

Silicon Interstitial Driven Loss of Substitutional Carbon from SiGeC Structures

M. S. Carroll and J. C. Sturm, Dept. of Electrical Engineering, Princeton University, Princeton, NJ; E. Napolitani, D. De Salvador and M. Berti, INFN and Dept. of Physics, University of Padova, Padova, Italy; J. Stangl and G. Bauer, Institute for Semiconductor Physics, Johannes-Kepler University Linz, Linz, Austria; D. J. Tweet SHARP Laboratories of America Inc., Camas WA

Abstract

The effect of annealing silicon capped pseudomorphic $\text{Si}_{0.7865}\text{Ge}_{0.21}\text{C}_{0.0035}$ or $\text{Si}_{0.998}\text{C}_{0.002}$ layers on silicon substrates in nitrogen or oxygen at 850°C was examined using x-ray diffraction (XRD) and secondary ion mass spectrometry (SIMS). Most substitutional carbon is lost from the alloy layers due to carbon out-diffusion rather than from precipitation. The carbon is found to diffuse more rapidly out of the SiGeC layer than the SiC layer after nitrogen and the carbon is found to leave the sample entirely, an effect that is enhanced by oxidation and thin cap layers. All substitutional carbon can be removed from the sample in some cases implying negligible formation of silicon-carbon complexes. Furthermore, it is found that each injected silicon interstitial atom due to oxidation causes the removal of one additional carbon atom for the SiGeC layer.

Introduction

Substitutional carbon incorporation in silicon and SiGe has drawn significant attention because of reduced boron diffusion in carbon's presence, due to its ability to consume silicon interstitials, which mediate boron diffusion [1]. However, the potential that the interstitial-carbon product is a defect (i.e. β -SiC precipitation or carbon clusters [2,3]) may limit the usefulness of carbon for diffusion engineering. Previous studies of carbon thermal stability in SiGeC confirm that carbon can precipitate in SiGeC [2,4]. In this letter carbon out-diffusion from thin SiGeC layers is examined and carbon out-diffusion is found to be the dominant mechanism of carbon loss for samples close to the surface, even in the regime of carbon concentration far above solid solubility or in the presence of excess interstitials injected during oxidation.

Experiment

Two test structures with 25 nm thick $\text{Si}_{0.7865}\text{Ge}_{0.21}\text{C}_{0.0035}$ layers capped by 50 or 280 nm of silicon and one 150 nm thick $\text{Si}_{0.998}\text{C}_{0.002}$ layer capped by a 45 nm silicon layer were grown on $\langle 100 \rangle$ silicon substrates by rapid thermal chemical vapor deposition (RTCVD) at temperatures between 550°C and 750°C using dichlorosilane, disilane, germane, and methylsilane as the silicon, germanium, and carbon sources respectively [5]. Samples of the as-grown and annealed structures were examined using secondary ion mass spectrometry (SIMS), which were sputtered using 1-2 keV Cs^+ (Fig. 1) or O^+ (Fig. 2) ions. Depths were determined using standard profilometry of the sputtered craters leading to a 5% uncertainty in depths, a 20% (Fig. 1) or 10% (Fig. 2)

uncertainty in carbon concentrations and approximately a 2% uncertainty in the absolute germanium fraction.

