Quantification of substitutional carbon loss from $Si_{0.998}C_{0.002}$ due to silicon self-interstitial injection during oxidation

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The empirical reaction of substitutional carbon with silicon self-interstitials in $Si_{0.998}C_{0.002}$ layers pseudomorphically grown on Si (100) substrates has been quantified at 850 °C. During annealing of a sample with a thin $Si_{0.998}C_{0.002}$ layer capped with a thin crystalline silicon layer, in either oxygen or nitrogen ambient, carbon diffuses from the surface edge of the $Si_{0.998}C_{0.002}$ layer towards and out of the silicon surface. The extra number of carbon atoms lost during oxidation is found equal to the number of silicon interstitials injected by the oxidation process, strongly suggesting that each substitutional carbon reacts with a single self-interstitial to form a mobile interstitial carbon, whereby it diffuses to the surface. The mechanism appears the same in $Si_{1-x-y}Ge_xC_y$ and $Si_{1-x}C_x$ films. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1500411]

The incorporation of substitutional carbon in silicon is of technological interest for its potential to locally reduce boron diffusion in silicon or in $Si_{1-x}Ge_x$,[1–3] which is critical for device structures with ultranarrow boron doped regions.[4] The effect of carbon on boron diffusivity has been attributed to its ability to locally suppress the silicon self-interstitial concentration, which is primarily responsible for mediating boron diffusion.[5–9] However, neither the product of the reaction of self-interstitial and substitutional carbon (e.g., precipitate or mobile interstitial-carbon[10]) nor the empirical relationship between the self-interstitial and substitutional carbon has been firmly established. Such knowledge is critical for device design with carbon. This letter uses self-interstitial injection during oxidation, already previously quantified,[11–13] to show that the reaction between a single self-interstitial and single substitutional carbon in a buried $Si_{0.998}C_{0.002}$ layer forms one mobile carbon atom (presumably interstitial-carbon[6,10]).

A pseudomorphic 150 nm $Si_{0.998}C_{0.002}$ layer was grown on both sides of a double-side-polished ⟨100⟩ float-zone silicon substrate by rapid thermal chemical vapor deposition and capped with 45 nm of crystalline silicon. The $Si_{1-x}C_x$ layer was grown at 550 °C and 10 Torr using 50 sccm of a disilane mixture (10% disilane in hydrogen) and 20 sccm of methylsilane (1% methylsilane in hydrogen) as the silicon and carbon source gases, respectively. After the silicon caps were grown, at or below 700 °C, the structure was annealed in-situ for 5 min at 800 °C in 10 Torr of H_2. Further details about the chemical vapor depostion (CVD) reactor can be found elsewhere.[14]

The total carbon in the silicon film was determined by secondary ion mass spectroscopy (SIMS). The substitutional carbon fraction in the $Si_{0.998}C_{0.002}$ film was 100% substitutional determined by x-ray diffraction[15] and Fourier transform infrared (FTIR) spectroscopy.[16] Samples of the as-grown wafer were annealed in nitrogen or dry oxygen

ambient at 850 °C for 2–8 h and also were examined with SIMS, and FTIR absorption spectroscopy. The oxide thicknesses were measured using SIMS and ellipsometry and the growth rate was nearly constant during the entire oxidation, 0.9 nm/min. No appreciable difference in oxidation rate was observed between pure silicon samples and those samples with the buried $Si_{0.998}C_{0.002}$ layer.

After annealing in nitrogen, the carbon concentration in the $Si_{0.998}C_{0.002}$ layer redistributes due to diffusion out of the high carbon concentration region, depleting the surface edge of the $Si_{0.998}C_{0.002}$ layer of carbon increasingly with longer annealing time (Fig. 1). The profiles were translated to account for consumption of silicon by oxidation using the Pilling–Bedworth ratio of 2.22,[17] so that the same physical location in the $Si_{1-x}C_x$ appears at the same abscissa in all profiles.

The layer is depleted of carbon much more rapidly during annealing in the oxygen ambient, consistent with previous reports of carbon enhanced diffusion due to self-interstitial injection from the oxidizing surface in silicon[18] and $Si_{1-x}Ge_x$[19] structures. Loss of carbon entirely from the silicon via the surface has also been reported after annealing in either nitrogen or oxygen ambient.[18,19] After oxidation, carbon is found in high levels in the oxide with a concentration of about 10^{20} cm^{-3}, demonstrating that the carbon primarily leaves via the silicon surface into the oxide rather than diffusing into the substrate (Fig. 2).

