THE EFFECT OF CARBON/SELF-INTERSTITIAL CLUSTERS ON CARBON DIFFUSION IN SILICON MODELED BY KINETIC MONTE CARLO SIMULATIONS

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ABSTRACT

A new model for carbon diffusion in silicon that explains carbon diffusion during annealing at 850ºC and 900ºC in superlattice carbon structures grown by MBE is implemented using the Monte Carlo atomistic simulator DADOS. Carbon concentrations in the delta layers are 2x10^{20} cm^{-3}, exceeding by far the solid solubility. The simple kick-out mechanism which incorporates the well established values of the product of diffusivity and equilibrium concentrations of intrinsic point defects and in-diffusion experiments of carbon in silicon does not explain the observed C diffusion profiles. A more detailed analysis of the experiments shows that, in order to fit them, a more unstable C\textsubscript{i} is required. Therefore, we include the formation of clusters in the simulations. The formation of carbon/Si self-interstitial clusters promotes the premature break-up of C\textsubscript{i} and the increase of the Si self-interstitial concentration in the carbon rich regions and, consequently, provides a better fit to the experiments. The low solubility of carbon in silicon at the annealing temperatures explains why these clusters are formed, even under conditions where the self-interstitial concentration is below the equilibrium value.

INTRODUCTION

Carbon (C) is present in silicon (Si) as a substitutionally dissolved isovalent impurity, introduced during the crystal growth. It appears in high concentrations, ranging from 10^{16} cm^{-3} to 10^{18} cm^{-3}, well above its solubility at the usual annealing temperatures. Previous experiments have shown that C can reduce the implantation-induced supersaturation of Si self-interstitials (I) and thus prevent the so-called transient enhanced diffusion (TED) of interstitially diffusing dopants such as boron (B) [1]. Recently, it has been also shown that, even in the absence of I supersaturation, the presence of C in Si in concentrations • 10^{19} cm^{-3} leads to an undersaturation of I which, in turn, cause retarded boron diffusion [2].

The diffusion of C in Si occurs via the kick-out mechanism [3, 4]:

\[ C_s + I \leftrightarrow C_i \]  

where C\textsubscript{s} denotes a carbon in a substitutional position that can be considered immobile while C\textsubscript{i} is the highly mobile specie that is either a carbon in an interstitial position or a pair composed of a carbon and a self-interstitial. In addition to being the mobile specie of carbon, C\textsubscript{i} is believed to be the trap of self-interstitials that produces the reduction of boron diffusion even in conditions of thermal generation of point defects [2, 5].

To reproduce carbon diffusion experiments in absence of I supersaturation, continuum simulations, based on standard partial differential equations for the concentrations of I, C\textsubscript{i} and C\textsubscript{s}.

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in terms of the kick-out mechanism, were developed by different groups [4,5,2]. The reaction constants for Equation (1) can be extracted from well-established experiments of radio-tracers of silicon self-diffusion [6], of carbon solubility [7] and in-diffusion [8,9] in addition to measurements of the diffusivity of C [10,11]. These experimental values do not allow any free parameters in the model. All of the authors reached the same conclusion: once all the experimental constrains are included, the flux of C from the carbon-rich regions is too high and, therefore, it is necessary to introduce an extra source of self-interstitials to reproduce the carbon diffusion, otherwise the model predicts a reduced diffusion of carbon and an too low concentration of self-interstitials in the carbon-rich regions.

In this work, we show both that Kinetic Monte-Carlo simulations performed with the DADOS [12] simulation package produce the same results as the continuum simulations, and that the experiments can not be explained using the kick-out mechanism alone. In fact, a detailed analysis of carbon diffusion in MBE-grown spikes allows the extraction of the distance run by a C before its break-up, the so-called long hop of C (λ), and shows a clear discrepancy between the experiment and the kick-out model. Finally, we will propose a new model that includes, in addition to the kick-out mechanism, the formation of carbon/self-interstitials clusters. In this new model, the long-hop of C is reduced while self-interstitials are released in the carbon-rich region, providing a better explanation of the experimental results.

For this purpose, we utilized a super lattice structure (SL) of carbon spikes in Si. Similar to extensively used boron doping SL [1,13], the carbon SL’s [4] include 6 C spikes, 10 nm wide with carbon concentrations of 2x10^{20} cm^{-3}, spaced 100 nm apart, capped with 50 nm silicon, which were epitaxially grown by MBE on FZ (100) Si substrates. Carbon was evaporated in elemental form from a special high-temperature carbon source. It is assumed that carbon is fully substitutional incorporated during growth at a temperature of 450ºC. Samples were annealed in a tube furnace at 850ºC and 900ºC in Ar (accuracy 10K). The diffusive behavior of C was monitored before and after annealing by secondary ion-mass spectroscopy (SIMS).

