APPLIED PHYSICS LETTERS VOLUME 72, NUMBER 7 16 FEBRUARY 1998

Carbon incorporation in $Si_{1-y}C_y$ alloys grown by molecular beam epitaxy using a single silicon–graphite source

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(Received 2 October 1997; accepted for publication 16 December 1997)

Pseudomorphic $Si_{1-y}C_y$ alloys on silicon (100) were grown by molecular beam epitaxy using a single effusion source of silicon contained in a graphite crucible, producing carbon concentrations of $y=0.008$. The behavior of carbon incorporation using this source was studied as a function of growth temperature using x-ray diffraction and infrared spectroscopy, and was compared to previous studies, where $Si_{1-y}C_y$ was grown from separate silicon and graphite sources. An increased energy barrier for the surface diffusion of carbon was observed using the single silicon–graphite source. An infrared absorption mode near 725 cm^{-1}, observed for growth temperatures up to 700 °C, was attributed to a transitional phase between the loss of substitutional carbon and the formation of silicon carbide precipitates. © *1998 American Institute of Physics.*
[S0003-6951(98)03707-3]

Recently, the alloying of C with Si and $Si_{1-x}Ge_x$ has attracted attention because of its ability to control the strain associated with the lattice mismatch to Si.[1,2] Carbon in the $Si_{1-y}C_y$ and the $Si_{1-x-y}Ge_xC_y$ systems modifies the alloy band structure and the band offsets for Si based heterostructures.[3] An increase of the substitutional C concentration in Si, by nearly four orders of magnitude more than the equilibrium solubility, has been predicted to arise from an enhanced surface solubility during epitaxial growth.[4] This result has been demonstrated by molecular beam epitaxy (MBE), but only for a small ‘‘growth window’’ where conditions such as the substrate temperature and growth rate are optimal for substitutional C incorporation.[5] The most common method of producing a C flux during MBE growth of $Si_{1-y}C_y$ is by sublimating high purity graphite in the presence of a Si flux.[1,5] However, previous studies have shown that the evaporation of Si in a graphite container will yield a molecular beam predominantly of Si, Si_2C, and SiC_2 species due to the reaction between Si and graphite.[6] Equivalent species were also obtained by the evaporation of SiC.[6,7]

In this letter, we report the structural properties of MBE grown $Si_{1-y}C_y$ on (100) Si using a single effusion cell of silicon contained in a graphite crucible. The behavior of C incorporation in the lattice for different substrate growth temperatures was studied using infrared absorption spectroscopy and x-ray diffraction. The amount of substitutional C was observed to decrease with increasing substrate temperature. Infrared absorption showed that the loss of substitutional C is due to the formation of an intermediate Si–C phase and SiC precipitates. Compared to previous studies using separate Si and graphite sources,[5] alloys grown with a single silicon–graphite source had an increased barrier to diffusion of C at the surface. We attributed this change to the difference in the C containing species of the molecular beam.

We grew 150 nm thick $Si_{1-y}C_y$ layers by MBE on the 2×1 reconstructed surface of Si (100) at substrate temperatures ranging from 400 to 750 °C, holding all other growth parameters constant. The MBE system was a model 620 manufactured by EPI Corporation, with a base pressure of less than 10^{-11} Torr.[8] Three in. diam float zone Si substrates were prepared by chemical degreasing and oxidation of the surface, followed by removal of the oxide in dilute hydrofluoric acid. Prior to growth, samples were heated to 200 °C for 45 min, then to 250 °C for 15 min, and finally the substrate was ramped to the growth temperature. Reflection high energy electron diffraction (RHEED) confirmed the 2×1 reconstruction of the Si surface prior to growth. X-ray diffraction was measured using a Philips Xpert-x-ray diffraction (XRD) diffractometer, using Cu $k\alpha_1$and $k\alpha_2$ radiation. Infrared absorption was measured with a Nicolet-740 Fourier transform infrared spectrometer.

The silicon–graphite effusion source was constructed from a high-temperature effusion cell manufactured by EPI. High purity Si pieces were heated inside a pyrolytic graphite crucible to produce the reaction forming the molecular beam. This resulted in a growth rate of approximately 0.33 A°/min at an effusion cell temperature of 1400 °C. At this temperature, the graphite crucible itself will have negligible vapor pressure for any C containing species.[9] Only the Si which reacted with the graphite crucible will have a significant vapor pressure, resulting in a molecular beam consisting of Si and C bonded with Si.

