Boron Segregation in Single-Crystal Si$_{1-x-y}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$

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It has been reported that boron segregates to single-crystal Si$_{1-x}$Ge$_x$ layers from silicon during thermal anneals. In this work, we find that boron segregates even more strongly into single-crystal Si$_{1-y}$C$_y$, as has been previously reported for polycrystalline films. This effect is also observed in single-crystal Si$_{1-x}$C$_x$. Segregation coefficients range from 1.7 to 2.9 for annealing temperatures in the 800-850°C range. In a Si$_{1-x}$C$_x$ layer with 0.4% carbon, most of the segregation is reversible if the carbon is removed by an oxidation-enhanced out-diffusion process. This argues against the formation of immobile B-C defects as the driving force for the segregation. Gradients of interstitial silicon atoms, created by high concentrations of substitutional carbon, are presented as a driving force capable of causing the segregation seen in the experiments.© 2005 The Electrochemical Society. [DOI: 10.1149/1.1915209] All rights reserved.


It has been shown that by adding small amounts of substitutional carbon (~0.1-1.0%) to silicon or Si$_{1-x}$Ge$_x$, the diffusivity of boron and phosphorus atoms can be reduced by an order of magnitude below normal levels. This is useful for devices where very sharp dopant profiles must be created and then maintained during subsequent high-temperature fabrication steps. Si$_{1-x}$Ge$_x$ has been used most notably as a base material for a heterojunction bipolar transistor; other potential applications include metal oxide semiconductor field effect transistor (MOSFET) channels and source/drain.$^{3,4}$

In addition to reducing diffusion, carbon has also been shown to induce boron segregation. In polycrystalline Si/Si$_{1-x-y}$Ge$_x$C$_y$ multilayer structures with carbon levels ranging from 0.05-1.5%, boron strongly segregates from the polysilicon layers into the polycrystalline Si$_{1-x}$Ge$_x$C$_y$ during 800-900°C thermal anneals. Segregation increases with increasing carbon level, and can be much stronger than previously reported segregation to single-crystal Si$_{1-x}$Ge$_x$. This effect provides additional control over dopant profiles, as boron not only diffuses more slowly but is also drawn into carbon-containing regions. It has been exploited in the gates of p-channel MOSFETs, where devices with polycrystalline Si$_{1-x}$Ge$_x$C$_y$ layers in the gate show increased resistance to boron penetration effects (and thus enhanced threshold voltage stability) due to the suppression of boron out-diffusion from the gate.$^5$

In this work, we study boron segregation in single-crystal Si$_{1-x-y}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$. We find that, similar to the polycrystalline case, boron accumulates in both Si$_{1-x}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$ layers (vs. Si) during thermal anneals. The segregation process is shown to be mostly reversible by removing the carbon from the Si$_{1-x}$C$_x$ layer. Driving mechanisms for the segregation are discussed in light of this data. Interstitial gradients, created by out-diffusion of substitutional carbon, are then presented as a driving mechanism for segregation.

Boron Segregation to Single-Crystal Si$_{1-x-y}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$

