

## Thermal Stability and Substitutional Carbon Incorporation far above Solid-Solubility in $\text{Si}_{1-x}\text{C}_x$ and $\text{Si}_{1-x-y}\text{Ge}_y\text{C}_x$ Layers Grown by Chemical Vapor Deposition using Disilane

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### Abstract

Growth conditions for epitaxy of  $\text{Si}_{1-x-y}\text{Ge}_y\text{C}_x$  and  $\text{Si}_{1-x}\text{C}_x$  alloy layers on (100) silicon substrates by rapid thermal chemical vapor deposition (RTCVD) with disilane as the silicon source gas are described and the  $\text{Si}_{1-x}\text{C}_x$  conditions are compared to previously reported RTCVD growth conditions for epitaxy of  $\text{Si}_{1-x}\text{C}_x$  using silane as the source gas. The thermal stability of the layers at 850°C in nitrogen is examined using x-ray diffraction as a measure of the average substitutional carbon concentration in the layers after annealing. A characteristic time constant to describe the reduction of average substitutional carbon concentration in the layer is extracted from the XRD measurements. The characteristic time constants are found to agree within a factor of 3 with that observed in previous reports. However, the time constants are found to depend more strongly on the as-grown substitutional carbon concentration than what is predicted by simple precipitation kinetics, assuming carbon diffusion to a constant number of nucleation centers.

### Introduction

The incorporation of high concentrations (> 0.1%) of carbon in silicon and SiGe is of wide technological interest for its potential use to engineer dopant diffusion [1], engineer the conduction band in silicon based materials [2, 3], and strain compensation [4]. However, because the solid solubility of substitutional carbon in silicon is  $\sim 10^{17} \text{ cm}^{-3}$  and carbon at concentrations above this can incorporate on interstitial sites or precipitate as  $\beta$ -SiC, special non-equilibrium epitaxial growth conditions are required to grow metastable films with substitutional carbon concentrations greater than 0.1 atomic percent.

It has been shown that the incorporation of substitutional carbon increases with reduced growth temperature and higher growth rates [5, 6]. Because the growth rate of silicon and SiGe by rapid thermal chemical vapor deposition is strongly dependent on the choice of silicon source gas and disilane is known to produce higher silicon epitaxial growth rates for similar partial pressures and temperatures as silane and dichlorosilane, disilane is a promising candidate for expanding the available parameter space of growth conditions that produce 100% substitutional carbon alloys with silicon and SiGe, which in turn could allow for increased throughput and an extension of the maximum total carbon concentration that can be incorporated entirely as substitutional carbon grown by RTCVD.

This paper characterizes the growth of  $\text{Si}_{1-x-y}\text{Ge}_y\text{C}_x$  and  $\text{Si}_{1-x}\text{C}_x$  layers using a mixture of 10% disilane in hydrogen as the silicon source gas. Growth conditions are

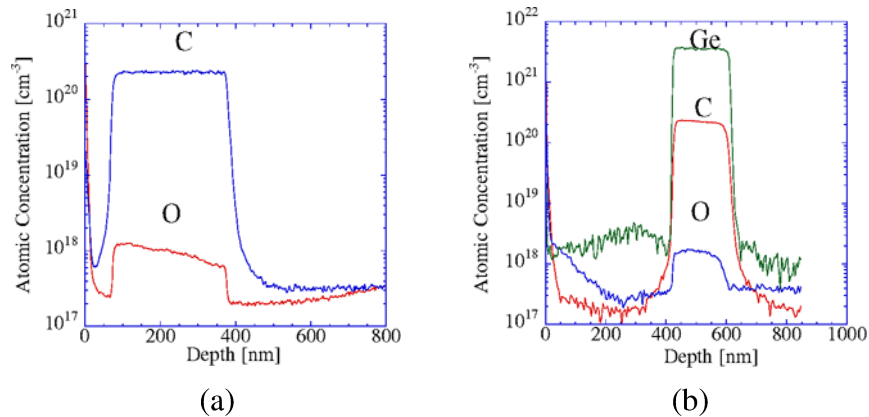
described to obtain  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_x$  and  $\text{Si}_{1-x}\text{C}_x$  films with as much as 0.81 and 0.45 atomic percent, respectively, that are 100% substitutional, and the thermal stability of the  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_x$  and  $\text{Si}_{1-x}\text{C}_x$  alloy layers is examined at 850°C for up to 10 and 16 hours of annealing in nitrogen, respectively. X-ray diffraction is used as a measure of the average substitutional carbon concentration in the layers during annealing and characteristic time constants are extracted to describe the carbon concentration dependence on time.