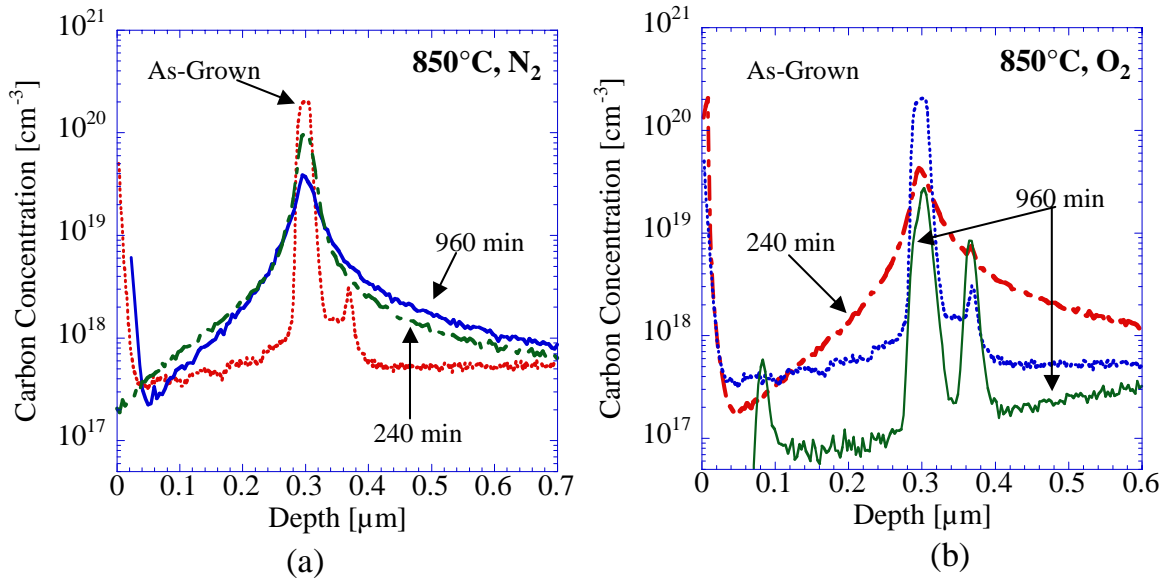


Figure 1. Carbon concentration profiles of the 280 nm silicon capped SiGeC layers before and after annealing at 850°C in nitrogen or oxygen ambient for 240-960 minutes overlaid on the as-grown carbon profile, (a) and (b) respectively.

All as-grown samples were examined by x-ray diffraction (XRD) using a double crystal rocking curve geometry around the (004) Bragg reflection to determine the amount of carbon that was substitutional in the buried alloy layers. The as-grown carbon was 100% substitutional in all three samples [6]. The substitutional carbon in the SiGeC layers after oxidation was also examined using XRD. Rocking curves of as-grown and oxidized samples of the SiGeC sample with a 50 nm cap were fit by simulations and agreed well with germanium and carbon profiles obtained by SIMS indicating that the carbon in the SiGeC layer compensated the strain as if it was all substitutional. As-grown and 960 minute nitrogen or oxygen annealed samples of the 280 nm silicon capped SiGeC layer were also examined for relaxation in the plane parallel to the growth surface by scanning around the (224) Bragg reflection. No relaxation was observed.

Carbon profiles from the SiGeC samples with a 280 nm silicon cap, annealed in nitrogen ambient for 240 or 960 minutes are overlaid on the as-grown carbon profile, Fig. 1 (a). Carbon diffusion in silicon is believed mediated by an interstitial kick-out [7],



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 distinct non-gaussian broadening of the carbon profiles after nitrogen annealing has been explained as a result of a depleted interstitial concentration in the carbon-rich region. The carbon reaction with the self-interstitial is believed to proceed so rapidly that it produces an undersaturation of interstitials locally [7]. Because the interstitial population is depleted

in the carbon region, a “quasi-stationary” profile is observed surrounded by tails of carbon “kicked-out” by the transport-limited diffusion of interstitials from the surrounding silicon [7].