Table I summarizes the values of the energies of diffusion and formation of the different species involved in carbon diffusion assuming the kick-out model alone. Diffusivities and concentrations relate to the general form D=D_0 \exp(-E_D/kT) and C=C_0 \exp(-E_C/kT). The parameters of C required for the DADOS simulations are its diffusivity D_{Ci}, experimentally measured [10, 11], and its binding energy E_{bCi}, related to its stability and its capability to trap self-interstitials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>D_0 (cm^2/s)</th>
<th>E (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_I</td>
<td>5</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>C_I</td>
<td>2.95e25</td>
<td>3.9</td>
<td>6</td>
</tr>
<tr>
<td>D_V</td>
<td>1e-3</td>
<td>0.43</td>
<td>14</td>
</tr>
<tr>
<td>C'_V</td>
<td>4.6e25</td>
<td>3.66</td>
<td>6</td>
</tr>
<tr>
<td>D_{Ci}</td>
<td>4.4e-3</td>
<td>0.87</td>
<td>10, 11</td>
</tr>
<tr>
<td>D_{bCi}</td>
<td>5</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

E_{bCi} can be calculated in the following manner: from the well established experiments of carbon diffusion, the solubility of C can be easily extracted using the calculations shown in ref.4. Once this solubility is obtained, the binding energy of C can be calculated from
equilibrium conditions, under which, the frequency of break-up of C_1 (kick-in) must be equal to the frequency of formation of C_1 (kick-out) that, as in the continuum model, is diffusion-assisted. Assuming an energy of 1 eV for the migration of I [14], the binding energy of C_1 is obtained as 1.6 eV, in good agreement with recent ab-initio calculations [15].

SIMS measurements of the as-grown (dashed line) and annealed, 900 ºC, 30 min. (open circles), carbon profile of one of the MBE spikes is shown in Figure 1 as well as the simulated profile obtained assuming the kick-out mechanism (line with crosses). As can be clearly seen, the kick-out mechanism alone does not provide a good fit to the experiment. Similar results are obtained for other times and temperatures.

![Figure 1. Secondary-ion-mass-spectroscopy, SIMS, profiles of an as-grown (---) and 900 ºC, 30 min, annealed Carbon spike (-----).DADOS simulations results are also included, either assuming the kick-out mechanism alone, with the parameters extracted from well-established experiments (----), or showing the best fit of the experiment, which provides a value of the long-hop of C_1 (λ) of 14 nm.](image)

Further review of the experimental data, Figure 1, clarifies that the diffused profiles do not follow a Gaussian distribution. In the case of substitutional impurities that diffuse via a fast-diffusing intermediate species, for short times, few atoms migrate and the solution of an initial δ-function impurity profile behaves exponentially [16]. In such a regime and using nanometer-scale doping profiles, the discrete nature of the diffusion can be visualized. A detailed analysis of this effect was performed by Cowern et al. [16, 17] for the boron diffusion in silicon in the temperature range 600-800 ºC. From the two equations that describe the impurity transport with the assumption that the initial impurity profile is composed of δ-functions, the experimental diffused spikes can be reproduced, and the values of both the long hop of the mobile specie (λ) and the average number of the particles that jump (θ) can be extracted. Similar analyses for the carbon profiles annealed at different temperatures and times yielded the long hop values for C. As an example, Figure 1 plots the obtained fit for 900 ºC, 30 min, and the associated long hop value, λ = 14 nm.

On the other hand, the long hop value can be determined from the frequencies of migration and break-up of C_1, using the relationship

\[ \dot{c} = \sqrt{6D_{nc}\delta} \]  \hspace{1cm} (2)

where \( D_{nc} \) is the diffusion coefficient of C_1 and \( \tau \) its life time, which is related with its binding energy. Equation 2 shows an exponential dependence with the inverse of temperature. Using the values in Table I, the long hop distance must be

\[ \lambda = 1.14e^{-2} \exp(0.865eV/kT) \text{ nm}. \] \hspace{1cm} (3)
In Figure 2, this dependence of $\lambda$ (solid line) is plotted and compared to the values obtained from the experimental fits. It is clear that the extracted values from the experiments do not follow this predicted trend. In order to interpret this discrepancy, we propose that the smaller values of $\lambda$ extracted from the experiments are not directly related to the lifetime of C$_i$ but rather to an effective $\lambda$ caused by the premature break-up of C$_i$ by a trap that reacts with C$_i$, quickly releasing a self-interstitial. The distance between two of these traps must be $\leq$ to the value of the effective $\lambda$. This means that a minimum concentration $\approx 10^{18}$ cm$^{-3}$ is expected for these traps, thus excluding the thermal generated vacancies as possible candidates because their concentration at the annealing temperatures have a value around $2 \times 10^7$ cm$^{-3}$ (730 °C) and $9 \times 10^9$ cm$^{-3}$ (900 °C).