### $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_x$ and $\text{Si}_{1-x}\text{C}_x$ epitaxy using disilane as the silicon source

$\text{SiGeC}$  alloy layers were grown by rapid thermal chemical vapor deposition (RTCVD) on (100) silicon substrates. All  $\text{SiGeC}$  and  $\text{SiC}$  layers discussed in this work were grown in a homemade reactor described elsewhere [7]. Sources gasses for silicon, germanium and carbon were disilane (10% mixture in hydrogen), germane (0.8% mixture in hydrogen) and methylsilane (1% mixture in hydrogen), respectively. Epitaxy of the alloy layers was done at temperatures ranging from 550-625°C at 10 torr with 3 slpm of hydrogen and 50 sccm of disilane mixture.

The chemical composition of all alloys was determined by secondary ion mass spectroscopy (SIMS) leading to an uncertainty of approximately 15-20% in the total carbon concentrations and 1-2 atomic percent in the germanium concentration. The substitutional carbon concentrations in the alloys were deduced from x-ray diffraction rocking curves around (004) silicon reflection and a linear interpolation between  $\beta\text{-SiC}$  and silicon is used to estimate the lattice constant and elastic constants for carbon in silicon [6].

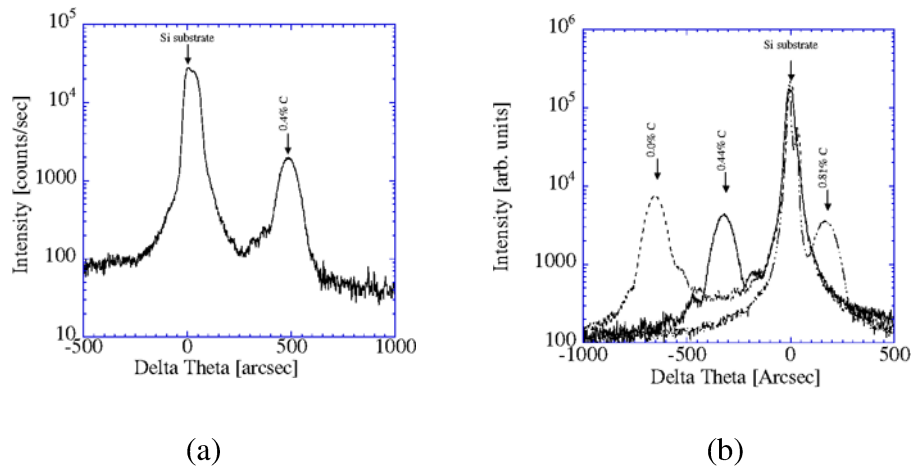
Two  $\text{Si}_{1-x}\text{C}_x$  alloy layers were grown with 20 sccm of methylsilane at 550°C and 625°C resulting in growth rates of 2.5 and 27.7 nm/min and having thicknesses of 100 and 300 nm, respectively. Each of the  $\text{Si}_{1-x}\text{C}_x$  layers were capped with ~ 50 nm of silicon and subjected to a subsequent 5 minute 800°C anneal. Sharp interfaces between the  $\text{Si}_{1-x}\text{C}_x$  and silicon and uniform carbon concentrations in the  $\text{Si}_{1-x}\text{C}_x$  are measured by SIMS, Fig. 1(a). The rocking curve of the  $\text{Si}_{0.9955}\text{C}_{0.0045}$  layer, furthermore, shows a well defined



**Figure 1.** Carbon, germanium and oxygen concentration profiles of the as-grown (a)  $\text{Si}_{0.996}\text{C}_{0.004}$  layer and (b)  $\text{Si}_{0.9255}\text{Ge}_{0.07}\text{C}_{0.045}$  layer.

