Thermal stability of Si/Si$_{1-x-y}$Ge$_x$C$_y$/Si quantum wells grown by rapid thermal chemical vapor deposition

C. W. Liu[a)] and Y. D. Tseng
Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan

M. Y. Chern
Department of Physics, National Taiwan University, Taipei, Taiwan

C. L. Chang and J. C. Sturm
*Department of Electrical Engineering and Center for Photonics and Optoelectronic Materials,
Princeton University, Princeton, New Jersey 08544*

The thermal stability of Si/Si$_{1-x-y}$Ge$_x$C$_y$/Si quantum wells was studied by high resolution x-ray diffraction, Fourier transform infrared spectroscopy, and defect etching. There are different pathways of strain relaxation in this material system, depending on the annealing temperature. The lattice structure of Si$_{1-x-y}$Ge$_x$C$_y$ was as stable as the Si$_{1-x}$Ge$_x$ alloys at an annealing temperature of 800 °C for 2 h. At an annealing temperature of 900 °C for 2 h, the structures of both Si$_{1-x-y}$Ge$_x$C$_y$ and Si$_{1-x}$Ge$_x$ started to relax. The addition of C enhanced the Ge outdiffusion in Si$_{1-x-y}$Ge$_x$C$_y$, compared to that of Si$_{1-x}$Ge$_x$. For the annealing temperatures of 950 and 1000 °C for 2 h, the Si$_{1-x}$Ge$_x$ continued to relax with the decrease of strain in the quantum wells, but the Si$_{1-x-y}$Ge$_x$C$_y$ relaxed with the *increase* of the strain due to the formation of SiC precipitates. Misfit dislocation formation was observed in the Si$_{1-x-y}$Ge$_x$C$_y$ alloys with initial thicknesses below the critical thickness after annealing at 1000 °C for 2 h. This relaxation is probably caused by the SiC precipitation, since SiC precipitates can reduce the strain compensation and, therefore, decrease the critical thickness. © *1999 American Institute of Physics.* [S0021-8979(99)06704-3]

I. INTRODUCTION

Recently there has been impressive progress in the growth[1,2] and characterization[3–6] of Si$_{1-x-y}$Ge$_x$C$_y$ alloys, which offer great flexibility in tailoring the strain and the electronic properties of group IV heterostructures.[7,8] Because the lattice constant of cubic carbon (diamond) is 0.356 683 nm,[9] which is 34% smaller than that of Si, substitutional incorporation of C can compensate in the compressive strain of Si$_{1-x}$Ge$_x$ layers grown on Si substrates, where the lattice constant of Ge is 4.17% larger than that of Si. This leads to an increase in the critical thickness of pseudomorphic Si$_{1-x-y}$Ge$_x$C$_y$ layers on Si. Since the formation of SiC precipitates is thermodynamically favored, the thermal stability of the Si$_{1-x-y}$Ge$_x$C$_y$ alloys will not only be affected by the misfit dislocation formation and Ge(C)/Si interdiffusion, which are inherent in Si$_{1-x}$Ge$_x$ alloys,[10–13] but also by the SiC precipitation. It was also reported that the carbon incorporation into Si$_{1-x}$Ge$_x$ layers has the effect of suppressing the boron outdiffusion in Si/Si$_{1-x-y}$Ge$_x$C$_y$/Si heterojunction bipolar transistors.[8] Therefore, it is important to investigate the thermal stability of Si$_{1-x-y}$Ge$_x$C$_y$ alloys for further device applications. Previous study[14] on Si$_{1-x}$C$_x$/Si superlattices grown by molecular beam epitaxy (MBE) showed that SiC precipitated at annealing temperatures of 1000 °C and above, and that the structure relaxed only by interdiffusion at 900 °C and below. The low temperature annealing (<800 °C)

of the single thick MBE-grown Si$_{1-x}$C$_x$ sample[15] showed no significant change in the strain and thickness. In this article, we have investigated the stability of Si$_{1-x-y}$Ge$_x$C$_y$ alloys grown by rapid thermal chemical vapor deposition (RTCVD) at different annealing temperatures by using high resolution x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and defect etching.