Variation in the thickness of the $Si_{0.998}C_{0.002}$ layer across the wafer and from sample to sample due to growth nonuniformity makes it difficult to quantitatively compare the change in the total integrated carbon in the $Si_{0.998}C_{0.002}$ layer from one annealing condition to another when integrating the entire carbon profile from the entire $Si_{0.998}C_{0.002}$ layer. The thickness of the thinner silicon cap is, however, better controlled. Therefore, the profiles are aligned as described above, and the total amount of carbon in the top 125 nm (as measured from the original silicon surface) is reported. Since the carbon concentration remains unchanged at this depth, this method should accurately capture the carbon loss to the

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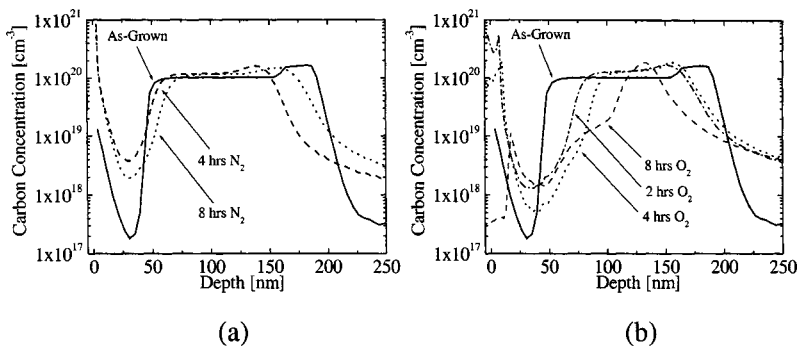[b)]Electronic mail: malcolmc@alumni.princeton.edu

FIG. 1. Carbon concentration depth profiles in silicon before and after annealing at 850 °C in either (a) nitrogen or (b) oxygen ambient for 2–8 h. The carbon profiles have been shifted so that the origin represents the location of the original silicon surface before oxidation. Carbon concentrations in the oxide are not accurate.

surface even if the total $Si_{0.998}C_{0.002}$ layer thickness differs significantly.

The integrated carbon found in the top 125 nm of silicon measured by SIMS shows relatively little ($\sim 12\%$) carbon loss after annealing in nitrogen up to 8 h, (Fig. 3). The substitutional carbon in both the $Si_{0.998}C_{0.002}$ layers was also monitored using FTIR absorption.[16] As measured by FTIR, the total substitutional carbon concentration in the silicon decreased less than 10% after 8 h in nitrogen. This shows that the substitutional carbon that remains in the silicon is relatively stable at 850 °C during annealing in nitrogen up to 8 h.

In the case of oxidation, the integrated amount of carbon in the $Si_{0.998}C_{0.002}$ and the Si cap decrease linearly with time (Fig. 3). The integrated carbon that is removed from the $Si/Si_{0.998}C_{0.002}$ structure after oxidation is compared to that found in the oxide (Fig. 4). The carbon that is lost from the $Si/Si_{0.998}C_{0.002}$ layers can be completely accounted for by the increase in carbon in the thermally growing oxide, within the uncertainty of the two SIMS measurements. The carbon that leaves the silicon is trapped in the oxide rather than leaving the silicon and oxide as a volatile species such as CO_2.

A primary application of substitutional carbon incorporation in silicon or $Si_{1-x}Ge_x$ devices is to capture excess self-interstitials that are introduced by processing steps such as implantation[4,7] or oxidation.[8,9] Therefore, it is desirable to establish the relationship between the self-interstitial and the substitutional carbon. The self-interstitial concentration is suppressed well below its intrinsic concentration in the $Si_{0.998}C_{0.002}$ layer, so that it can be treated as a sink for diffusing interstitial silicon atoms even for carbon concentrations as low as 10^{19} cm^{-3}.[2,20] The surface concentration of

self-interstitials is constant during oxidation,[11,13] so the resulting self-interstitial concentration will, to a first approximation, be a linearly decaying interstitial profile from the surface supersaturation value to approximately zero at the $Si_{0.998}C_{0.002}$ layer.[2,11] The interstitial flux can therefore be calculated as

$$J_I = -D_I \frac{dI}{dx} = n_{surf} \times \frac{D_I I^*}{\Delta x}, \tag{1}$$

where, n_{surf} is the ratio of the interstitial surface concentration to the bulk intrinsic interstitial concentration ($I/I^* = 12.7$) at 850 °C, $D_I I^*$ is the interstitial transport product measured by metal tracer diffusion (1×10^4 cm^{-1} s^{-1}),[11,19,21] and Δx is the silicon cap layer thickness.

The silicon cap thickness is, however, not constant during the oxidation. The effective cap layer thickness depends on two competing processes, the loss of carbon from the top of the $Si_{0.998}C_{0.002}$ layer (increasing the cap) and the consumption of silicon by the oxide (decreasing the cap). However, even after losing 40 nm of the $Si_{0.998}C_{0.002}$ layer after 8 h of oxidation, the silicon cap thickness (evaluated as the thickness between the oxide–silicon interface and the depth at which the carbon increases to $\sim 10^{19}$ cm^{-3}) remains relatively constant for the entire oxidation time (50–60 nm). In Fig. 3 the effective cap thicknesses are shown next to their respective carbon values. This may be because the two competing processes proceed towards a steady-state resulting in a relatively constant silicon cap thickness.