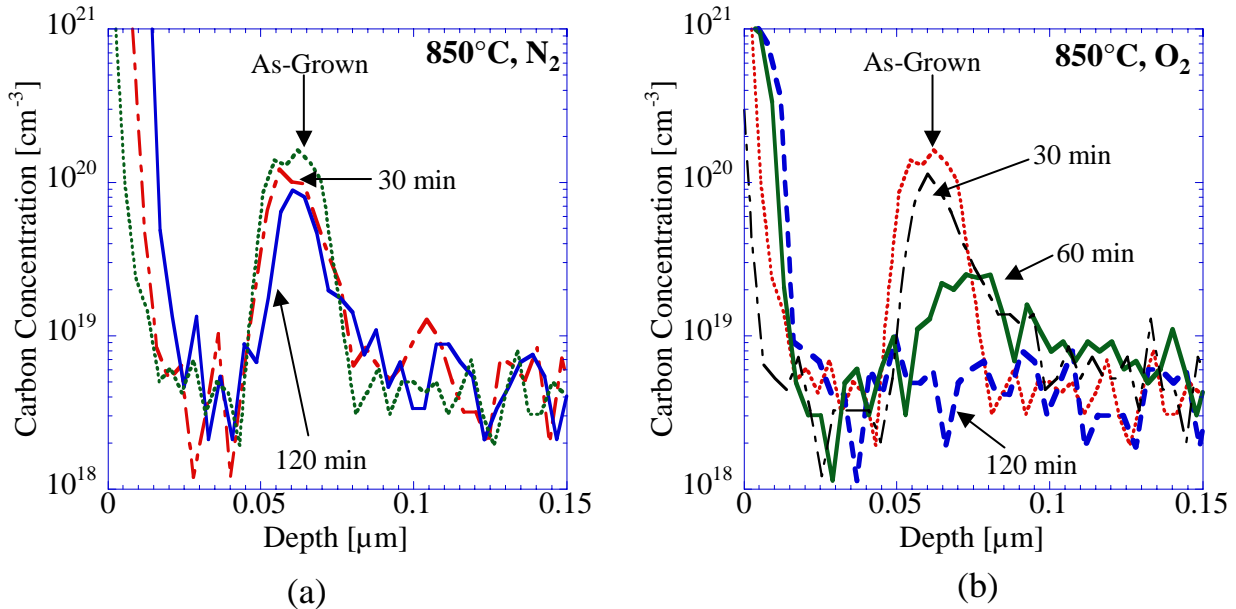


Figure 2 Carbon concentration profiles from 50 nm silicon capped SiGeC layers before and after annealing at 850°C in nitrogen or oxygen ambient for 30-120 minutes overlaid on the as-grown carbon profile, (a) and (b) respectively.

The carbon concentration of the out-diffusing tail on the surface side is notably less than that on the substrate side of the SiGeC layer. No sign of carbon build-up on the surface side combined with a relatively constant concentration gradient towards the surface over the entire 16 hour anneal, indicates that carbon is diffusing towards and out the surface from the SiGeC layer. Previous studies have also reported loss of carbon from slightly carbon enriched ($8 \times 10^{17} \text{ cm}^{-3}$) crystalline silicon out the surface after annealing in either oxygen or nitrogen ambient [8].

The rate of carbon loss from the SiGeC layer is enhanced by oxidation, Fig. 1 (b), and the carbon is reduced well below the as-grown background concentration ($3 \times 10^{17} \text{ cm}^{-3}$) except two spikes of immobile carbon, which persist after 960 minutes of oxidation located at 300 and 370 nm. The oxide-silicon interface after 960 minutes of oxidation is indicated by the carbon spike located at a depth of 100 nm in this sample.

Carbon concentration profiles of the SiGeC layer with a 50 nm Si cap after annealing for 30 or 120 minutes in nitrogen ambient are overlain on the as-grown profile, Fig. 2 (a). A clear reduction of the total carbon concentration is observed although very little broadening of the profile is observable. Presumably, the primary mechanism of loss is diffusion to the surface and the carbon tails are obscured by the higher carbon detection limits ($3 \times 10^{18} \text{ cm}^{-3}$). The carbon concentration profiles after oxidation of 30 to 120 minutes, Fig. 2 (b), shows a more rapid decrease of the carbon concentration resulting in no detectable carbon in this sample after 120 minutes of oxidation.

Immobile carbon (density of $\sim 2 \times 10^{19} \text{ cm}^{-3}$) is observed in the SiGeC layer with a 300 nm silicon cap after oxidation, but is not observed in the SiGeC layer capped with a 50 nm silicon cap. The formation of immobile carbon in the SiGeC layer structure with the 50 nm cap is likely prevented by the rapid carbon out-diffusion to the surface. The carbon concentration is above the

solid solubility in the SiGe layer for a shorter time in the 50 nm capped layer not allowing time for carbon to condense into its immobile form. Previous reports of carbon precipitation or immobile carbon are typically from much thicker carbon layers in $\text{Si}_{1-x}\text{C}_x$ or $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ [2,3,4]. In these cases the carbon concentration in the middle of the layer remains near the as-grown value longer (typically far above the solid solubility) because the carbon out-diffusion in nitrogen is slower and the carbon concentration decreases only near the edges of the layers. Indeed, in the thick (150 nm) $\text{Si}_{1-x}\text{C}_x$ layer in this study SIMS does show immobile carbon formation after 8 hours of oxidation, but only after the top 100 nm of carbon layer has eroded away with no sign of immobile carbon.

The carbon detected by SIMS in the alloy layers after annealing in either nitrogen (solid) or oxygen (hollow) was integrated over the layer thickness for all annealing times. The change in carbon content in the 50 nm Si capped $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ and 45 nm Si capped $\text{Si}_{1-x}\text{C}_x$ layer is shown in Fig 3 (a) and (b), respectively. After 120 minutes of annealing the 50 nm Si capped SiGeC layer $\sim 1.5 \times 10^{14} \text{ cm}^{-2}$ carbon diffuses out due to the intrinsic carbon diffusion mechanism in SiGeC. The carbon out-diffusion from the SiC layer is, however, much slower and even after 8 hours of annealing in nitrogen only $\sim 1 \times 10^{14} \text{ cm}^{-2}$ is lost from the layer. Furthermore, the carbon in the layer during the nitrogen anneal remains substitutional, measured by XRD. The source of the extra carbon out-diffusion from the SiGeC layer remains to be identified. The extra carbon lost due to oxidation (carbon in alloy layer after nitrogen anneal subtracted from that after oxidation) is due to the extra silicon self-interstitials injected by the oxidation process and increases with decreasing silicon cap thickness, Fig. 4.

