The effect of composition on the thermal stability of $Si_{1-x-y}Ge_xC_y/Si$ heterostructures

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The thermal stability of molecular beam epitaxy grown $Si_{1-x-y}Ge_xC_y/Si$ heterostructures ($0 \leqslant x < 0.30$, $y \sim 0.008$) was studied using infrared absorption spectroscopy. The local vibrational mode of C in Si and $Si_{1-x-y}Ge_x$ was used to quantify the loss of C atoms from substitutional sites with high temperature annealing. The activation energy ($E_a = 4.9$ eV) for the loss of substitutional C achieved a maximum for the strain compensated alloy ($x \sim 0.1$). An additional increase of Ge content resulted in a rapid decrease in E_a, which was found to be 3.4 eV for $x \sim 0.27$. The nonmonotonic behavior of E_a on Ge content is explained by the effect of the interface strain between the epitaxial layer and Si substrate. © *1998 American Institute of Physics.*
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Band-gap tailoring and lattice matching of $Si_{1-x-y}Ge_xC_y/Si$ heterostructures have the potential to improve the performance and capabilities of Si based optoelectronics.[1] Although remarkable progress in molecular beam epitaxy (MBE),[1,2] chemical vapor deposition (CVD),[3] and solid phase epitaxy (SPE)[4] of $Si_{1-x-y}Ge_xC_y/Si$ heterostructures has been achieved, important questions concerning growth kinetics and thermal stability are not yet fully understood. These growth techniques occur far from equilibrium forming metastable alloys with C concentrations exceeding the equilibrium solubility by up to four orders of magnitude. The magnitude of the C supersaturation in these alloys imposes limitations on thermal processing, beyond which the alloy will relax to its equilibrium state. Under high temperature treatment, the relaxation of metastable $Si_{1-y}C_y$ alloys occurs by the formation of thermodynamically stable β-SiC precipitates of small grain size (3–5 nm).[5] However, post-growth device processing of these heterostructures requires that the structural properties and alloy compositions remain stable during heat treatments. There have been a number of reports on the measurements of thermal stability of $Si_{1-y}C_y/Si$ heterostructures,[5–7] but little is known of $Si_{1-x-y}Ge_xC_y/Si$ alloys.[7] We report on the effect of Ge on the thermal stability of $Si_{1-x-y}Ge_xC_y/Si$ heterostructures in the most technologically interesting region of Ge contents ($0 \leqslant x < 0.30$).

$Si_{1-x-y}Ge_xC_y$ layers were grown by MBE on p-type float zone Si(100) substrates. The Si–C beam was formed by thermally heating a float zone refined silicon ingot contained in a pyrolytic graphite crucible. Zone refined intrinsic Ge was evaporated from a pyrolytic BN crucible. The substrate temperature during growth was 400 °C. All layers were grown approximately 150 nm thick and were recrystallized at 650 °C for 30 min prior to the annealing experiment and compositional analysis. The recrystallization temperature and time were chosen so to maximize the integrated absorption of the local vibrational mode (LVM) of substitutional C in the layer. The procedure is similar to that used by Strane during the SPE growth of implanted $Si_{1-x-y}Ge_xC_y$ layers which resulted in nearly all C atoms occupying substitutional sites.[4] X-ray diffraction and Raman spectroscopy were applied to quantify the amount and uniformity of substitutional C and Ge in our samples. X-ray rocking curve analysis of the symmetric (004) and asymmetric (224) reflections revealed that the $Si_{1-x-y}Ge_xC_y$ layers with $x < 0.2$ were fully strained. Further details on the MBE growth conditions can be found in Ref. 8

Samples were cut into 1 cm^2 pieces and annealed in a quartz furnace purged by pure N_2 at atmospheric pressure in the temperature region from 750 to 1000 °C for various times. Fourier transform infrared spectroscopy (FTIR) was used to analyze the amount of substitutional C during annealing through the integrated absorbance of the local vibrational mode of C in Si.

The left inset in Fig. 1 displays the room temperature FTIR spectra of the $Si_{0.992}C_{0.008}$ (solid line). The full width at half maximum (FWHM) of the substitutional C local vibration mode (C-LVM) at 607 cm^{-1} of $Si_{0.992}C_{0.008}$ is about 14 cm^{-1}, close to that found by Strane *et al.*[5] The dashed line shows the absorbance of the $Si_{0.722}Ge_{0.27}C_{0.008}$ alloy, illustrating the spectral shift of the C-LVM to lower energies due to the effect of Ge on the bonding strength.