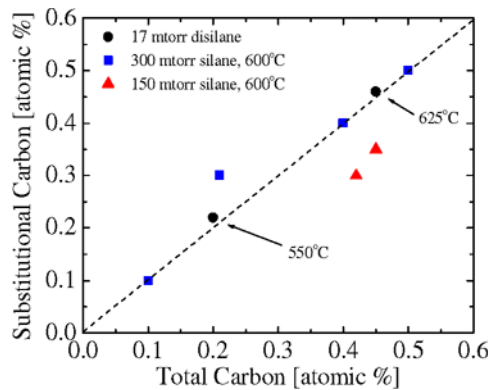
(004) reflection centered at ~ 500 arcseconds from the silicon (004) diffraction peak indicating a tensilely strained single crystal layer, Fig 2 (a). The substitutional carbon concentrations extracted from the XRD measurements of both layers agree well with the

total carbon concentration measured by SIMS demonstrating that 100% substitutional carbon layers may be grown at 625°C with up to at least 0.45% substitutional carbon.



**Figure 2.** X-Ray diffraction rocking curves around the (004) Bragg reflection of the (a)  $\text{Si}_{0.996}\text{C}_{0.004}$  layer and (b) and the  $\text{Si}_{0.93-x}\text{Ge}_{0.07}\text{C}_x$  layers with  $x$  varying from 0 to 0.008.

These results are compared to those reported by Mitchel et al. at 600°C, who studied substitutional carbon incorporation in  $\text{Si}_{1-x}\text{C}_x$  epitaxial layers grown by RTCVD using silane. With the exception of using silane as the silicon source gas their growth conditions were similar to those used in this work (i.e. 12 torr, 2 or 8 slpm of  $\text{H}_2$  and methylsilane was the source gas for carbon). It was found in that work that it was necessary to use high silane partial pressures, 300 mtorr, to incorporate all carbon



**Figure 3.** Summary of substitutional carbon incorporation in epitaxial  $\text{Si}_{1-x}\text{C}_x$  for different silane partial pressures and different disilane growth temperatures. The dashed line represents 100% substitutional carbon. Conditions for carbon incorporation using silane were obtained from reference [6].

substitutionally in silicon up to 0.5% atomic percent of carbon at 600°C, Fig. 3. However, using a disilane partial pressure 17 times lower and at a higher temperature, 625°C, a similar amount of carbon was incorporated entirely substitutionally, Fig. 3, which is encouraging as restrictions on both critical growth parameters for 100% substitutional carbon incorporation, low temperature and high partial pressures of the silicon source gas, appear to be relaxed with the use of disilane.

Silicon capped  $\text{Si}_{0.93-x}\text{Ge}_{0.07}\text{C}_x$  layers were grown at  $625^\circ\text{C}$  with the addition of 25 sccm of germane and either 0, 20 or 50 sccm of methylsilane, while using the same hydrogen and disilane flows and partial pressures. Sharp interfaces and uniform concentrations of carbon and Ge were also obtained for these conditions, Fig 1 (b) (SIMS) and X-ray diffraction rocking curves around the (004) reflection again show well defined reflections from the alloy layers that shifts from the compressively strained lattice constant of the  $\text{Si}_{0.93}\text{Ge}_{0.07}$  to the tensilely strained  $\text{Si}_{0.922}\text{Ge}_{0.07}\text{C}_{0.008}$  layer, Fig 2 (b), which further demonstrates that fully strain compensated SiGeC layers up to at least 7 atomic percent germanium may be grown by RTCVD using disilane. The growth rates for all three layers was  $\sim 30$  nm/min and little change in growth rate due to the introduction of carbon was observed. The substitutional carbon concentrations were extracted from the XRD using Ge concentrations obtained from SIMS and found to be 100% substitutional in all of the layers.

