

## Boron Diffusion and Silicon Self-Interstitial Recycling between SiGeC layers

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### ABSTRACT

Substitutional carbon is known to locally reduce silicon self-interstitial concentrations and act as a barrier to self-interstitial migration through the carbon rich regions. A silicon spacer between two carbon rich SiGe layers is fabricated in this work to examine self-interstitial generation in a region that is isolated from self-interstitial formation at the surface or in the silicon bulk. Boron marker layers above, below and in between two SiGeC layers are used to monitor the self-interstitial concentration between the substitutional carbon. No evidence of self-interstitial depletion in the silicon spacer is observed, despite annealing in conditions believed sufficient to allow the self-interstitials to reach and react with surrounding substitutional carbon. Simulations of the self-interstitial and carbon indicate that the silicon self interstitial concentration in the spacer layer can be sustained in part due to a silicon self-interstitial recycling process through a reverse “kick-out” reaction.

### INTRODUCTION

Accurate modeling of silicon front-end processes has become increasingly important because of the increasing expense of trial and error experiments for advanced complementary metal oxide semiconductor (CMOS). A necessity for simulation of dopants like boron is the ability to predict relative silicon self-interstitial concentrations, which promote boron diffusion [1]. However, critical parameters like self-interstitial diffusivities and generation rates are still under investigation [2-4].

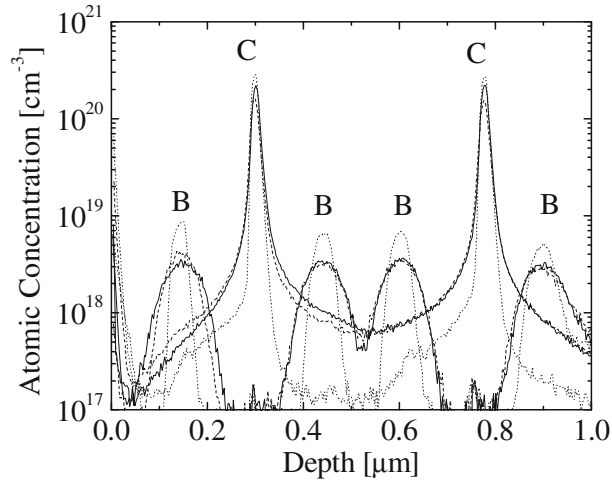
Previously it has been shown that a SiGeC layer efficiently getters interstitials that migrate to the carbon layer. This effect can be used to effectively insulate the silicon below the SiGeC layer from interstitials introduced from the surface. Therefore, a region of silicon between two SiGeC layers is effectively insulated from interstitials injected from the surface and the bulk. Furthermore, self-interstitials in a silicon region between two SiGeC layers will diffuse to the surrounding carbon layers, where they would be expected to react with the carbon removing them from the silicon spacer. Because it is believed that the SiGeC layers insulate the silicon spacer from the bulk and the surface, the interstitial concentration in the spacer will depend entirely on a detailed balance between the self-interstitial generation rate in the spacer and the rate of interstitials that diffuse to the surrounding carbon layers where they are consumed. This novel structure offers a method to probe the generation rate of silicon self-interstitials.

### EXPERIMENT

Single crystal, 25 nm thick boron marker layers located at 150, 440, 600, and 900 nm below the surface were grown by rapid thermal chemical vapor deposition at temperatures of 550-750°C on Czochralski silicon substrates with or without two 25 nm Si<sub>0.775</sub>Ge<sub>0.22</sub>C<sub>0.005</sub> layers at depths of 300 and 750 nm. The samples were subsequently annealed in either nitrogen for 30, 120 or 240 minutes at 850°C, or oxygen for 30, 60 or 120 minutes at 850°C. Carbon, germanium and boron concentrations before and after annealing are measured by secondary ion mass spectrometry (SIMS) with 20% and 5% uncertainties in concentration and depth, respectively.