Figure 1 shows absorption spectra of $Si_{0.892}Ge_{0.10}C_{0.008}$ annealed at 908 °C for different times. The spectra consists of two main lines at 602 and at 815 cm^{-1}. The asymmetric line at 815 cm^{-1} with FWHM $\sim$66 cm^{-1} is associated with the vibration of coherent SiC precipitates.[5] The line at 602 cm^{-1} is the vibrational mode of substitutional C. With progressive annealing, the absorbance at 602 cm^{-1} decreases while that of the 815 cm^{-1} mode increases showing that C atoms transfer from substitutional sites to SiC precipitates. Samples were annealed until the C vibrational mode disappeared (the uppermost spectrum in Fig. 1). The spectrum without the C mode was then subtracted from the others as a reference to remove all irrelevant spectral features when determining the integrated absorbance of the C-LVM. This procedure was especially important for $Si_{1-x-y}Ge_xC_y/Si$ het-

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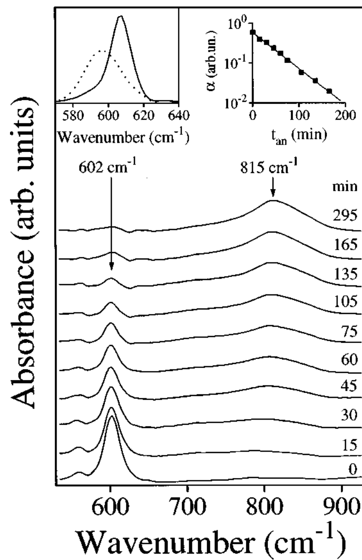

FIG. 1. Effect of annealing at 908 °C on FTIR spectra of $Si_{0.892}Ge_{0.10}C_{0.008}$/Si heterostructure. Annealing times (t_{an}) are shown on the right side of the figure. The right inset shows the integrated absorption coefficient of substitutional C vibration mode (α) vs t_{an}. Solid line is the best fit of the experimental points. The left inset shows the FTIR spectra of substitutional C vibration mode in $Si_{1-x-y}Ge_xC_y$/Si heterostructures with $x=0$ (solid line) and 0.27 (dashed line).

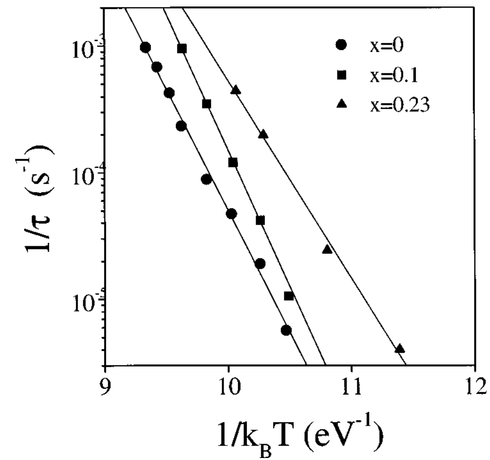

FIG. 2. Arrhenius plot of the rate of substitutional C loss for three different Ge contents ($x=0$, 0.1, 0.23). Solid lines are the best fits of the experimental points.

erostructures because of the strong difference between refractive indexes of the layers and the Si substrates.

The integrated absorption of the C-LVM (α) for $Si_{0.892}Ge_{0.10}C_{0.008}$ alloys versus annealing time at 908 °C is presented in the top right inset to Fig. 1. It can be fit with an exponential decay function

$$\alpha=\alpha_0\times\exp\left\{-\frac{t}{\tau}\right\}, \tag{1}$$

with α_0 and τ being the initial absorption coefficient and decay constant, respectively. To ensure the accuracy of the fitting procedure, α was measured over a duration in which its magnitude decreased by at least one order of magnitude; see the right inset in Fig. 1. Similar to Strane *et al.*,[5] we found a rapid nonexponential decrease in α during the initial annealing steps at annealing temperature less than 900 °C, which was followed by a continuous exponential decay of α for the remainder of the annealing sequence. X-ray diffraction measurements, however, showed the layer strain decreased exponentially for the entire annealing sequence with the same decay constant as the exponential part of α decay. We believe that the initial drop of α is the result of the formation of a transitional Si–C phase partially preserving the layer strain, which precedes the precipitation of β-SiC.[5,8] In fact, during the initial drop of α, no characteristic β-SiC absorption was observed in FTIR spectra. Therefore, only the onset of the exponential part of the α decay curve will be considered further.

