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STABILITY AND PRECIPITATION KINETICS IN $\text{Si}_{1-y}\text{C}_y/\text{Si}$ AND
 $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ HETEROSTRUCTURES PREPARED BY
SOLID PHASE EPITAXY

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ABSTRACT

This study investigates the stability of metastable $\text{Si}_{1-y}\text{C}_y/\text{Si}$ heterostructures during rapid thermal annealing (RTA) over a temperature range of 1000 - 1150° C. Heterostructures of $\text{Si}_{1-y}\text{C}_y/\text{Si}$ and $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ ($x=0.077$, $y \leq .0014$) were formed by solid phase epitaxy from C implanted, preamorphized substrates using a 30 minute 700° C anneal in N_2 . The occupancy of C in substitution lattice sites was monitored by Fourier Transform Infrared Absorption spectroscopy. The layer strain was monitored by rocking curve x-ray diffraction and the structural changes in the layers were determined using plan-view and X-sectional transmission electron microscopy (TEM). For anneals of 1150° C or above, all the substitutional C was lost from the Si lattice after 30 seconds. TEM verified that the strain relaxation was the result of C precipitating into highly aligned βSiC particles rather than by the formation of extended defects. No nucleation barrier was observed for the loss of substitutional C. Preliminary results will also be discussed for $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ heterostructures where there is the additional factor of the competition between strain energy and the chemical driving forces.

INTRODUCTION

Tailoring of electronic band structures and strain in Si heteroepitaxial structures can be accomplished by creating IV-IV alloys¹. We have recently shown that C can be alloyed into Si and $\text{Si}_{1-x}\text{Ge}_x$ in concentrations several orders of magnitude above the solid solubility limit using solid phase epitaxy (SPE) of amorphous layers^{2,3}. In these alloys C resides primarily on substitutional lattice sites and strains Si and SiGe as predicted by Vegard's law ($\delta a_0/\delta c \approx 2.0 \times 10^{-3}$ nm/at. % C where $\delta a_0/\delta c$ is the change in lattice parameter per addition of substitutional C). In order to introduce C into device structures a good understanding of the stability limits of C in Si and $\text{Si}_{1-x}\text{Ge}_x$ is needed. Our initial studies on the SPE produced $\text{Si}_{1-y}\text{C}_y/\text{Si}$ heterostructures investigated the stability over the temperature range of 700° C-950° C³. It was found that heat treatment induced the loss of substitutional C by the precipitation of 2-4 nm diameter particles of cubic βSiC . The βSiC precipitates were oriented in the same directions as the Si matrix. It was proposed that these precipitates form through the loss of coherency of Guinier-Preston zones. The loss of substitutional C showed no incubation period which would be indicative of a transformation barrier. As the substitutional C was lost from the alloy, the layer strain correspondingly was reduced. No extended defects were found in the microstructure indicating that the clustering of C and precipitation was responsible for the strain relaxation. It was concluded that chemical rather than mechanical driving forces induced layer relaxation. In

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the present work we extend the study of the thermal stability of $\text{Si}_{1-x}\text{C}_y/\text{Si}$ heterostructures to higher temperature through the use of rapid thermal annealing (RTA). Finally preliminary results on the stability of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ heterostructures are reported. In the ternary system the effects of strain and chemical instability can be separately evaluated.

EXPERIMENTAL PROCEDURE

Metastable $\text{Si}_{1-y}\text{C}_y$ alloy layers were prepared by ion implantation of C into preamorphized layers of $\langle 100 \rangle$ float zone Si ($\rho = 100\text{-}150\ \Omega\text{-cm}$). Carbon was implanted at 25 keV and a dose of $5.25 \times 10^{15}/\text{cm}^2$. This implant procedure was expected to yield a peak C concentration of 1.0 at. %. Surface contamination from the amorphization and implantation processes was removed with a 4 min 1000 watt rf generated O_2 plasma. Regrowth of the implanted layers was obtained using a two anneal sequence in an N_2 ambient. First, a 30 minute 450°C anneal was used to clean-up end of range damage from the implantation and smooth the amorphous/crystalline interface. Next, a 30 minute 700°C anneal was used for SPE regrowth. The regrowth of the layer and C incorporation was confirmed by ion channeling and Fourier Transform Infrared Absorption (FTIR) prior to annealing. To study the high temperature stability, rapid thermal anneals (RTA) were performed over the temperature range 1000°C - 1150°C for times of 30 to 150 seconds.

The $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloy layers were formed by C implantation into 100 nm of $\text{Si}_{0.923}\text{Ge}_{0.077}$ deposited by chemical vapor deposition on $\langle 100 \rangle$ Si. Silicon implantation was used to first amorphize a 150 nm thick layer. The C was implanted with multiple energies to make a flat profile where the C resides primarily in the SiGe epilayer. Layers with C concentrations of 0.46, 0.93 and 1.4 at. % were created. The cleaning and annealing procedures were the same as for the $\text{Si}_{1-y}\text{C}_y$ layers.