II. GROWTH

The Si$_{1-x-y}$Ge$_x$C$_y$ single quantum wells were grown on Si ⟨100⟩ substrates by RTCVD. The Si$_{1-x-y}$Ge$_x$C$_y$ layers were grown at 625 °C using methylsilane as the C source. The growth pressure was 6 Torr. The gas flows were 3 slpm for a hydrogen carrier, 26 sccm for dichlorosilane, and 0.8 sccm for germane. The maximum content of carbon incorporation is around 2%. The Si cap layer was grown at 700 °C using a 26 sccm dichlorosilane flow and a 3 slpm hydrogen flow. The Ge fraction and thickness of Si$_{1-x}$Ge$_x$ were determined by fitting x-ray rocking curves. Details of the Si$_{1-x-y}$Ge$_x$C$_y$ growth can be found in Ref. 2. As small amounts of methylsilane were added to the source gases, we observed a shift in the (400) x-ray diffraction peak of the resulting Si$_{1-x-y}$Ge$_x$C$_y$ layers away from that of a similar layer without the addition of methylsilane. Vegard's law with a compensation ratio of 1% C to 8.3% Ge was used[1,2] to estimate the carbon concentration in the alloys. The carbon content was obtained from the shift of (400) peak by assuming the Ge concentration was unchanged as the methylsilane was added. The thickness of the as-grown Si$_{1-x-y}$Ge$_x$C$_y$

a)Electronic mail: chee@cc.ee.ntu.edu.tw

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quantum well was also determined by fitting the rocking curves, which had been calibrated by Auger electron spectroscopy depth profiles on thick samples. Secondary ion mass spectroscopy (SIMS) also has confirmed the existence of flat C profiles, and that Ge concentration was unchanged by adding the methylsilane on calibrated samples.

Three quantum well structures were investigated in this study. The well compositions were $Si_{0.77}Ge_{0.23}$, $Si_{0.762}Ge_{0.23}C_{0.008}$, and $Si_{0.758}Ge_{0.23}C_{0.012}$ with thicknesses of 20, 18, and 18 nm, respectively. The nominal thickness of the Si cap was about 60 nm. The Ge content and thickness were obtained from dynamic simulation of the rocking curves, assuming a box profile. All as-grown samples were pseudomorphic and fully strained due to the low temperature growth (625 °C). No defect was observed in these as-grown films after defect etching, using four parts of 49% HF and five parts of 0.3 M CrO_3. For a reference, the critical thicknesses of the $Si_{0.77}Ge_{0.23}$, $Si_{0.762}Ge_{0.23}C_{0.008}$, and $Si_{0.758}Ge_{0.23}C_{0.012}$ samples were 10, 17, and 23 nm, respectively, estimated from Matthews and Blakeslee's theory.[12,16,17] The thickness of the $Si_{0.77}Ge_{0.23}$ control sample was above its critical thickness, indicating that further relaxation could be caused by dislocation formation and/or atomic interdiffusion. The thickness of the highest carbon-content sample ($Si_{0.758}Ge_{0.23}C_{0.012}$) is well below its critical thickness, indicating that the relaxation mechanism could be interdiffusion and/or SiC precipitation. However, misfit dislocation formation can be also observed in these thin $Si_{1-x-y}Ge_xC_y$ films, if the SiC precipitates can reduce the strain compensation and thus decrease the critical thickness. Please note that the interdiffusion and/or the misfit dislocation formation would decrease the vertical lattice constant, but the SiC precipitation can increase the vertical lattice constant because of the consumption of Si and C atoms during the formation of SiC precipitates. The increase of the vertical lattice constant by 1 at.% of SiC formation in $Si_{1-x-y}Ge_xC_y$ is effectively the same as that by 8.3 at. % of Ge incorporation.

