Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 532–535 (2003) 905–910
SURFACE SCIENCE
www.elsevier.com/locate/susc

The effects of carbon incorporation during GSMBE of $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$: growth dynamics and segregation

R.W. Price [a], E.S. Tok [a,b], N.J. Woods [a], J. Zhang [a,*]

[a] *Department of Physics, Centre for Electronic Materials and Devices, Blackett Laboratory, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BW, UK*

[b] *Department of Material Science, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Singapore*

Abstract

$Si_{1-y}C_y(0\,0\,1)$ and $Si_{1-x-y}Ge_xC_y(0\,0\,1)$ layers were grown using gas source molecular beam epitaxy (GSMBE) with three precursors; methylsilane (CH_3SiH_3), disilane (Si_2H_6) and germane (GeH_4). The effect of carbon on growth was studied by observing the change in period of the intensity oscillations of reflection high energy electron diffraction (RHEED) during the formation of $Si/Si_{1-y}C_y$ heterojunctions. $Si_{1-x-y}Ge_xC_y$ layer thickness (growth rate) changes were measured ex situ using X-ray diffraction (XRD). A decrease in growth rate was measured in the presence of carbon and evidence for carbon segregation was collected. Temperature programmed desorption (TPD) was used to study the limiting effect carbon has on H_2 desorption and disilane adsorption. The flux dependence of the growth rate was modelled and compared to experiment to highlight the relative importance of the sticking probability of disilane to the hydrogen desorption rate constant. The growth rate decrease during $Si_{1-y}C_y(0\,0\,1)$ growth compared to that of $Si(0\,0\,1)$ was shown to be dominated by a decrease in the sticking probability of disilane.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Reflection high-energy electron diffraction (RHEED); Molecular beam epitaxy; Thermal desorption spectroscopy; Adsorption kinetics; Carbon; Germanium; Silicon

1. Introduction

During semiconductor device processing heat treatments such as rapid thermal anneals may be used to activate implanted dopants, reduce implantation damage or to grow oxides. However, these anneals can have a detrimental side effect on device performance since the dopants can diffuse into regions where they can cause parasitic barriers in the conduction band which drastically reduce the collector current enhancement in heterojunction bipolar transistors [1]. Boron is found to diffuse by an interstitial mechanism and any species which can remove Si self-interstitials will limit this out diffusion of boron. Substitutional carbon is found to have this effect [2] but any epitaxial film with a substitutional C concentration above the bulk solubility limit is thermodynamically metastable and can only be produced by growth techniques such as molecular beam epitaxy (MBE), gas source MBE (GSMBE) or chemical vapour deposition.

Previous studies have reported $Si_{1-y}C_y(0\,0\,1)$ film growth exceeding the equilibrium soluble limit

* Corresponding author. Tel.: +44-20-7594-7594; fax: +44-20-7581-3817.
E-mail address: jing.zhang@ic.ac.uk (J. Zhang).

0039-6028/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0039-6028(03)00466-7

[3] with y ranging from 0.5% to 1.16% depending on the substrate temperature during growth. The growth rate was found to decrease with increasing y over the temperature range 550–650 °C and speculated that this was due to both a reduction in the sticking probability of silane and a decrease in the rate of hydrogen desorption due to the higher energy C–H bond.

In the work reported here we demonstrate the effect of carbon on the Si(0 0 1) surface on both the adsorption of disilane and the desorption of hydrogen using temperature programmed desorption (TPD). The consequential effects on the steady state growth of $Si_{1-y}C_y$ are probed by measuring the period of reflection high energy electron diffraction (RHEED) intensity oscillations and X-ray diffraction (XRD) measurements are performed ex situ to measure the thickness of grown layers.

TPD measures the rate of desorption of adsorbed surface species as a function of substrate temperature. The temperature at which the maximum rate of desorption occurs is dependent on the kinetics governing the desorption process and also on the temperature ramp rate. By keeping the ramp rate constant the effect of different surface species can be directly measured by observing any change in the position of the maximum rate of desorption. For less facile desorption the peak in the desorption rate should move to a higher temperature and this is indeed found to be the case for hydrogen on a carbon contaminated surface. TPD can also be used to probe the effect of carbon on the adsorption of disilane by providing a measure of the amount of hydrogen that adsorbed on the surface during the adsorption of the associated silicon. It is found that on a hydrogen free surface previously exposed to methylsilane (MS), the subsequent rate of disilane adsorption is significantly reduced.

RHEED intensity oscillations are additionally recorded during growth from MS and disilane on clean Si(0 0 1) and also during the adsorption of disilane on a carbon contaminated surface. In both cases the growth rate is seen to vary gradually during deposition. This suggests the carbon surface population builds up or is depleted over the growth of many monolayers and is direct evidence for the segregation of carbon during growth.