The concentration of substitutional C in the heterostructures was measured using a Nicolet 60SX Fourier Transform Infrared Spectrometer. The localized vibrational mode (LVM) for substitutional C lies directly on top of the Si-Si two phonon absorption mode, therefore, in order to characterize the C content subtraction of an identical reference without C implantation was performed. Rocking curve double crystal X-ray diffraction was used to characterize the strain in the heterostructures. The evaluation of the scans was performed using kinematical theory and has been previously reported⁵. The final microstructure was examined using transmission electron microscopy (TEM) on a JEOL 200CX. Both plan view and cross-section specimens were prepared. Final thinning for these specimens was performed using ion milling.

RESULTS

I. RTA of $\text{Si}_{1-y}\text{C}_y/\text{Si}$ Heterostructures

For the 1000°C RTA, the reduction of the LVM absorbance signal for C substitutional in Si was measured by taking the full width half maximum multiplied by the height. Triangles (Δ) in Figure 1 mark the evolution of this signal with increasing anneal time. This signal has been shown to be directly related to the substitutional C content in the epitaxial layer.⁵ The loss of substitutional C initiates immediately after annealing begins with the most rapid loss of substitutional C occurring in the first stages of annealing. After 150 seconds of annealing the substitutional C signal has been reduced by over 50%. The reduction of the LVM absorbance peak is accompanied by the appearance of a broad

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Figure 1 Thermal stability of $\text{Si}_{0.99}\text{C}_{0.01}/\text{Si}$; the (Δ) corresponds to the remaining substitutional fraction of C; the (+) corresponds to the amount of strain relaxation.

Figure 2 The relative absorbance corresponding to the substitutional C LVM plotted versus the residual layer strain in the $\text{Si}_{0.99}\text{C}_{0.01}/\text{Si}$ layer.

absorbance band located at $12.2 \mu\text{m}$. During furnace anneals of supersaturated C in Si, this band has been previously correlated with the βSiC phonon absorption mode⁶.

X-ray rocking curve scan for $\{004\}$ and $\{224\}$ reflections were used to show that the layer remained commensurate with the substrate and did not develop lattice tilt during the anneals. The relaxation of the layer strain in the (004) planes is shown in Figure 1 with the crosses(+). After 150 seconds, approximately 40% of the layer strain was relaxed. The relaxation of the strain did not exhibit the rapid reduction in the initial stages that was observed for the loss of substitutional C. Plan-view and cross-section TEM of the annealed layers indicated that extended defects such as misfit dislocations were not formed and therefore could not account for the strain relaxation. This relaxation occurs exclusively via the loss of substitutional C and eventual clustering and precipitation of βSiC .

Figure 2 plots the loss in absorbance signal versus the residual strain for the annealed layers. After the initial rapid loss in absorbance signal, the strain and absorbance signal tail off in an almost linear fashion. The large loss in absorbance signal relative to the strain relaxation during short anneals, indicates that initial C lost from the lattice does not relax the layer. Formation of coherent precipitates (i.e. Guinier-Preston zones) would explain this behavior.

The 1000°C RTA results from the absorbance measurements are compared to those for a similar layer annealed in a conventional furnace in Figure 3. The plot shows the time for 50% reduction

Figure 3 Arrhenius plot of the time to 50% loss in substitutional C versus reciprocal Temperature.

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of the substitutional C versus reciprocal temperature in Arrhenius fashion. The furnace results extrapolate well to the RTA result, indicating an activation energy of 3.3 ± 0.5 eV. The activation energy of C diffusion in C is 3.1 eV⁴. The similarities in activation suggest that the loss of substitutional C from Si is diffusion limited.

The absorbance spectra for alloys annealed above 1000°C (i.e. 1075 and 1150°C) showed a complete loss of the LVM absorbance peak for substitutional C. The complete loss of this signal took place in less than 30 seconds. The loss in the peak is accompanied by high absorbance changes over the full infrared range, indicating that the heat treatments are altering the absorbance in the substrate. These changes in the absorbance spectra were accompanied by the loss of a side peak due to the epilayer in the X-ray rocking curve spectra. This verifies that the higher temperatures anneals relax the film and substitutional C is completely lost for RTA anneals as short as 30 seconds.