III. CHARACTERIZATION AND DISCUSSION

To study the thermal stability of the $Si/Si_{1-x-y}Ge_xC_y/Si$ quantum wells, the x-ray rocking curves from as-grown and annealed samples were measured. The samples were annealed at temperatures from 800 to 1000 °C in nitrogen. To avoid nonuniformity of the 100 mm wafer, an accumulative annealing scheme was adopted. In other words, the annealing treatment was performed on the same pieces of samples at different temperatures. For all three samples annealed at 800 °C for 2 h, there was no change in the rocking curves, indicating that these structures are stable during a low-temperature process. This is similar to previous results.[14] The C incorporation into $Si_{1-x}Ge_x$ does not degrade the thermal stability of the lattice structure at 800 °C. However, for all samples continuously annealed at 900 °C for 2 h, we observed a shift toward the Si peak in the (400) x-ray rocking curves shown in Figs. 1, 2 and 3 for the $Si_{0.77}Ge_{0.23}$, $Si_{0.762}Ge_{0.23}C_{0.008}$, and $Si_{0.758}Ge_{0.23}C_{0.012}$ quantum well samples, respectively, indicating that all the structures started
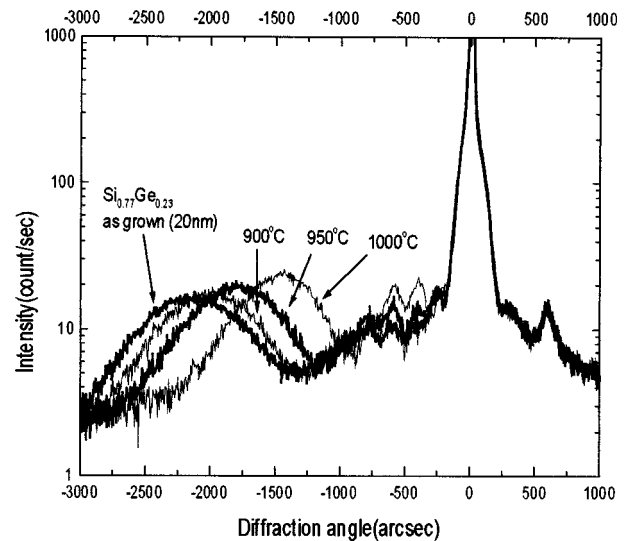

FIG. 1. High resolution x-ray diffraction spectra of $Si/Si_{0.77}Ge_{0.23}/Si$ quantum wells annealed at different temperatures. The well thickness is 20 nm. The (400) diffraction peak of the $Si_{0.77}Ge_{0.23}$ layer continued to shift towards the (400) Si peak as the annealing temperature increased.

to relax. To further probe the relaxation, the x-ray rocking curves were fitted with simulation profiles. The diffused Ge profile was taken from the solution of the one dimensional interdiffusion equation,[18]

$$x_{Ge}(z) = x_{Ge}^0/2\{-\text{erf}[(-W/2+z)/2L]$$
$$+\text{erf}[(W/2+z)/2L]\},$$

where x_{Ge}^0 is the initial Ge concentration, W is the quantum well thickness, z is the position along the growth direction ($z=0$ at the well center), erf is the error function, and L is the diffusion length. As the result of the SIMS profile,[19] the width of carbon profile is relatively unchanged during the annealing. We, therefore, assume a box carbon profile and
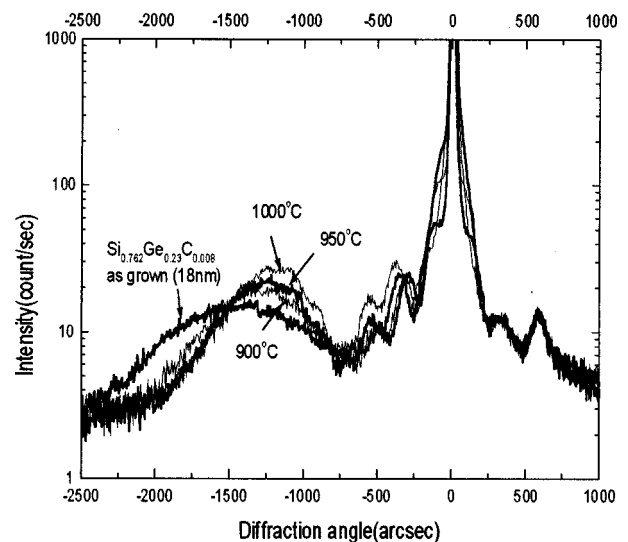

FIG. 2. High resolution x-ray (400) diffraction spectra of $Si/Si_{0.762}Ge_{0.23}C_{0.008}/Si$ quantum wells annealed at different temperatures. The well thickness is 18 nm.