The resulting boron profiles were fit using a standard process simulator [5] to extract boron diffusivities for each of the conditions. X-ray diffraction of single SiGeC layers grown using similar conditions and annealed under the same conditions show that the carbon is 100% substitutional before and after annealing [6].

Boron and carbon concentration depth profiles before and after annealing for 30 minutes in either nitrogen (dashed lines) or oxygen (solid lines) ambients in a sample with two SiGeC layers are shown in Fig. 1. Enhanced broadening due to oxidation is observed in the surface region of the sample with the SiGeC layers, but no sign of enhanced diffusion is observed in the region between the SiGeC layers. In the sample without SiGeC the boron diffusion enhancement during oxidation was also observed.



**Figure 1.** Carbon and boron concentration profiles before (dotted) and after 30 minutes annealing at 850°C in either nitrogen (dashed) or oxygen (solid) ambients.

The boron diffusivity in silicon is believed to be mediated nearly 100% by a self-interstitial mechanism around 800°C [1] and the boron diffusivity is believed to depend on the self-interstitial super saturation as:

$$\frac{D_B^{meas}}{D_B^*} \cong \frac{I}{I^*} \quad (1)$$

where  $\frac{D_B^{meas}}{D_B^*}$  is the average boron diffusivity enhancement during oxidation with respect to

intrinsic diffusion (\* indicates intrinsic value taken from literature),  $\frac{I}{I^*}$  is the interstitial super-saturation. Oxidation enhanced diffusion results from extra self-interstitials injected at the oxide/silicon interface, and the enhanced diffusion is a consequence of the subsequent self-interstitial migration into the boron doped regions, which promotes additional boron diffusion [7, 8].

The suppression of oxidation enhanced diffusion below SiGeC layers has previously been reported [9, 10] and the efficient formation of mobile interstitial-carbon formed through self-interstitials reacting with substitutional carbon has been proposed as the explanation for this phenomena [11]. This reaction is sometimes called the “kick-out” (KO) reaction:

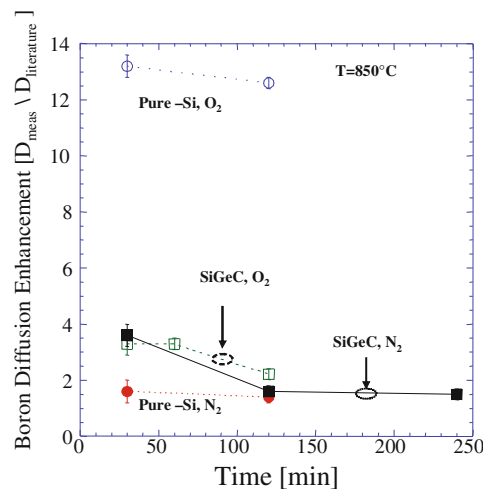


where  $C_s$  is a carbon atom in a substitutional site,  $I$  is the silicon interstitial,  $C_i$  is the mobile interstitial carbon defect. The resulting carbon out-diffusion due to the creation of the mobile

carbon can insulate the underlying silicon from the injected excess self-interstitials.

A single boron diffusivity was used to fit the diffusion in the all silicon samples and between the SiGeC layers for each annealing time and for each ambient. The diffusivities are compared to those found in the pure silicon sample grown on the same day and annealed in identical conditions in Fig. 2. The boron diffusivity in the pure silicon samples after annealing in a nitrogen ambient agrees relatively well with previous reports (e.g.,  $2.3 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$  at  $850^\circ\text{C}$  [12]), while during annealing in oxygen the boron diffusivity is found to be an average of 12-14 times greater than the literature value, Fig. 2. This is in relatively good agreement with previous reports of oxidation enhanced diffusion at  $850^\circ\text{C}$  [13, 14].

The boron diffusivity between the SiGeC layers after annealing in nitrogen was found to be indistinguishable from that after annealing in oxygen for the same time, Fig. 1 & 2. The absence of enhanced diffusion in the silicon spacer between the SiGeC layer during the oxidation indicates that the SiGeC layer effectively insulates the spacer from self interstitials in the surface region.