Finally, in all layers grown with high carbon concentrations a proportional increase in oxygen concentration is also observed. Oxygen is an undesirable contaminant in the presence of carbon, as it is known to facilitate carbon precipitation [8, 9], however, TEM of all the as-grown  $\text{Si}_{0.93-x}\text{Ge}_{0.07}\text{C}_x$  layers showed no evidence of precipitates. The resulting oxygen background is consistently about 200 times less than the carbon concentration at  $625^\circ\text{C}$  and the source is as of yet unidentified, Fig 1 (a & b). Because a similar magnitude of increase in oxygen concentration is observed in SiGeC layers grown with dichlorosilane and low oxygen backgrounds are observed in pure silicon grown with disilane, disilane is not suspected as the source of oxygen contamination. Residual oxygenated species in the methylsilane are a potential source of the contamination and different purification schemes for the methylsilane source are currently being examined.

### Thermal Stability of Carbon Alloys

Reduction of tensile strain in alloy layers that contain carbon after annealing in nitrogen has been correlated with the formation of precipitates and a decrease in carbon on substitutional sites [10, 11]. Therefore, the thermal stability of the carbon in the SiGeC and SiC layers after annealing at  $850^\circ\text{C}$  in a nitrogen ambient for up to 10 and 16 hours, respectively, was monitored by XRD, Fig. 4. To evaluate the contribution of just the Ge to the change of strain over the annealing times the pure  $\text{Si}_{0.93}\text{Ge}_{0.07}$  sample was measured and the strain in the layer was found to be indistinguishable from the as-grown layer within the uncertainty of the Ge concentration due to growth non-uniformity.

However, a rapid increase in compressive strain is observed in the  $\text{Si}_{0.9219}\text{Ge}_{0.07}\text{C}_{0.0081}$  layer after 10 hours of annealing indicating a loss of approximately 59% of the average substitutional carbon in the layer. In contrast, the strain in the layers with less carbon are significantly more stable despite differing in concentration by only 2-4 times. The carbon profiles after annealing, measured with SIMS, show out-diffusion of the carbon from the SiC and SiGeC layers affecting the concentration only within the first 10-20 nm of the edges of the carbon layers, however, the carbon concentration in the rest of the layer remains indistinguishable from the as-grown layer. The observed shift in the XRD peak positions, therefore, can not be explained by carbon out-diffusion.

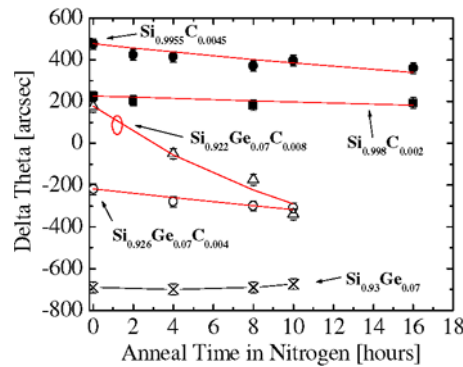
Based on classical theory of phase transitions, the rate of precipitation in supersaturated mixtures can often be described by the semi-empirical Avrami relation,

$$y(t) = \exp[-(t/\tau)] \quad (1)$$

where  $y(t)$  is the number of solute atoms that remain unprecipitated  $t$  is the time and  $\tau$  is the characteristic time constant of the reaction. Loss of substitutional carbon after annealing has indeed been described relatively well by this relationship [12]. Furthermore, the time constant dependence on temperature and carbon concentration have been described previously with some success with the following relationship [10, 12]:

$$\frac{1}{\tau} \sim D \left( \frac{y_o - y^{eq}}{y_{SiC}} \right)^{\frac{1}{3}} \sim D \left( \frac{y_o}{y_{SiC}} \right)^{\frac{1}{3}} \quad (2)$$

where  $y_o$  is the initial carbon concentration,  $y_{SiC}$  is the carbon concentration in  $\beta$ -SiC (i.e.  $y_{SiC} = 0.5$ ),  $D$  is the diffusivity of the carbon, and  $y^{eq}$  is the solid solubility of carbon in silicon, which is negligible compared to the initial carbon concentrations in the layers of this work. This relationship can be derived from the assumption that the precipitation reaction is a diffusion limited process with a fixed number of nucleation sites.