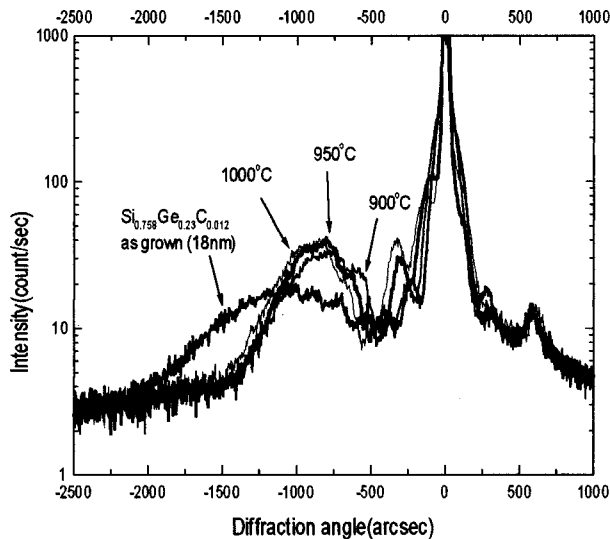FIG. 3. High resolution x-ray (400) diffraction spectra of Si/Si$_{0.758}$Ge$_{0.23}$C$_{0.012}$/Si quantum wells annealed at different temperatures. The well thickness is 18 nm.

FIG. 4. Typical simulation curve to fit the (400) diffraction spectrum. The insert shows the Ge and C profiles used in the simulation.

the width remaining constant, but the carbon concentration is left as a fitting parameter. The diffused Ge profile and the box carbon profile yield the narrowing of (400) diffraction peak of Si$_{1-x-y}$Ge$_x$C$_y$ in the diffraction spectra after successive annealings. The simulation also shows that the carbon box profile enhances the amplitude of the thickness fringe in the (400) diffraction spectra. Therefore, the fringes are more visible in the carbon-containing samples than in the Si$_{1-x}$Ge$_x$ samples. The relaxation parameter R, describing the misfit dislocation formation, is defined by