All samples used in this study were grown by rapid thermal chemical vapor deposition using SiCl$_4$H$_2$ and SiH$_4$ as silicon sources and GeH$_4$, SiCH$_4$, and B$_2$H$_6$ as sources for germanium, carbon, and boron, respectively. Si$_{1-x-y}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$ layers were grown at 625°C, and silicon was deposited at temperatures ranging from 625 to 750°C. Previous work shows that for films grown under similar conditions most of the carbon is incorporated substitutionally.$^9,10$ Two samples were used to study segregation in single-crystal Si$_{1-x-y}$Ge$_x$C$_y$, shown in Fig. 1. For the first sample (Fig. 1a), thin (15 nm) epitaxial layers of Si$_{0.95}$Ge$_{0.05}$ and Si$_{1-y}$Ge$_y$C$_{0.01}$ were sandwiched between thicker (100 nm) silicon in situ doped Si layers ([B] = 2 × 10$^{15}$ cm$^{-3}$), all on top of an n-type substrate and undoped buffer (500 nm). This structure was annealed at 800°C for 28 h to allow boron to move from the silicon into the Si$_{1-x}$Ge$_x$C$_y$ layers. The second sample (Fig. 1b) was similar to the first, except that the Si$_{1-y}$Ge$_y$C$_{0.01}$ layers were thicker (25 nm), initially in situ doped higher (not lower) than the silicon, and the carbon level was much lower (0.05%). (There were several other layers on either side of the region of interest, which did not affect our study and are not discussed here.) This sample was annealed for 18 h at 800°C. Secondary-ion mass spectrometry (SIMS) analysis was used to measure germanium, carbon, boron, and oxygen profiles in all samples. Figure 2 shows SIMS profiles of these two structures before and after annealing. For the first sample (Fig. 2a), the Si$_{1-x}$Ge$_x$C$_y$ layers initially have much less dopant than the surrounding silicon. However, after the anneal, boron has moved into these layers and reached levels higher than the original silicon concentration. Defining a segregation coefficient $m$ as the ratio of boron in the Si$_{1-x}$Ge$_x$ vs. Si after the anneal, we find $m = 1.7$ for the Si$_{1-x}$Ge$_x$C$_y$ layer. Boron segregation to Si$_{1-y}$C$_y$ is well known, and the magnitude of this result is consistent with previous reports.$^{7,11}$ However, additional segregation occurs in the Si$_{1-y}$C$_{0.01}$C$_y$ layer ($m = 2.3$), showing that carbon enhances the effect. This confirms that the enhanced segregation seen in polycrystalline Si$_{1-x-y}$Ge$_x$C$_y$ in a previous report is not (at least exclusively) due to polycrystalline or grain boundary effects. (Note: In the as-grown profile there is a boron peak in the top Si layer at ~120 nm. This was unintentionally incorporated during growth and should not affect the rest of the experiment.)

The second sample (Fig. 2b) demonstrates a similar effect at a much lower carbon concentration (0.05%). As mentioned, the as-grown profiles show that during growth a higher boron concentration was initially placed in the Si$_{1-x}$Ge$_x$ and Si$_{1-y}$Ge$_y$C$_{0.01}$ layers than in the silicon. This would normally be expected to flatten out during the anneal. However, as shown in Fig. 2b, boron concentration in the Si$_{1-x}$Ge$_x$C$_y$ layer actually increases during the anneal, again indicating segregation. Interestingly, although the carbon concentration is much lower in this sample, the amount of segregation is higher ($m = 2.9$) than before. This is discussed later in the paper.

A third sample was grown to study boron segregation in Si$_{1-y}$C$_y$, whose structure and as-grown SIMS profile are shown in Fig. 3. On top of an n-type (100) substrate, an undoped 500 nm buffer layer was first grown, followed by a sandwich structure consisting of a thin (20 nm) Si$_{0.99}$Ge$_{0.01}$C$_{0.04}$ layer in between two boron-doped ([B]
observed in the Si$_{1-x}$ Ge$_x$ layers compared to Si$_{1-x}$ Ge$_x$, which is the opposite of what is observed. Segregation is also observed in Si$_{1-x}$ Ge$_x$ layers, indicating that carbon by itself can drive the segregation (Ge-B interactions not required). Thus these mechanisms used to explain boron segregation to Si$_{1-x}$ Ge$_x$ cannot be used to explain the segregation to Si$_{1-x}$ C$_y$ or the enhanced segregation to Si$_{1-x}$ Ge$_x$ vs. Si$_{1-x}$ Ge$_y$ seen here.

One possibility unique to Si$_{1-x}$ Ge$_x$ and Si$_{1-x}$ C$_y$ is that boron is becoming trapped at a carbon-related defect. For example, silicon carbide (SiC) precipitates can form in Si$_{1-x}$ Ge$_x$ layers with carbon levels and annealing conditions similar to those used in this study.\textsuperscript{7,18} and boron could become immobilized either inside or at the surfaces of these defects. A direct boron-carbon interaction may also be occurring, such as the B-C-I cluster proposed by Liu et al.\textsuperscript{19} Either of these defects may be expected to render the boron (and carbon) atoms immobile. This possibility is considered in the next section.