**Figure 4.** Summary of the positions of the XRD reflections from all alloy layers with respect to the silicon (004) substrate diffraction peak before and after annealing in nitrogen ambient at 850°C. Best fits using a single time constant are shown for all layers except the  $Si_{0.93}Ge_{0.07}$  layer.

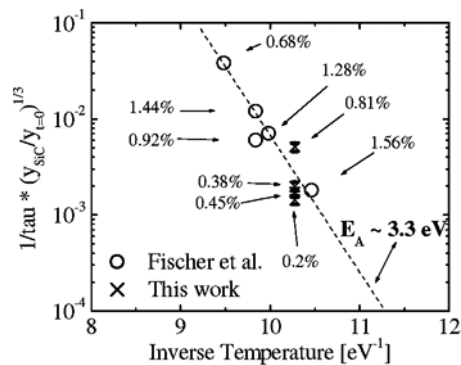
Characteristic time constants were extracted for the  $Si_{1-x-y}Ge_xC_x$  and  $Si_{1-x}C_x$  layers annealed in this work and are normalized according to their respective concentrations, eqn. 2, so that they may be compared with one another and previous work, Fig. 5 [12]. The agreement of normalized time constants between this work and that expected from Fischer et al. is within a factor of 3, which is consistent with the observation that the time constant is dominated by a temperature dependent diffusivity with an activation energy similar to that of the diffusivity of carbon in silicon, 3.3 eV.

However, the spread of normalized time constants for different concentrations shows that the time constants are significantly more sensitive to the carbon concentrations than is predicted by this simple classical theory. The presence of 7 atomic percent germanium does not appear to change the time constant more than 20% for layers containing approximately the same carbon concentration, (i.e. the  $Si_{0.9955}C_{0.0045}$  and the  $Si_{0.9262}Ge_{0.07}C_{0.0038}$ ), and previous reports indicate a faster rate of carbon loss in  $Si_{0.892}Ge_{0.1}C_{0.008}$  compared to  $Si_{0.992}C_{0.008}$  of only about 2 at similar temperatures [13], which is not enough to explain the factor of 5 difference that is observed between the lowest and highest carbon content layers in this work. It is not clear, from this limited set of observations, whether the increased sensitivity to carbon concentration may be caused

by the increased oxygen concentration observed in these layers, a known catalyst for precipitation [8], or perhaps because of an intrinsic aspect of the carbon precipitation itself.

## Conclusion

Growth conditions for SiC and SiGeC layers using disilane as the silicon source gas are presented and carbon concentrations that are 100% substitutional are incorporated into silicon and Si<sub>0.93</sub>Ge<sub>0.07</sub> up to 0.45 and 0.81 atomic percent, respectively. It is found that a similar carbon content film may be grown at a higher temperature and lower partial pressure of disilane than what is reported for growth with silane. The thermal stability of



**Figure 5.** Summary of characteristic time constants normalized according to eqn. 2 so that they may be compared to the work of Fischer et al. [12]. The carbon content in each of the layers is indicated beside the normalized time constant.

all layers grown with disilane, is furthermore, examined and the rate of loss of substitutional carbon from these layer is found to be within a factor of 3 of what would be expected from previous reports. However, the characteristic time constant of the precipitation is found to depend more strongly on the carbon concentration than what is predicted by simple precipitation kinetics assuming carbon diffuses to a fixed number of nucleation centers.

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