$$R = (a_p - a_{Si})/(a_r - a_{Si}), \tag{1}$$

where a_p is the in-plane lattice constant of Si$_{1-x-y}$Ge$_x$C$_y$ alloys, a_r is the lattice constant of fully relaxed Si$_{1-x-y}$Ge$_x$C$_y$ layers, and a_{Si} is the lattice constant of the Si substrates. The shape of the (400) diffraction is determined by the diffusion length L. The relative position of the (400) diffraction peak with respect to the Si (400) peak is determined by the carbon concentration, the relaxation parameter, and the diffusion length which changes the center concentration in Ge profiles after the annealing. The diffusion length L can be extracted by fitting the simulation profiles with rocking curves. The carbon concentrations and relaxation parameters cannot be extracted individually without further measurements. A typical simulation curve is shown in Fig. 4, where the relaxation parameter is assumed to be zero. Note that we can have different sets of carbon concentrations and relaxation parameters to fit the experimental curves. The extracted diffusion length increases as the carbon content increases in the alloys (Fig. 5) for all the annealing temperatures. This indicates that the incorporation of carbon can enhance the Ge diffusion in Si. Since transient enhanced diffusion was observed in CVD-grown SiGe quantum wells,[11] the diffusion coefficients could not be extracted directly from the diffusion length. We have also observed some nonlinear diffusion in our samples, but details of it are still under investigation.
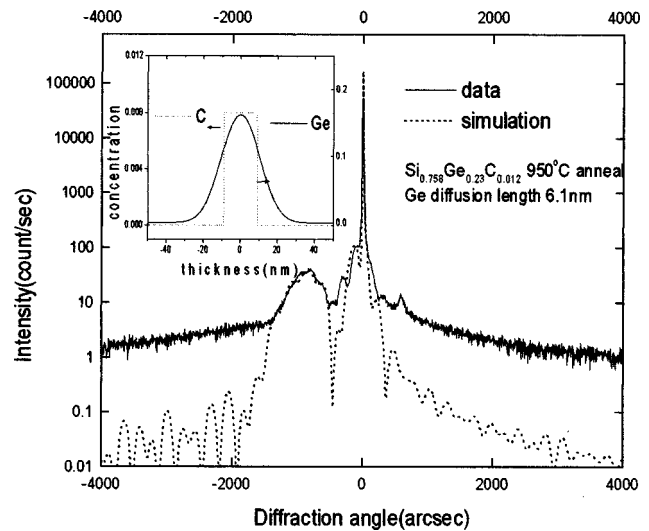
The same pieces of samples were annealed again at 950 °C for 2 h. The (400) peak of the Si$_{0.77}$Ge$_{0.23}$ control sample continued to shift towards the Si (400) peak. The peak of the Si$_{0.762}$Ge$_{0.23}$C$_{0.008}$ sample shifted less than the control samples. The peak of high carbon-content sample (Si$_{0.758}$Ge$_{0.23}$C$_{0.012}$) even had a slight tendency to shift towards the opposite direction, which indicated that the lattice constant of this sample started to *increase*. This is probably due to the formation of SiC precipitates, since only a decrease of carbon content in the Si$_{1-x-y}$Ge$_x$C$_y$ can increase the vertical lattice constant. To confirm this observation, we annealed these samples at 1000 °C for another 2 h. Similar behavior was observed. The vertical lattice constant of the Si$_{0.77}$Ge$_{0.23}$ control sample continued to decrease, and that of the Si$_{0.762}$Ge$_{0.23}$C$_{0.008}$ sample decreased very slightly, but that of the Si$_{0.758}$Ge$_{0.23}$C$_{0.012}$ sample continued to increase (Fig. 6).
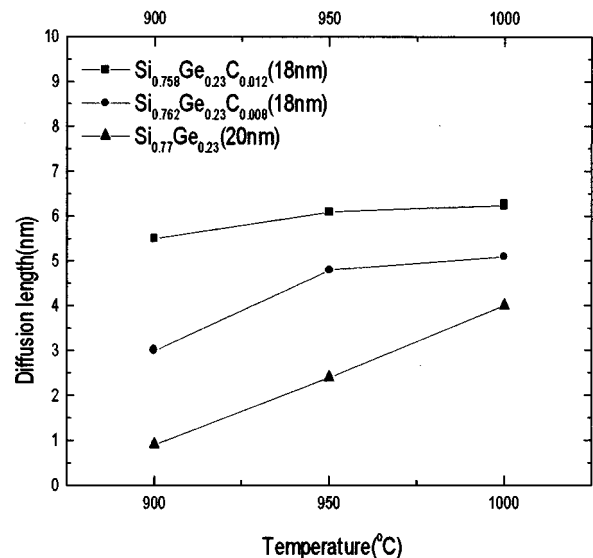

FIG. 5. Extracted diffusion length at different annealing temperatures.