Reversibility of Boron Segregation

If boron is becoming immobilized at carbon-related defects, then once boron has segregated to a Si$_{1-x}$ Ge$_x$ layer, it should not be able to diffuse out again (assuming the defects are stable). Therefore, an experiment was performed to test the reversibility of the segregation process. The same structure shown in Fig. 3 (to study segregation to Si$_{1-x}$ C$_y$) was first annealed at 850°C for 2 h in N$_2$, as before. In this section, the sample was also subjected to an additional 2 h dry oxidation at 850°C. The purpose of the initial N$_2$ anneal was, as before, to allow the boron to segregate to the Si$_{1-x}$ C$_y$ layer. The second step (oxidation) was designed to drive the carbon out of the Si$_{1-x}$ C$_y$ layer. When the silicon surface is oxidized, it is known that silicon self-interstitials are injected into the sample. These silicon interstitials diffuse down to the Si$_{1-x}$ C$_y$ layer and interact with the substitutional carbon atoms through the following reaction\textsuperscript{20}

\begin{equation}
C_3 + I \rightarrow C_1
\end{equation}

where C$_3$ is a substitutional carbon atom, I is a silicon interstitial atom, and C$_1$ is a carbon-silicon interstitial pair, or “interstitialcy.” The resulting carbon interstitialcies are very mobile and diffuse quickly compared to the substitutional carbon. As the Si$_{1-x}$ C$_y$ layer is positioned so close to the surface, they can rapidly diffuse to the surface and into the growing oxide. (SIMS profiles confirm that
carbon is accumulating in the oxide. It has been previously shown that, by this mechanism, almost all of the carbon can be removed from a Si$_{1-x}$Ge$_x$C$_y$ layer with the same carbon level ($\sim 0.4\%$) thickness, and oxidation conditions. In addition, for the same rate of interstitial injection, the loss of carbon has been shown to be the same for Si$_{1-x}$Ge$_x$C$_y$ and Si$_{1-y}$C$_y$ layers.

In Fig. 5, carbon and boron profiles in this sample, which was subjected to both the N$_2$ anneal and oxidation, are compared to the sample from the previous section, which was subjected to only the N$_2$ anneal. It is seen in Fig. 5a that, as anticipated, most of the carbon is removed from the Si$_{1-x}$C$_y$ layer during the oxidation step. 84% of the integrated carbon has been removed from the region of the original Si$_{1-x}$C$_y$ layer, with 74% removed from the sample entirely. Figure 5b shows that, at the same time, most of the boron segregation has gone away, with the profile largely flattening out. The decrease near the surface is caused by boron evaporation and/or segregation into the oxide layer on the surface. The ability to reverse the segregation in this structure via the oxidation step argues against the formation of immobile boron-carbon defects as the driving force for the segregation. In particular, it is unlikely that the segregation was caused by SiC precipitates, which were then caused to be removed by the oxidation. The presence of excess interstitials is known to drive the formation of SiC precipitates in silicon, not their removal. (Note: A small residual boron peak does remain in the region of the original Si$_{1-x}$C$_y$ layer; whether this simply has not had enough time to diffuse away, or is potentially associated with defects, is not clear.)

**Segregation Driven by Gradients of Silicon Interstitial Atoms**

We propose that the reaction of carbon with silicon interstitials, and the resulting gradients of interstitials that are produced inside Si$_{1-x}$Ge$_x$C$_y$ layers, is driving boron segregation into these layers. Carbon (at low concentrations) is a substitutional impurity in silicon and requires the presence of silicon self-interstitials to diffuse. A substitutional carbon atom (C$_S$) pairs with a silicon self-interstitial (I) to form a carbon-interstitial pair, or “interstitialcy” (C$_I$) (Reaction 1), which is mobile and can rapidly diffuse. Eventually it dissociates, with the carbon atom returning to a substitutional site and the silicon interstitial diffusing away. As a result of silicon interstitials being consumed through Reaction 1, and the subsequent diffusion of the carbon-interstitial pairs out of the layers, the population of silicon interstitials is depressed in Si$_{1-x}$Ge$_x$C$_y$ regions. In the adjacent silicon layers, the dissociation of C$_I$ to form substitutional carbon and silicon interstitials raises the silicon interstitial population there. In the next subsection, we use simulations to model this reaction and diffusion of carbon and interstitial silicon during thermal anneals. In the following subsection, we model the effect that the resulting interstitial profiles have on boron diffusion. Finally, the simulations are compared to data.