**Figure 2.** Summary of the average boron diffusivities in the pure silicon sample (circles) or in the silicon spacer between the SiGeC layers (squares) after annealing in either nitrogen (solid) or oxygen (hollow) ambients at  $850^\circ\text{C}$ .

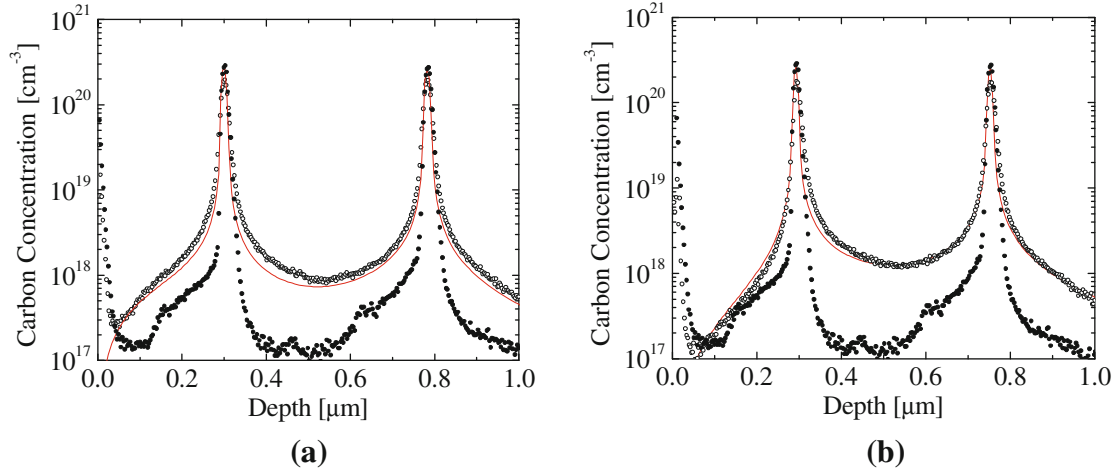
Although there is no evidence of oxidation enhanced diffusion, the boron diffusivity in the silicon spacer layer is found to be greater ( $\sim 4$  times) than in the pure silicon case at early annealing times, Fig. 2. Because the SiGeC layers have sufficient substitutional carbon to insulate the spacer from the surface and bulk self-interstitials a different source of self interstitials is believed to cause the enhanced boron diffusion between the SiGeC layers.

Estimates of the self-interstitial diffusivity vary over a large range [4], however, the diffusion length for a single self-interstitial after annealing at  $850^\circ\text{C}$  for 30 minutes is expected to far exceed the width of the silicon spacer between the SiGeC layer in this experiment. A conservative estimate of the diffusion length of the self-interstitial is  $\sim 800 \text{ nm}$  for the case of  $[\text{C}] \sim 10^{18} \text{ cm}^{-3}$  [15]. Almost all the silicon self-interstitials in the silicon spacer layer are, therefore, expected to have time to diffuse to the surrounding SiGeC layers and react with the substitutional carbon within the annealing times examined in this work. Self interstitials, therefore, are being generated in the spacer during these anneals to maintain the observed boron diffusivity. Saturation of the carbon with self-interstitials from the spacer is ruled out as a possibility because the oxidation enhanced diffusion is suppressed also at longer times.

To explain the anomalous non-gaussian carbon diffusion and reduced boron diffusivities observed around the SiGeC layers a combined KO (eqn. 2) and Frank-Turnbull mechanism has previously been proposed:



where  $V$  is a silicon vacancy [16]. Using a combination of experimentally obtained values and assuming a mass action relationships between carbon and the silicon point defects, values for the forward and reverse reaction rates for eqn.'s 2 & 3 can be derived and used to simulate self-interstitial, vacancy, interstitial-carbon and substitutional carbon concentrations and diffusion [16, 17]. To test this model's predictions for our case the carbon diffusion was simulated by numerically solving the coupled partial differential equations describing the linked diffusion and generation/recombination relationships of all the elements [5].