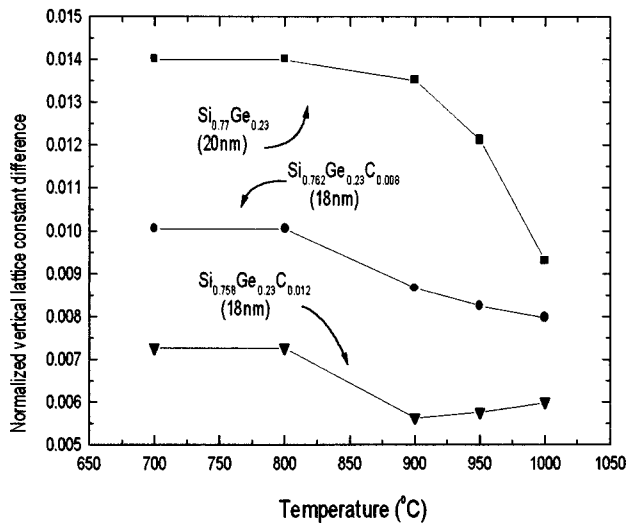FIG. 6. Difference between the vertical lattice constant of $Si_{1-x-y}Ge_xC_y$ and the Si substrate, normalized with respect to the Si lattice constant at different annealing temperatures. The 700 °C data are from the as-grown samples because the Si cap is grown at 700 °C.

FIG. 8. Asymmetrical (422) diffraction spectra of the 1000 °C annealed samples. With the peak positions of (400) and (422) diffraction, the in-plane lattice constants can be obtained.

To study the change of the material structures after 1000 °C annealing, FTIR absorption measurements were performed. The FTIR spectrum (Fig. 7) of an as-grown 40 nm $Si_{0.698}Ge_{0.28}C_{0.022}$ layer shows a sharp absorption peak at 600 cm^{-1}, which is characteristic of the vibration frequency of substitutional carbon in silicon.[2] Note that in the FTIR measurement a thick layer is used to increase the absorption signal. However, in the spectrum of the same sample after annealing at 1000 °C, the 600 cm^{-1} absorption peak vanished within the detection limit, and a broad peak from 670 to 900 cm^{-1} was observed, very similar to the absorption spectrum of amorphous silicon carbide.[2,20] This indicated that some carbon atoms came out of the substitutional lattice and formed silicon carbide precipitates.
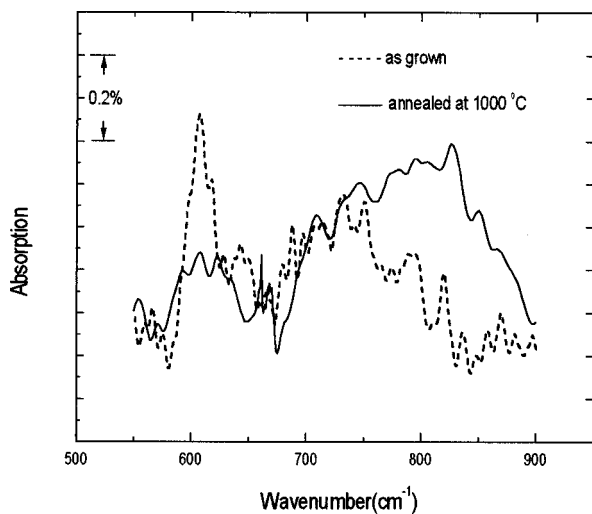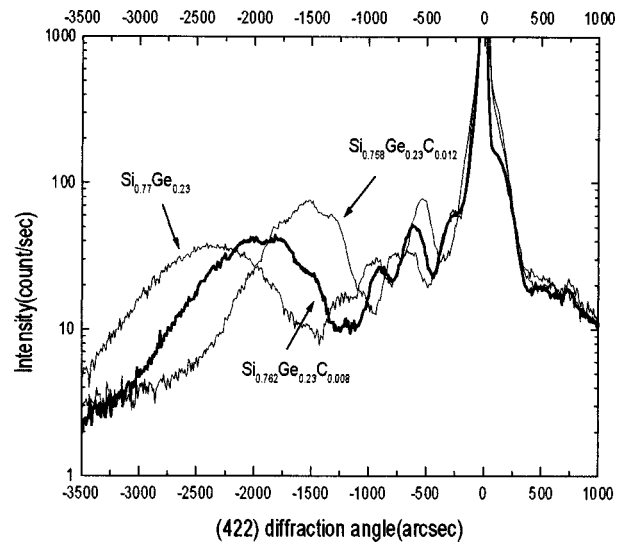
To further resolve the relaxation due to misfit dislocation formation and the residual carbon content in the $Si_{1-x-y}Ge_xC_y$ alloys, we measured the asymmetrical (422) diffraction of all three 1000 °C-annealed samples (Fig. 8). Following the approach in Ref. 21, the in-plane lattice constant can be obtained, which is a function of the relaxation parameter and the residual carbon content [Eq. (1)]. Note that the Ge content at the center of the quantum well is determined by the diffusion length, and is not a free parameter. To fit the relative position of the (400) diffraction of the $Si_{1-x-y}Ge_xC_y$ alloys with respect to the (400) Si substrate, we can have different sets of relaxation parameters and carbon contents. A unique solution to the relaxation parameter and residual carbon content can be determined to satisfy both the in-plane lattice constants and the (400) diffraction spectra of the $Si_{1-x-y}Ge_xC_y$ alloys. The results of the relaxation parameters and the residual carbon contents are given in Table I. The difference between the initial carbon concentration and the residual carbon content is the amount of SiC precipitates. The atomic fractions of SiC precipitates are 0.0072 and 0.0084 for $Si_{0.762}Ge_{0.23}C_{0.008}$ and $Si_{0.758}Ge_{0.23}C_{0.012}$, respectively. The degree of relaxation increased with the amount of SiC precipitates. The SiC precipitates may be responsible for the misfit dislocation formation in the thin layers, because the precipitates reduce the strain compensation and decrease the critical thickness to approximately 15 nm for these two $Si_{1-x-y}Ge_xC_y$ samples. Therefore, after annealing, the thickness of these two $Si_{1-x-y}Ge_xC_y$ samples (18 nm) was beyond the critical thickness and misfit dislocation formation occurred. These