II. $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ Heterostructures

The LVM for substitutional C in Si can also be used in Si-Ge-C ternary systems to quantify C content. Significant broadening of the absorption peak relative to $\text{Si}_{1-y}\text{C}_y$ was observed, therefore, quantification requires calibration to the implant doses. It was found that the full width half maximum multiplied by the peak height yields a signal which is linear with C content up to nearly 1.5 at. % C. This absorbance signal was used to monitor the substitutional C content in SPE formed $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ heterostructures. Figure 4 shows the loss of the substitutional C during a 925°C anneal for $\text{Si}_{0.986}\text{C}_{0.014}/\text{Si}$ and $\text{Si}_{0.91}\text{Ge}_{0.076}\text{C}_{0.014}/\text{Si}$ heterostructures. The shape of the depletion curves are similar for both the ternary and binary structures, both having sharp losses in C content during the initial anneal times. After 150 minutes both the heterostructures have lost all substitutional C from the Si lattice. During the annealing, a broad absorption band forms at $12.2 \mu\text{m}$. This band is identical to the one which formed in the $\text{Si}_{1-y}\text{C}_y/\text{Si}$ heterostructures and is due to the formation of small βSiC precipitates⁵. There is no shift in shape or position in the SiC phonon band for the Ge containing alloys, suggesting the precipitates are similar. Note that despite the reduction of lattice strain in the heterostructure, the ternary alloy loses substitutional C at least as fast as the binary. This indicates that the strain energy plays a very small role in the transformation process.

TEM was used to investigate the microstructure after annealing under the conditions of Figure 4 to the point where absorption measurements indicated all substitutional C is lost. Figure 5a shows the cross-section of a $\text{Si}_{0.915}\text{Ge}_{0.076}\text{C}_{0.009}$ layer

Figure 4 Comparison of the depletion of the absorbance signal for $\text{Si}_{0.91}\text{Ge}_{0.076}\text{C}_{0.014}$ and $\text{Si}_{0.986}\text{C}_{0.014}$ versus annealing time at 925°C.

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Figure 5 a) TEM X-section of $\text{Si}_{0.913}\text{Ge}_{0.076}\text{C}_{0.009}/\text{Si}$ heterostructure annealed at 925°C for 130 min. b) Diffraction pattern from plan-view of same layer. The small satellite spots around the Si spots are from βSiC .

after annealing 925°C for 130 minutes. In the micrograph the implant region is speckled with small 2-4 nm particles. The diffraction pattern from the plan-view of the same specimen (Figure 5b) show that these particles are cubic βSiC . βSiC has the diamond structure and the precipitates are observed to be aligned with the Si matrix lattice. There is no evidence of strain around the precipitates indicating the interface between the Si lattice and the precipitates must be incoherent. The precipitates reside primarily in the top 100 nm thus there is no significant diffusion of C into the bulk. There is a thin line of precipitates along the initial amorphous/crystalline interface. This layer of precipitates results from the gettering of C by the Si interstitials in the end of range region of the implant. This C gettering at the end of range region has been also observed in the $\text{Si}_{1-x}\text{C}_x/\text{Si}$ heterostructures grown by SPE³. In short, the TEM micrographs show that the loss in substitutional C follows the same

Figure 6 (004) Rocking curve X-ray diffraction scans for $\text{Si}_{0.913}\text{Ge}_{0.076}\text{C}_{0.009}/\text{Si}$ before and after 925°C for 130 min. The as grown $\text{Si}_{0.913}\text{Ge}_{0.076}$ is also shown

path in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ as previously observed in $\text{Si}_{1-y}\text{C}_y$.

Figure 6 shows the changes in the rocking curve diffraction scan along the (004) reflection with the depletion of substitutional C by annealing. The uppermost scan is from the as deposited $\text{Si}_{0.923}\text{Ge}_{0.077}$ layer and is included as a reference. The middle and bottom scans are from $\text{Si}_{0.91}\text{Ge}_{0.076}\text{C}_{0.014}/\text{Si}$ heterostructures just after SPE growth and after 925°C for 130 min respectively. Evaluations of all three of these heterostructures using rotated (004) and (224) reflections revealed that all the layers are nearly commensurate and have no lattice tilt. The as deposited $\text{Si}_{0.923}\text{Ge}_{0.077}$ layer has compressive strain due to the incorporation of Ge. The SPE ternary heterostructure has an average X-ray strain of (0.28 % tensile) due to the overcompensation of the Ge with the smaller C atom. After annealing at 925°C for 130 min., the strain has become compressive (0.4 %). Thus, the layer strain nearly returns to the strain expected by the $\text{Si}_{0.923}\text{Ge}_{0.077}$ binary heterostructure on Si. Thus, Ge appears to act essentially as a spectator to the precipitation and strain evolution in the layers heavily supersaturated with C.

CONCLUSIONS

We have extended the study of $\text{Si}_{1-y}\text{C}_y/\text{Si}$ heterostructure stability to rapid thermal processing temperature regime. These results show that extrapolation of the lower temperature furnace results adequately describes the stability up to 1000°C . At temperatures above 1000°C , the heterostructures lose substitutional C by C clustering into G. P. zones and precipitation of βSiC . The $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ heterostructures were found to lose substitutional C identically to $\text{Si}_{1-y}\text{C}_y/\text{Si}$. The strain compensation of Ge has little effect on the kinetics involved in the loss of substitutional C.

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