Figure 1 shows the x-ray diffraction and the infrared absorption spectra of $Si_{1-y}C_y$ layers grown by evaporation from the single silicon–graphite source. The $Si_{1-y}C_y$ alloy grown at 400 °C was amorphous, but was re-crystallized prior to both measurements by annealing at 750 °C for 20 min in N_2 gas, resulting in practically all C atoms occupying substitutional sites.[10] For samples grown at higher tempera-

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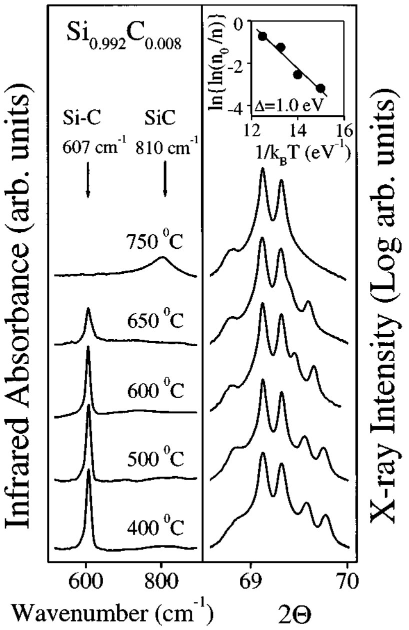

FIG. 1. Infrared absorption spectra and (004) x-ray reflections for pseudomorphic $Si_{1-y}C_y$ alloys grown on (100) silicon for substrate temperatures of 400–750 °C. The inset plots the substitutional carbon concentration normalized to the total carbon concentration vs the reciprocal growth temperature.

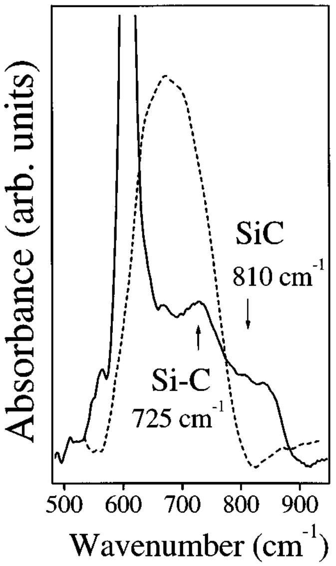

FIG. 2. The infrared absorption spectra of the as-grown amorphous $Si_{1-y}C_y$ alloy grown at 400 °C (dashed line) and crystalline $Si_{1-y}C_y$ grown at 650 °C (solid line). The alloy grown at 650 °C exhibits infrared peaks characteristic of the LVM of carbon in silicon, SiC precipitation, and an intermediate Si–C phase with an absorption peak centered at 725 cm^{-1}.

tures, annealing produced no significant change in infrared absorption or x-ray diffraction. The percentage of substitutional carbon in the layers was co-determined by the angular shift between the $k\alpha_2$ (004) reflections of silicon and $Si_{1-y}C_y$, and by the absorbance of the 607 cm^{-1} local vibrational mode (LVM) of C in Si. The C content of $y = 0.008$ for the layer grown at 400 °C was measured after re-crystallization. X-ray rocking curve analysis of the symmetric (004) and asymmetric (224) reflections revealed that the layers were fully strained. X-ray diffraction and Raman measurements indicated that the C concentration was uniform across the wafer.

Infrared absorption measurements indicated that substitutional C exists in the layers for growth temperatures up to 700 °C. At a growth temperature of 750 °C, the LVM of C disappeared and the absorption peak at 810 cm^{-1} indicated that C had transformed to a SiC precipitate phase.[11] For intermediate growth temperatures (400–700 °C) the (004) x-ray diffraction peak of the $Si_{1-y}C_y$ layer shifted to smaller angles relative to the substrate peak with increased growth temperature (Fig. 1). The LVM of C in Si at 607 cm^{-1} experienced a decrease in intensity as the growth temperature was increased. These two measurements indicate a decrease in substitutional C versus increasing substrate temperature. An absorption peak near 725 cm^{-1} appeared for the intermediate temperatures along with a small SiC characteristic peak at 810 cm^{-1}. Figure 2 shows the infrared absorption spectra of $Si_{1-y}C_y$ alloys grown at 650 and 400 °C, where the infrared spectra of the layer grown at 400 °C was measured prior to recrystallization. Three distinct absorption features for the $Si_{1-y}C_y$ layer grown at 650 °C are the 607 cm^{-1} LVM of C, a small 810 cm^{-1} SiC precipitate peak, and the broad peak near 725 cm^{-1} resembling that of the as-grown amorphous $Si_{1-y}C_y$. The 725 cm^{-1} peak increased in intensity with growth temperature up to 700 °C, but disappeared for a growth temperature of 750 °C. At 750 °C, only the 810 cm^{-1} SiC peak remained. Our observation of the 725 cm^{-1} peak is consistent with a Si–C transitional phase, intermediate between the loss of substitutional C sites on the silicon lattice and the formation of SiC precipitates. The disordered nature of this transitional phase is supported by the results of Kimura *et al.*[12] who observed an absorption peak near 725 cm^{-1} for Si implanted with C ions which existed for annealing temperatures up to 900 °C.

The behavior of C incorporation during MBE growth of $Si_{1-y}C_y$ can be explained by the diffusion and formation of Si–C interstitial defects near the surface.[5] The number of C atoms, n, on substitutional lattice sites can be modeled by:

$$n(T,r) = n_o(r,f)\exp\left(\frac{-ak}{4r}\right), \tag{1}$$

where n_o is the total C concentration, r is the silicon growth rate, f is the carbon flux, a is the Si lattice constant, T is the growth temperature, and the exponential rate term

$$k = k_o \exp(-\Delta/k_B T) \tag{2}$$

describes the transfer of C from substitutional sites to interstitial Si–C defects at the surface. The activation energy is designated by Δ and k_B is the Boltzmann constant. The term $a/4r$ in Eq. (1) is the time for 1 monolayer of material to be grown, after which C will be effectively ''frozen in'' the lattice and thus subject only to bulk diffusion.