FIG. 7. FTIR spectra of a 40 nm $Si_{0.698}Ge_{0.28}C_{0.022}$ sample before and after annealing at 1000 °C. After annealing, the substitutional carbon absorption peak at 600 cm^{-1} vanished, and a broad peak from 670 to 900 cm^{-1} was observed, very similar to the absorption spectrum of amorphous silicon carbide.

TABLE I. Summary of the rocking curve simulation results after 1000 °C annealing for 2 h.

Sample	Relaxation parameter	Residual carbon content	Atomic fraction of SiC precipitates
$Si_{0.77}Ge_{0.23}$	0.17	0	0
$Si_{0.762}Ge_{0.23}C_{0.008}$	0.21	0.0008	0.0072
$Si_{0.758}Ge_{0.23}C_{0.012}$	0.26	0.0036	0.0084

1000 °C-annealed films also showed a lot of dislocation network after defect etching, while no misfit dislocation was observed in the as-grown films after defect etching. This confirms that misfit dislocation is formed after the annealing.

IV. CONCLUSIONS

We have observed that C enhanced the Ge outdiffusion at 900–1000 °C in the Si/Si$_{1-x-y}$Ge$_x$C$_y$/Si quantum wells. At 800 °C annealing for 2 h, the lattice structure was stable for both the Si$_{1-x}$Ge$_x$ and the Si$_{1-x-y}$Ge$_x$C$_y$ layers. The thermal budget of device processing would not be degraded due to the C incorporation. After annealing at 1000 °C for 2 h, the substitutional carbon absorption in the FTIR spectra vanished, and the amorphous-like absorption peak was observed, indicating the formation of SiC precipitates. The vertical lattice constant of the Si$_{0.758}$Ge$_{0.23}$C$_{0.012}$ layer increased due to the consumption of Si and C atoms after annealing at 1000 °C for 2 h. The strain in the strained Si$_{1-x-y}$Ge$_x$C$_y$ layers can increase after thermal treatment. This may offer an alternative design for strained layer applications. The Si$_{1-x-y}$Ge$_x$C$_y$ layer with an initial thickness below the critical thickness shows misfit dislocation formation after annealing at 1000 °C for 2 h. This is probably due to the decrease in strain compensation by SiC precipitates.

ACKNOWLEDGMENTS

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