**Figure 3.** Experimental (circles) and simulated (solid lines) carbon concentration profiles before (solid) and after (hollow) annealing for 120 minutes at 850°C in (a) nitrogen or (b) oxygen ambients

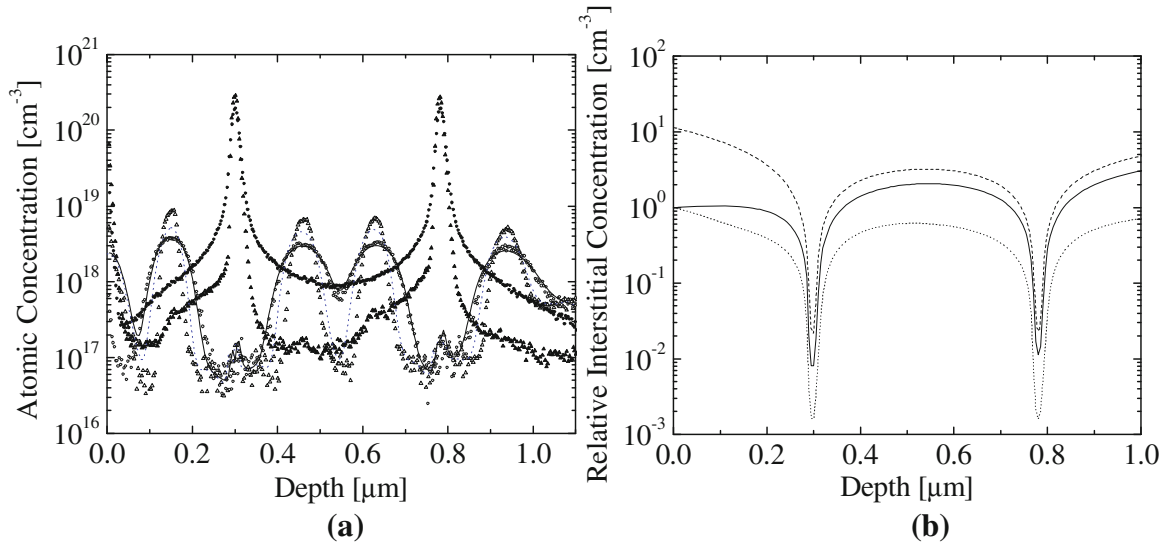
Using values from Bracht [4] and Ural [18] for the equilibrium point-defect concentration & diffusivities (see Table 1), and setting the surface boundary condition for all elements at their experimentally or calculated thermal equilibrium values during nitrogen anneals, the experimentally obtained carbon diffusion profile after 120 minutes of annealing in nitrogen can be relatively well reproduced, Fig. 3 (a). During oxidation the self-interstitial surface boundary condition changes because of the self-interstitial injection. The self-interstitial concentration has been found to be fixed at  $\sim 12.4$  times its intrinsic value at 850°C independent of the proximity of the SiGeC layer [9]. Using this boundary condition, very good agreement between the experimental and simulated carbon profiles is also achieved, Fig 3 (b). Because the simulation also tracks the self-interstitial concentration, the boron diffusion can also be simulated and very good agreement can be obtained between the observed and simulated boron diffusion after 120 minutes in nitrogen when both KO and FT mechanisms are considered, Fig. 4 (a). The simulated self-interstitial concentrations, furthermore, show a predicted super-saturation within the silicon spacer layer during both the nitrogen and oxidation case in good agreement with the experimental observation of enhanced boron diffusion between the SiGeC layers, Fig. 4 (b).