**Interstitial undersaturations created by carbon diffusion.**—

Previously, a complete model of coupled carbon and point-defect diffusion was developed. Substitutional carbon is assumed to undergo two reactions: Reaction 1, known as the “kick-out” reaction, and the Frank-Turnbull reaction.
where $V$ is the concentration of vacancies in the lattice. This describes substitutional carbon directly forming an interstitialcy and leaving a vacancy behind. The simultaneous reaction and diffusion of all four species $C_S, C_I, I, V$ was modeled by solving a set of partial differential equations in the PROPHET 23 simulator, using parameters from Ref. 20,24,25. Previously, this model was successfully used to simulate high-concentration carbon diffusion in silicon and Si$_{1-x}$Ge$_x$ under various conditions. We find that it also can accurately model carbon diffusion in our samples. Figure 6 shows the SIMS profile of carbon in a structure identical to the one from the previous section, except that no boron was present anywhere in the sample. This sample was annealed at 850°C for 2 h in N$_2$, and the resulting data compared with simulations. The profiles match well; in particular, the pronounced diffusion in the tails of the profile, compared to the very slow diffusion in the peak, is modeled very accurately. The good match with the data gives us confidence that the simulation accurately predicts the concentration profile of silicon interstitials in the regions where the carbon is out-diffusing. As seen, the region of high carbon concentration is severely depleted of silicon interstitials, by at least two orders of magnitude compared to the equilibrium value. The adjacent region at a depth of $300$ nm has a slightly enhanced concentration (above the equilibrium value of $1.86 \times 10^{10}$ cm$^{-3}$ at 850°C) due to interstitials being released by the reverse of Reaction 1 in this region.

**Theory of boron segregation to regions of low interstitial concentration.**—Boron diffusion depends on silicon interstitials in the same manner as carbon. Similar to Reaction 1, substitutional boron atoms ($B_S$) react with silicon self-interstitials ($I$) to form mobile boron-interstitial pairs, or “interstitialcies” ($B_I$). It is typically assumed that this reaction and its inverse occur much faster than the diffusion process, and hence can always be considered in equilibrium$^{26}$

$$B_S + I \rightarrow B_I$$  \[3\]

$$k B_S I = B_I$$  \[4\]

where $k$ is a constant. These boron interstitialcies diffuse much faster than substitutional boron, and dominate the process. As a result, the diffusion flux of boron atoms $F_B$ is given by

$$F_B = -D_{B0} \frac{d}{dx} B_I = -D_{B0} \frac{d}{dx} (kB_S)$$  \[5\]

where Reaction 4 was substituted for the boron interstitialcy concentration, and $D_{B0}$ is their diffusivity. Normalizing the silicon interstitial concentration by its equilibrium value $I_0$, an equilibrium diffusivity $D_{B0}$ can be defined as

$$D_{B0} = -D_{B0} k I_0$$  \[6\]

Assuming that only a small fraction of boron atoms is paired with interstitials ($B_{Total} = B_S + B_I \approx B_S$), the boron flux can then be expressed as

$$F_B = -D_{B0} \frac{d}{dx} \left( \frac{J}{I_0 B_{Total}} \right)$$  \[7\]
If the concentration of silicon interstitials (I) is assumed to be uniform with position, it can be taken out of the derivative, and the diffusivity becomes

\[
D_B = D_B0 \frac{I}{I_0} \quad F_B = -D_B \frac{dB}{dx}
\]

where \( B = B_{\text{total}} \). In this case, the effective boron diffusivity depends directly on the concentration of silicon interstitials. If it is enhanced, as in oxidation-enhanced diffusion\(^{27}\) or transient-enhanced diffusion,\(^{28}\) boron diffusion increases dramatically. If it is decreased, as in a Si\(_{1-x}\)Ge\(_x\)C\(_y\) layer, diffusion decreases dramatically.\(^3\) Boron diffusion has actually been used as a measure of the local interstitial concentration in a region.\(^{29}\)

However, as seen in Fig. 6, the concentration of silicon interstitials is not always constant. At the edges of a Si\(_{1-x}\)Ge\(_x\)C\(_y\) layer, there is a steep gradient in the silicon interstitial profile. In this case, Eq. 7 must be expressed as\(^{30,31}\)

\[
F_B = -D_B0 \frac{d B}{dx} \bigg/ D_B B_{\text{total}} \frac{d I}{dx}
\]

The first term on the right represents the standard diffusion flux of boron, driven by gradients in boron concentration. The second term states that a flux of boron atoms also results from a gradient in interstitial atoms, even if no gradient in boron exists. In particular, the flux is in the direction of a negative gradient. As a result, boron is driven from regions of high interstitial concentration to regions of low interstitial concentration, or in our case, into the Si\(_{1-x}\)Ge\(_x\)C\(_y\) layer. This provides a mechanism to drive boron segregation into Si\(_{1-x}\)Ge\(_x\)C\(_y\) or Si\(_{1-x}\)C\(_y\) layers from Si based solely on point-defect diffusion considerations.