Figure 2 presents the Arrhenius plot relating the measured decay constant for loss of substitutional C versus annealing temperature for $Si_{1-x-y}Ge_xC_y$/Si heterostructures with $x=0$, 0.1, and 0.23. For each value of Ge content, $1/\tau$ reveals thermally activated behavior over the entire temperature region

$$\frac{1}{\tau}=r_0\times\exp\left\{-\frac{E_a}{k_BT}\right\}. \tag{2}$$

The magnitude of E_a for the $Si_{0.992}C_{0.008}$ alloy found from the best fit of the experimental points is 4.45 ± 0.15. The E_a for the $Si_{0.892}Ge_{0.1}C_{0.008}$ layer is 4.9 ± 0.2 eV. The values of E_a for $Si_{1-y}C_y$/Si and $Si_{1-x-y}Ge_xC_y$/Si ($x\sim0.1$) heterostructures are in good agreement with the prior results measured in the high temperature annealing region (1000–1130 °C) for this same composition (4.5 and 5.3 eV, respectively),[7] and far exceeds the activation energy of C diffusion in bulk Si near the C solubility limit (3.1 eV).[9] A discrepancy between our activation energy for $Si_{1-y}C_y$ versus a lower value obtained by Fischer *et al.* ($E_a=3.3$ eV) may be due to surface oxidation during their annealing sequence.[6] Due to volume considerations, the formation of SiO_2 will inject one silicon self-interstitial for each of the two-oxygen atoms.[10] Carbon diffusion is enhanced in the presence of a supersaturation of Si self-interstitials, as C diffusion is believed to be dominated by a mobile interstitial C–Si pair.[10] For the temperature range of 800–1100 °C, Ladd *et al.* measured an increase in C diffusivity by approximately one to two orders of magnitude during annealing in an oxidizing ambient and during a phosphorus in-diffusion when compared to annealing in a nitrogen ambient.[11] The former two environments produce a Si self-interstitial concentration in excess of the equilibrium concentration. The surface oxide observed during Fischer's work may have been a source of excess Si self-interstitial defects, resulting in increased C diffusivity and thus a lower barrier to loss of substitutional C. During our experiments, we took great care to ensure all annealing was performed in a pure N_2 environment. Combining our results with those of Ref. 7, a unitary activation behavior for the loss of substitutional C for $Si_{1-y}C_y$/Si and $Si_{1-x-y}Ge_xC_y$/Si ($x\sim0.1$) heterostructures in the entire temperature region 830–1130 °C is concluded.

As shown in Fig. 3, the E_a vs Ge content achieves maximum at $x\sim0.1$, and decreases rapidly at higher x. Such a behavior can be understood as the competition of opposing contributions to E_a: (i) the mismatch between Si–Si and Si–C bonds becomes larger with Ge content which acts to decrease E_a,[12,13] and (ii) the interface strain between the

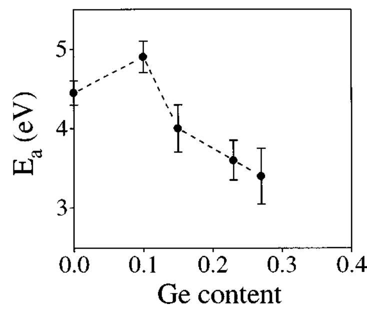

FIG. 3. Activation energy of substitutional C loss vs Ge content for annealed $Si_{1-x}Ge_xC_{0.008}$. The maximum at $x=0.1$ occurs for the strain compensated heterostructure.

layer and the Si substrate decreases as the small addition of Ge to $Si_{1-y}C_y$ compensates the tensile strain in the layer[2] thus increasing E_a. In our case the strain compensation is attained at $x\sim0.1$, which was verified by x-ray diffraction measurements. At $x\sim0.1$ when the C atoms leave substitutional lattice sites, the strain energy increases by a value ΔE, as opposed to in $Si_{1-y}C_y$ layers where the strain energy decreases with loss of substitutional C. From continuous elastic theory the contribution from interface strain at $x\sim0.1$ $(2\Delta E)$ could be estimated as ~0.1 eV per C atom.[14] This value is in reasonable agreement with the experimental results if one takes into account the limitations of the elastic theory approach for SiGeC alloys with large mismatch between Si–Si(Ge), and Si(Ge)–C bonds.[2,13]

In conclusion, we present temperature stability measurements of $Si_{1-x-y}Ge_xC_y/Si$ and $Si_{1-y}C_y/Si$ MBE grown heterostructures with $(0\leq x<0.30,\ y\sim0.008)$. The ternary alloy $Si_{1-x-y}Ge_xC_y/Si$ heterostructure with small $x\sim0.1$ was found to have higher activation energy for substitutional C loss than for the binary $Si_{1-x}C_y$ alloy. The activation energy achieves a maximum in the structure with zero interface strain between the Si substrate and $Si_{1-x-y}Ge_xC_y$ layers $(x\sim0.10$ and $y=0.008)$ and rapidly decreases as the Ge fraction is further increased. Thus, ternary unstrained layers grown on Si substrate might hold the greatest potential for device processing at elevated temperatures for Si based heterostructure technology.

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