the overall deformation of the implanted annealed layer. Indeed, first order estimation of the strain generated by such Si interstitials shows that, at such concentrations, the out-of-plane strain they would generate is less than $10^{-6}$ to $10^{-4}$ times the overall strain measured in the as-implanted layer. In other words, although we have

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Fig. 3. SIMS profiles showing the evolution of the boron delta layers. (a) After H+ implantation (b) before and after 850 °C (90 s) annealing.

Fig. 4. Weak beam dark field cross-sectional (1 -1 0) image taken with g = 004 of H+ implanted sample annealed at 850 °C (90 s).

Fig. 5. Graph showing the evolution of the loop density (left axis) and mean diameter (right axis) with annealing duration at 850 °C.

Fig. 6. Graph comparing the values of the Si supersaturations as deduced from the characteristics of the loop population measured by TEM (triangles) with those extracted from boron diffusivity measurements (squares).
proven the existence of quite large concentrations of silicon interstitials in the H implanted layers during annealing, we believe that these concentrations are not large enough to have a noticeable influence of the overall strain evidenced in these layers. However, it is possible that, in the as implanted layers, the initial concentration of Si interstitial atoms is significantly larger than that found after annealing. Indeed, Si interstitial atoms are known to recombine easily at the wafer surface during annealing and this could result in the massive loss of those Si defects, initially present in the as-implanted layer. This possibility will be examined in detail in a fore coming paper.

5. Conclusion

Up to now, the strain build up evidenced during annealing of H implanted Si layers has been exclusively ascribed to the behavior of V and H complexes. However, like every ion implantation, hydrogen implantation results in the formation of Frenkel pairs i.e., a large and same number of vacancies and interstitials. Very little was known about the existence and possible role of these Si interstitials. We have tried to estimate their concentrations during the annealing of such implanted layers following two approaches. One was based on the study of the diffusion of boron marker layers, which can be used as detectors of Si interstitials supersaturations, the other one based on the observation of the evolution of a population of dislocation loops, which can be related through the Gibbs–Thomson equation to the concentration of Si interstitials being in dynamical equilibrium with them. Both approaches give similar results. The concentrations of Si interstitials we have evidenced during annealing are large if one considers their effect on diffusion phenomena but small if one considers their possible contribution to the overall strain found in these layers. However, we cannot rule out that these concentrations could be much larger before annealing, in the as implanted layers. The demonstration of this possibility will require further work, mixing numerical simulations and experimental results. However, at present, we can conclude that since the Smart Cut™ process takes place during annealing, the contribution of the Si interstitial atoms to the strain build up driving this process is probably negligible.

References