Figure 2. C$_i$ long hop at different temperatures and times, the relationship determined from the experimental values in Table 1, assuming kick-out mechanism (---), and the values derived from the fit of the carbon superlattice experiments (♦).

Therefore, to resolve these inconsistencies, new simulations include the formation of clusters composed by carbon and self-interstitials, in a model similar to that proposed for the clustering of boron in conditions of self-interstitials supersaturation [14]. In the case of carbon, the formation of clusters could also occur in conditions of thermal generation of point-defects because of the low solubility of carbon in silicon. Evidence of a broad band absorption related to Carbon precipitates has been observed after thermal treatments [18]. Although the carbon precipitation mechanisms may be fairly complex, the purpose of this study is a proof of concept to explain the reduction of the C$_i$ long hops under high carbon concentration conditions. To determine potential energies for these clusters, iterative simulations were performed using a genetic algorithm to obtain the best fit, minimizing the error between the simulated profiles and the SIMS data, for the samples annealed at 900°C at three different times. The resulting values for the binding energies of the clusters are summarized in Table II.

Table II. Simulation parameters for carbon/self-interstitial clusters. $E_{nC,nI}$ (eV) is the potential energy of carbon/self-interstitial clusters, where nC and nI are the number of carbon atoms and self-interstitials, respectively.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$E$ (eV)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$</td>
<td>-1.51</td>
<td>Negligible concentration</td>
</tr>
<tr>
<td>C$_2$</td>
<td>-2.3</td>
<td></td>
</tr>
<tr>
<td>C$_2$I</td>
<td>-0.3</td>
<td></td>
</tr>
<tr>
<td>C$_2$I$_2$</td>
<td>-1.09</td>
<td>Negligible concentration</td>
</tr>
<tr>
<td>C$_3$</td>
<td>-1.09</td>
<td></td>
</tr>
<tr>
<td>C$_3$I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_3$I$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$I$_3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B7.2.4
The concentration of clusters with two self-interstitials or more are negligible. The potential energy for the cluster $C_2I$ (-2.3 eV) implies a binding energy for the emission of a $C_i$ or an I low enough to prevent the formation of bigger clusters. In fact, this cluster is formed at the very beginning of the annealing when a $C_i$ meets a $C_s$. It is very unstable and consequently does not retain the self-interstitial, and breaks up creating either a $C_i$ and a $C_s$ or a I and a $C_2$. In the latter case, it acts as the trap that reduces the $\lambda$ of $C_i$ and, at the same time increases the self-interstitial concentration in the carbon spikes.

The simulated carbon profiles produced by this model, which includes both the kick-out mechanism and C/I clustering, are shown in Figure 3a for 900°C (solid line) and in Figure 3b for 850°C (solid line). In addition, the simulated profile for 900°C and 850°C for the longest annealing times, assuming the kick-out mechanism alone, has been also included for comparison, (light solid line).

Figure 3. Experimental (°) and simulated (-----) carbon diffusion profiles assuming kick-out mechanism and the formation of Carbon/Self-Interstitials clusters for annealings at (a) 900°C at 17 m, 30 m and 1 h and (b) 850°C for 1 h and 3 h. For the longest times, the simulated profile assuming the kick-out mechanism alone has been included for comparison (——).
A good fit of the experiments is reached in all the cases. It is also worthy of note that the undersaturation of self-interstitials in the carbon-rich regions does not change with temperature in the range 700-900°C, in agreement with recent experiments [2].

DADOS simulations of C delta layers reiterate that the kick-out mechanism alone does not explain the carbon diffusion in silicon, and they establish that the formation of carbon/self-interstitial clusters with a low content of self-interstitials provides a compelling explanation of diffusion results. The model presented proposes the decrease of the long hop distance, \( \lambda \), of C\(_i\) and the associated release of a self-interstitial that increase the I concentration in the C layers and provides a better fit of C diffusion in MBE spikes with initial carbon concentrations of 2x10\(^{20}\) cm\(^{-3}\).

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