**Modeling of boron segregation due to interstitial gradients.**— We use the PROPHET simulations described previously to quantitatively model the effect of the interstitial gradients on boron profiles. In particular, we are interested in knowing if the flux produced by the second term in Eq. 9 is powerful enough to drive a significant amount of boron into a Si\(_{1-x}\)Ge\(_x\)C\(_y\) layer. All the carbon and interstitial models remained identical to those used for Fig. 6, and boron diffusion was added as described by Eq. 9, using coefficients from Ref. 32 for the equilibrium boron diffusivity \( D_{B0} \). In particular, no direct boron-carbon interactions were assumed.

A test structure (not modeled after an experimental sample) was first created in the simulator, consisting of three box-shaped 20 nm Si\(_{1-x}\)C\(_y\) layers of \( y = 0.1, 0.2, \) and 0.4% carbon surrounded and separated by 200 nm silicon layers. All silicon and Si\(_{1-x}\)C\(_y\) layers were initially doped with a uniform boron concentration of \( 1 \times 10^{19} \, \text{cm}^{-3} \). This was then subjected to a (simulated) 850°C, 14 h anneal. Plots of silicon interstitials and boron after the anneal are shown in Fig. 7, with the location of the Si\(_{1-x}\)C\(_y\) layers indicated by the arrows. First, note that, as expected, the carbon layers are creating large undersaturations of silicon interstitials. The magnitude of the undersaturation (compared to the adjacent silicon) increases as the carbon concentration increases, starting at ~1.2 times for 0.1% carbon and increasing to ~14 times for 0.4% carbon. Second, and most significantly, strong boron segregation to the regions of interstitial undersaturation is also observed. This increases with carbon level (due to the increasing interstitial undersaturation), starting at 1.6 for 0.1% carbon and increasing to 4.7 for 0.4% carbon. These levels are comparable to the amount of segregation we observed in both our single-crystal and polycrystalline Si\(_{1-x}\)Ge\(_x\)C\(_y\) and Si\(_{1-x}\)C\(_y\) samples, confirming that interstitial gradients alone (without any direct boron-carbon interactions) are powerful enough to drive the boron segregation. However, this is not a true equilibrium segregation effect, as it relies on the nonequilibrium process of carbon reacting with interstitials and out-diffusing. Once the carbon has finished diffusing out of the layer, the interstitial undersaturation, and hence boron segregation, goes away. This is consistent with the findings of the section on reversibility of boron segregation, where after the carbon was removed (in this case by oxidizing the surface) most of the segregation went away.

**Comparison of simulation with data.**— These simulations were then applied to model the boron profiles we measured in our experiments. Two samples were chosen for analysis: one with low carbon content (0.05%) and one with high carbon content (0.4%).

The segregation observed in Fig. 2 for a 0.05% Si\(_{1-x}\)Ge\(_x\)C\(_y\) layer was first simulated (800°C 18 h). The initial boron and carbon profiles were taken from the SIMS data and used as initial conditions for the simulation. Figure 8 shows a comparison of the modeled and experimental boron profiles after annealing. The agreement is fairly close. However, these results should be interpreted with some caution: germanium effects (which are known to influence both boron diffusion and segregation) are not included in the simulation, nor is the effect of boron on carbon diffusion. For example, we have observed that heavy boron doping (in the \( 10^{19} \, \text{cm}^{-3} \) range, the same as used for our experiments) can increase the rate of car-

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### Figure 7.
Boron and silicon interstitial profiles for the simulation test structure (not experimental data) after 850°C, 14 h anneal, showing strong boron segregation to the regions of low interstitial concentration.

### Figure 8.
Comparison of boron segregation simulation and SIMS data for low-carbon (0.05%) sample annealed at 800°C for 18 h.
substitutional carbon, are a strong driving force for boron segregation. Simulations predict that this effect can drive segregation similar to that seen in experiment; however, a more precise fit to the data may require additional considerations such as the effect of boron on carbon diffusion.

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