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

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ABSTRACT

H implantation results in the appearance of tensile out-of-plane strain in the implanted region which evolves during further annealing. V_nH_m complexes and/or larger platelets, both co-precipitates of vacancies and H atoms, are believed to be responsible for strain generation. However, during 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 H implantation at 12 keV with a fluence of 1×10^{16} H^+/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.

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 IH_2 for interstitials and V_nH_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 ⟨0 0 1⟩ 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

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and 900 nm, respectively, below the sample surface. The sample was implanted by 12 keV H^+ ions at a fluence of 1×10^{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 based 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^{-6} 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-interstitial during annealing:

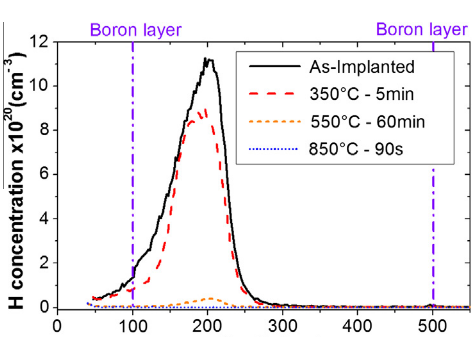

Fig. 1. SIMS profiles showing the evolution of hydrogen during annealing. The H profile after 850 °C is lost in the background.

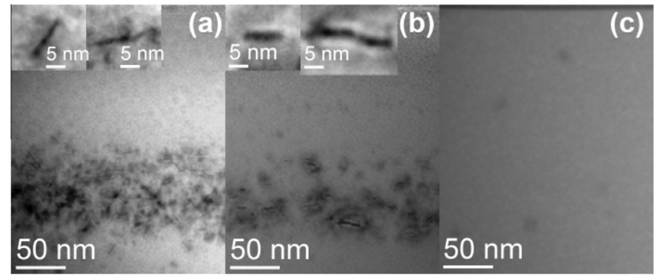

Fig. 2. Cross-sectional TEM micrographs taken under off-Bragg conditions of the samples implanted with H at 12 keV to a fluence of 10^{16} cm^2 and annealed, (a) at 350 °C, (b) at 350 °C and 550 °C, (c) at 350 °C, 550 °C and 850 °C (90s).

$$S = \frac{D_B}{D_B^*} = \frac{C_i}{C_i^*} \qquad (1)$$

where C_i and C_i^* 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_i^*. 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, λ the mean diffusion length of the boron-interstitial pair and g, the generation rate of those pairs per unit of time:

$$D_B = \lambda^2 . g \qquad (2)$$

According to the diffusion equations, each pair of λ 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 $D_B^* = 3.79 \times \exp(-\frac{3.64\text{eV}}{kT})$ [9]. D_B^* 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