**Table I.** Diffusivities and equilibrium concentrations used for simulations at 850°C

$D_{C_s}$ [cm <sup>2</sup> s <sup>-1</sup> ]	$C_s^*$ [cm <sup>-3</sup> ]	$D_{C_i}$ [cm <sup>2</sup> s <sup>-1</sup> ]	$C_i^*$ [cm <sup>-3</sup> ]	$D_V$ [cm <sup>2</sup> s <sup>-1</sup> ]	$V^*$ [cm <sup>-3</sup> ]	$D_I$ [cm <sup>2</sup> s <sup>-1</sup> ]	$I^*$ [cm <sup>-3</sup> ]
$2.3 \times 10^{-14}$	$1.9 \times 10^{14}$	$5.5 \times 10^{-5}$	$7.5 \times 10^4$	$2.5 \times 10^{-10}$	$1.5 \times 10^{14}$	$5.8 \times 10^{-7}$	$1.6 \times 10^{10}$

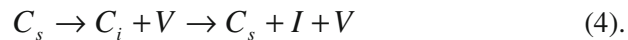
Two mechanisms lead to self-interstitial generation within the silicon spacer layer in the simulation. Silicon self-interstitials are, firstly, produced due to a reverse KO mechanism.

Mobile interstitial-carbon that is produced in the SiGeC layer is predicted to migrate out of the SiGeC layer and return to a substitutional site within the silicon spacer through “kicking-out” a substitutional silicon atom, which ultimately results in the return of silicon self-interstitials in the spacer region. Self-interstitials that migrate from the spacer and are consumed in the SiGeC layer as interstitial-carbon are, therefore, effectively recycled through the reverse migration of interstitial carbon back into the spacer.



**Figure 4.** (a) as-grown boron (hollow) and carbon (solid) concentrations before (triangles) and after 120 minutes annealing (circles) at 850°C in nitrogen compared to FT + KO (solid line) and KO only (dashed line) simulations; and (b) the simulated relative silicon self-interstitial concentrations after 120 minutes annealing at 850°C using both the FT and KO mechanism in nitrogen (solid) and oxygen (dashed) compared to the same simulation using only the KO mechanism in nitrogen (dotted).

This first mechanism of self-interstitial generation in the spacer layer does not, however, explain how a super-saturation of self-interstitials can occur because self-interstitials can only be recycled and extra are not produced by this mechanism. An undersaturation of self-interstitials is in fact predicted when only the KO mechanism is used, Fig. 4 (b). The second and only other source of self-interstitial generation in the silicon spacer layer, that is present in the simulation, is the conversion of interstitial-carbon into self-interstitials through a combined FT and reverse KO mechanism:



The reverse KO is predicted to be a significantly faster mechanism of annihilation of interstitial carbon than a reverse FT mechanism.

The simulated carbon diffusion using the combined FT and KO mechanisms predicts that the SiGeC layer will act as a source of self-interstitials and vacancies. Enhanced vacancy concentrations in the presence of SiGeC have been previously reported [17], which further supports the FT hypothesis. Finally, the super-saturations simulated using the combined KO and FT mechanisms are indeed quantitatively similar to the enhanced boron diffusivities observed in the experiment demonstrating that the over-saturation of self-interstitials in the silicon spacer region may be understood simply as a consequence of self-interstitial recycling of consumed self-interstitials via the reverse-KO mechanism, without need of an alternative mechanism of interstitial generation.

## CONCLUSION

Boron diffusion between two SiGeC layer has been used to monitor the silicon self-interstitial concentration in a region that is isolated from silicon self-interstitial generation and migration from the bulk and surface. Boron diffusivities between the SiGeC layers are found to be approximately equal or greater than that observed in silicon samples without substitutional carbon. Simulation of the carbon diffusion indicates that by considering both the Frank-Turnbull (FT) and the kick-out (KO) mechanism super-saturations of self-interstitials are predicted between the SiGeC layer in agreement with the enhanced boron diffusivities observed in experiment and furthermore the combined KO & FT model reproduces several novel effects of oxidation on both the boron and carbon diffusion. Self-interstitial recycling and generation through the reverse KO mechanism is, therefore, sufficient to explain the observed source of self-interstitial generation in this work.

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