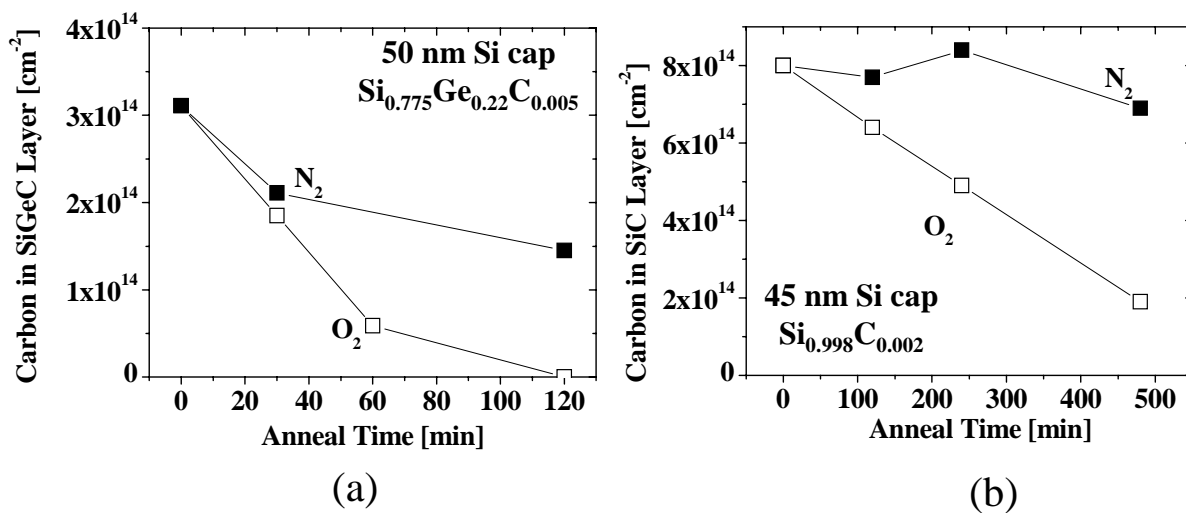


Figure 3. Total carbon in (a) SiGeC layers and (b) SiC layer after annealing in either nitrogen (solid symbol) or oxygen (hollow symbol) ambient at 850°C. Carbon concentrations measured by SIMS.

Interstitial Flux

Oxidation is known to inject interstitials into the silicon bulk at the surface and the enhanced carbon diffusion and carbon loss from the SiGeC layers after oxidation qualitatively can be explained by an increase in mobile carbon, C_i , due to the injected interstitials. For high carbon concentrations in buried SiGeC layers, similar atomic compositions as those in this work, SiGeC layers are near perfect interstitial sinks for all interstitials injected during oxidation [9]. Therefore the addi-

tional injected interstitials are expected to “kick-out” a similar number of carbon, since all injected interstitials are consumed at the SiGeC layer.

During oxidation the surface concentration of interstitials is constant [10], resulting in a linearly decaying interstitial profile from the surface supersaturation concentration to approximately zero at the SiC or SiGeC layer [11, 12]. The interstitial flux into the silicon during oxidation can therefore be calculated as:

$$J_I = -D_I \frac{dI}{dx} = n_{surf} \times \frac{D_I I^*}{\Delta x} \quad (2)$$

where, n_{surf} is the ratio of the interstitial surface concentration to the bulk interstitial concentration ($I/I^* = 12.7$) at 850°C, $D_I I^*$ is the interstitial transport product measured by metal tracer diffusion ($1 \times 10^4 \text{ cm}^{-1} \text{ s}^{-1}$) [11,13], and Δx is the depth of the SiGeC layer.