The top right inset of Fig. 1 displays the behavior of $\ln[\ln(n_o/n)]$ vs $1/k_B T$ for $Si_{1-y}C_y$ layers grown by the evaporation of Si in a graphite crucible, where the reference n_o was taken to be the substitutional C concentration of the layer grown at 400 °C after re-crystallization. The best fit to this data gives the energy of formation of interstitials Si–C defects of $\Delta = 1.0 \pm 0.2$ eV in the temperature range up to the threshold for SiC precipitation. The growth of $Si_{1-y}C_y$ layers on (100) Si by the sublimation of graphite from a heated filament separate from the pure silicon beam yields a smaller activation energy of $\Delta = 0.5$ eV.[5] The reason for the increased activation energy observed for $\mathrm{Si}_{1-y}\mathrm{C}_y$ grown from the single silicon–graphite source may be attributed to the chemical composition of the C containing species in the molecular beam. Evaporation from the single silicon–graphite source produces a molecular beam where the C containing molecular species is bonded to Si.[6] In contrast, evaporation from pure graphite does not.[9] We infer that the bonding of C to Si in the molecular beam tends to decrease surface diffusion of C, possibly by increasing the probability that the small C atom will be immediately buried under a Si atom. Once the C atom has been buried under 1 or more monolayers of Si, its position will be effectively ''frozen in'' and will be subject only to bulk diffusion.[4,5] Substitutional C incorporation has been shown to depend on the gas source used during rapid thermal chemical vapor deposition (RTCVD) of $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$.[13] Mi *et al.* reported high substitutional carbon incorporation efficiencies at growth temperatures up to 600 °C using methylsilane (SiCH_6), where it was speculated that C may be incorporated into the lattice without breaking the preformed Si–C bond.

In summary, we have grown pseudomorphic $\mathrm{Si}_{1-y}\mathrm{C}_y$ layers with $y = 0.008$ by evaporation of Si in a graphite crucible at an effusion cell temperature of 1400 °C. Evaporation from the single silicon–graphite source results in an energy barrier to the formation of interstitial Si–C defects of $\Delta = 1.0 \pm 0.2$ eV compared to the separate evaporation of graphite and silicon with $\Delta = 0.50$ eV.[5] An infrared absorption mode observed near 725 cm^{-1} was attributed to a transitional Si–C phase intermediate between that of C diffusing from substitutional lattice sites to the formation of SiC precipitates.

The authors gratefully acknowledge support from ONR Grant No. N00014-93-1-0393 and DARPA Contract No. F49620-96-C-0006. They thank P. Thompson and M. Fatemi of the Naval Research Laboratory for the x-ray rocking curve measurements.

[1] K. Eberl, S. S. Iyer, S. Zollner, J. C. Tsang, and F. K. LeGoues, Appl. Phys. Lett. **60**, 3035 (1992).

[2] H. J. Osten, E. Bugiel, and P. Zaumseil, Appl. Phys. Lett. **64**, 3440 (1994).

[3] K. Eberl, K. Brunner, and W. Winter, Thin Solid Films **294**, 98 (1997).

[4] J. Tersoff, Phys. Rev. Lett. **74**, 5080 (1995).

[5] H. J. Osten, M. Kim, K. Pressel, and P. Zaumseil, J. Appl. Phys. **80**, 6711 (1996).

[6] J. Drowart and G. De Maria, in *Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon, London, 1960), p. 16.

[7] J. Drowart, G. De Maria, and M. Inghram, J. Chem. Phys. **29**, 1015 (1958).

[8] B. A. Orner, A. Khan, D. Hits, F. Chen, K. Roe, J. Pickett, X. Shao, R. G. Wilson, P. R. Berger, and J. Kolodzey, J. Electron. Mater. **25**, 297 (1996).

[9] P. D. Zavitsanos and G. A. Carlson, J. Chem. Phys. **59**, 2966 (1972).

[10] J. W. Strane, H. J. Stein, S. R. Lee, B. L. Doyle, S. T. Picraux, and J. W. Mayer, Appl. Phys. Lett. **63**, 2786 (1993).

[11] J. W. Strane, H. J. Stein, S. R. Lee, S. T. Picraux, J. K. Watanabe, and J. W. Mayer, J. Appl. Phys. **76**, 3656 (1994).

[12] T. Kimura, S. Shigeru, and S. Yugo, Thin Solid Films **81**, 319 (1981).

[13] J. Mi, P. Warren, P. Letourneau, M. Judelewicz, M. Gailhanou, M. Dutoit, C. Dubois, and J. C. Dupuy, Appl. Phys. Lett. **67**, 259 (1995).