The calculated number of self-interstitials injected is compared to the carbon removed from the $Si/Si_{0.998}C_{0.002}$ (Fig. 3), assuming an average cap thickness of 56 nm. The
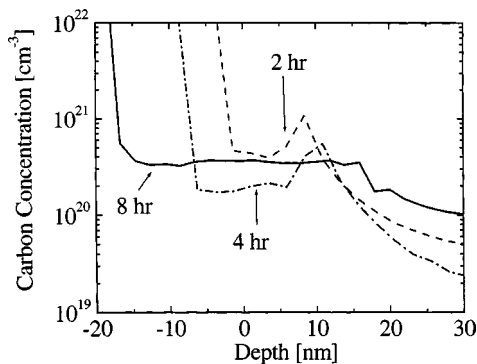

FIG. 2. Carbon concentration depth profiles in the thermally grown silicon dioxide after oxidation for 2–8 h. The carbon profiles have been shifted so that the origin represents the location of the original silicon surface before oxidation. Carbon concentrations in the silicon are not accurate.
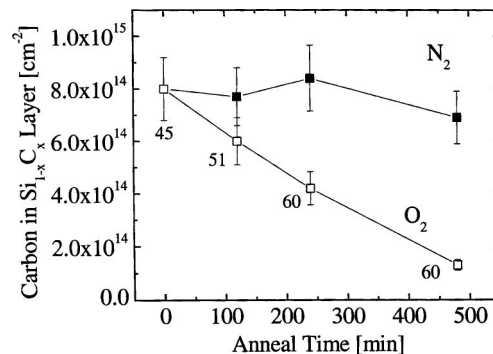

FIG. 3. Integrated level of carbon in the top 125 nm of the silicon measured by SIMS before and after annealing at 850 °C in either nitrogen or oxygen ambient for 2–8 h. The effective silicon cap thickness (in nanometers) after oxidation is written beside each point.
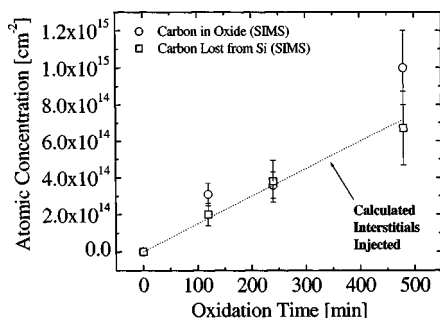
FIG. 4. The integrated carbon removed from the silicon and integrated carbon found in the silicon dioxide after oxidation at 850 °C as a function of oxidation time. The calculated number of silicon self-interstitials injected for the same oxidation conditions assuming an effective silicon cap thickness of 56 nm is also shown.

estimated number of self-interstitials injected (i.e., the time integrated flux) is nearly identical to the number of total carbon leaving the silicon. This suggests a one-to-one relationship exists between the mobile carbon produced and exiting the $Si/Si_{0.998}C_{0.002}$ and the self-interstitials injected. This conclusion is consistent with previously proposed explanations of carbon diffusion:[6,10]

$$C_s + I \rightarrow C_i \quad \text{(diffusing species)}, \tag{2}$$

that predict that substitutional carbon diffuses entirely by the formation of interstitial carbon C_i, which is formed in a one-to-one ratio with C_s and I. Furthermore, the formation of C_i at the $Si_{0.998}C_{0.002}$ layer by injected self-interstitials, and a sink for the interstitial carbon at the silicon surface, effectively creates a reverse flux of interstitial carbon towards the sample surface that removes the injected self-interstitials from the silicon and thereby acts to insulate the silicon layer below almost entirely from the injected self-interstitials at the surface. This effect has been observed using carbon in buried SiGe layers.[22] This 1:1 reaction has also been observed in similar structures when the injected silicon self-interstitials react with carbon in a compressively strained $Si_{1-x-y}Ge_xC_y$ layer ($x \sim 0.2$).[19] Because no appreciable deviation from a 1:1 ratio is observed also in this case, with tensilely strained $Si_{1-x}C_x$, it is concluded that the fundamental mechanism does not appear to be affected by germanium or strain.

In conclusion, silicon self-interstitials injected during oxidation react with substitutional carbon in silicon in a one-to-one ratio to form highly mobile interstitial carbon atoms.

The reaction does not directly form immobile carbon (e.g., silicon carbide precipitates). The mobile carbon rapidly diffuses to the silicon surface where it is absorbed in the oxide, shielding the region below the $Si_{0.998}C_{0.002}$ layer from any enhanced diffusion due to excess self-interstitials. The mechanism appears similar in $Si_{1-x-y}Ge_xC_y$ and $Si_{1-x}C_x$ random alloys.

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