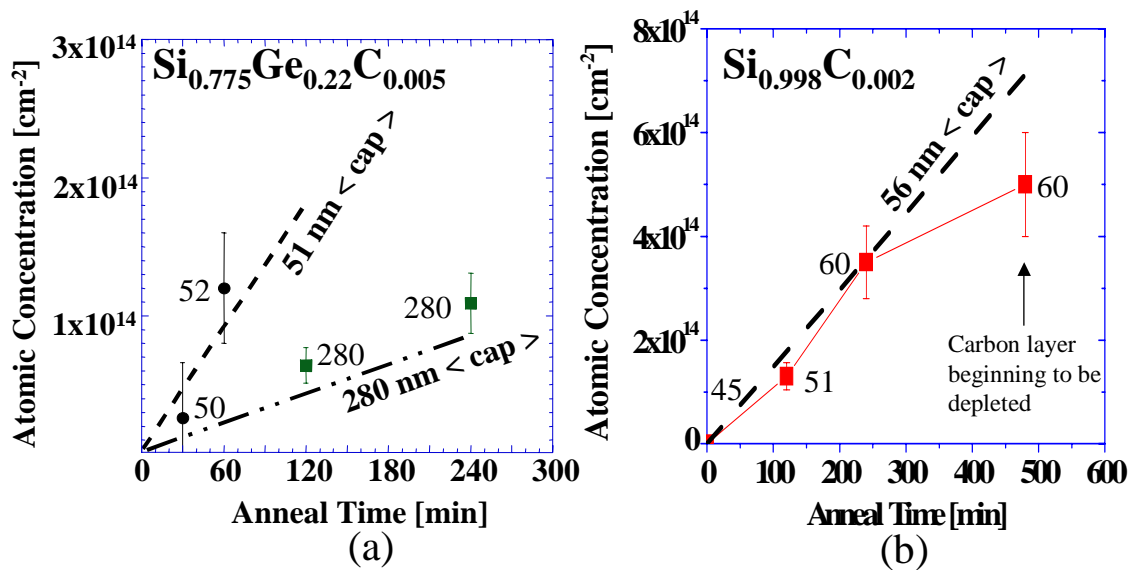


Figure 4. Summary of oxidation enhanced carbon loss from the (a) 50 nm and 280 nm silicon capped SiGeC layers and (b) the 45 nm silicon capped SiC layer. The number of injected interstitial silicon atoms after oxidation is calculated for each test structure using the average silicon cap thickness over the entire oxidation time. The silicon cap thicknesses are found next to each of the carbon loss data in nanometers for each oxidation condition, respectively.

A crude estimate of the total number of injected interstitials is made using an average silicon cap thickness for the entire oxidation time. The silicon cap thickness is, however, not constant during the oxidation. The cap layer thickness depends on two competing processes, the erosion of the carbon layer (increasing the cap) and the consumption of surface silicon by the oxidation reaction (decreasing the cap). This effect is greatest in the thick SiC layer that undergoes the longest oxidation times (8 hrs.). However, even after eroding approximately 100 nm of carbon from the SiC layer, the silicon cap thickness (the total silicon between the edge of the carbon layer and the silicon-oxide interface) remains nearly constant for the entire oxidation time (see cap thickness, Fig. 4, determined by SIMS). Apparently, the two competing processes naturally reach a temporary steady-state increasing or decreasing the total silicon cap until the carbon layer erosion rate matches the silicon consumption rate due to oxidation.

The calculated number of interstitials injected into each carbon layer is compared to the extra carbon removed due to oxidation, Fig. 4. The extra carbon out-diffusion and the calculated

number of injected interstitials both scale with the silicon cap thickness and agree reasonably well for all three oxidation cases considering the uncertainties involved indicating that nearly every injected self-interstitial removes one carbon from the carbon alloy layer. Note: the extra carbon loss after the longest oxidation time may deviate from the calculated number of injected interstitials because by this time the carbon layer is beginning to become completely depleted of carbon. For this reason the carbon loss from the SiGeC layers after the longest oxidation times is omitted because SIMS clearly shows that the SiGeC layers are nearly completely depleted of carbon.

Conclusion

Carbon out-diffusion from $\text{Si}_{0.998}\text{C}_{0.002}$ or $\text{Si}_{0.7865}\text{Ge}_{0.21}\text{C}_{0.0035}$ layers has been examined after annealing in nitrogen or oxygen ambient at 850°C. Carbon out-diffusion from carbon alloy layers is the dominant mechanism of carbon loss, not precipitation. Carbon is found to diffuse out the surface and the carbon diffusion from the SiC or SiGeC layer is enhanced by oxidation. Each injected interstitial leads to the removal of one carbon from the SiC or SiGeC layer. Finally, the rapid and complete loss of carbon from the 50 nm silicon capped SiGeC layer after oxidation clearly indicates that the end-product of the reaction between the injected silicon self-interstitials and the substitutional carbon is mobile carbon. No evidence of immobile carbon formation or precipitation is observed in this important case.

Acknowledgements

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