2. Experimental procedure

In this work Si and $Si_{1-x}Ge_x$ films containing small amounts of substitutional carbon (less than 2%) were grown using GSMBE with disilane, germane and methylsilane precursors. The growth apparatus is a purpose built double ended system based on the VG Semicon V80M and its basic configuration has been described previously [4]. Structural parameters such as layer thicknesses and substitutional germanium/carbon concentrations were obtained from rocking curve measurements and simulations using a Philips high resolution X-ray material research diffractometer and X'pert X-ray simulation software.

The growth chamber employed is also equipped with a line of sight mass spectrometer (VG Quadruple SXP300), associated counting electronics and a multi-channel scaler which enables the collection of TPD data using ion counting techniques [5]. The RHEED measurements were obtained using a VG LEG110 electron gun operating at 15 keV and a k-space data collection system.

The beam equivalent pressure (BEP) of MS used during the growth ranged from 5.0×10^{-7} to 5.0×10^{-5} mbar and that for disilane ranged from 5.0×10^{-5} to 2.0×10^{-4} mbar with the total system pressure remaining below 5.0×10^{-4} mbar.

3. Results and discussion

RHEED patterns were recorded from $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ surfaces during growth under normal GSMBE conditions in the temperature range 500–550 °C. The RHEED patterns displayed features indicative of good long range order with half order features seen in the $\langle 1\,1\,0 \rangle$ directions indicating a $(2 \times 1) + (1 \times 2)$ reconstruction. RHEED intensity oscillations could be easily recorded implying that growth proceeds in the two-dimensional layer by layer mode [6]. Three-dimensional growth, as indicated by the presence of transmission features in RHEED patterns, was observed at higher substrate temperatures or higher MS fluxes. Therefore, annealing a MS exposed surface to high temperatures was avoided and TPD measurements involving surfaces ex-

posed to MS were limited to a maximum temperature of 650 °C.

Dynamic changes in growth rate were recorded during the growth of Si from disilane on various starting surfaces and are shown in Fig. 1. In the first case (a) the growth was from disilane with a BEP of 1.0×10^{-4} mbar and a substrate temperature of 550 °C on a surface previously dosed with 1500 Langmuirs (L) of MS at 400 °C. In the second case (b) oscillations were recorded during the growth of $Si_{1-y}C_y$ from disilane (BEP $= 1.0 \times 10^{-4}$ mbar) combined with MS (BEP $= 1.0 \times 10^{5}$ mbar) at 550 °C on a clean Si(0 0 1) starting surface. The methylsilane flux was removed after approximately 7 monolayers (ML) where growth continued purely from disilane. The insert shows typical RHEED intensity oscillations recorded in the latter case (b). The flux dependence of the period of RHEED oscillations was also studied from growth

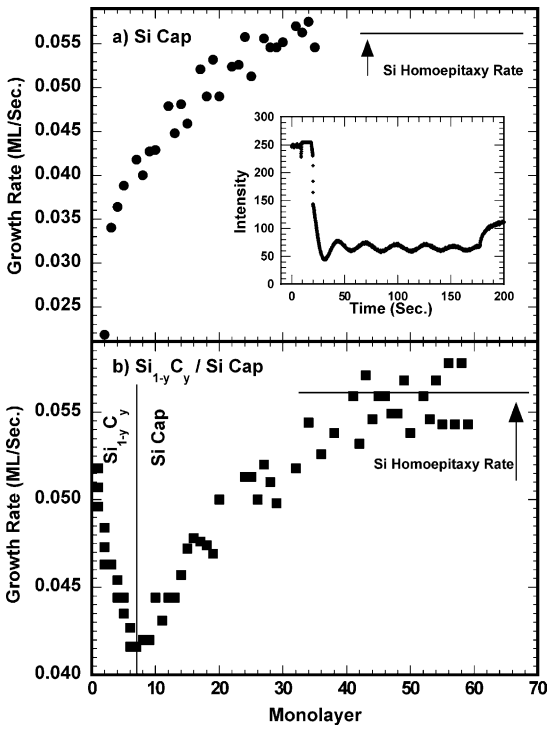


Fig. 1. (a) Si growth rate variation on a MS adsorbed Si(0 0 1) surface and (b) growth rate variation during growth of $Si_{1-y}C_y$ on a clean Si(0 0 1) surface followed by a Si capping layer. The insert shows typical RHEED intensity oscillations from which the results were obtained.

from disilane (BEP $= 2.0 \times 10^{-4}$ and 5.0×10^{-5} mbar) at 550 °C on clean Si(0 0 1) and on a Si(0 0 1) surface previously dosed with 1500 L of MS at 400 °C, this will be discussed later.

The initial growth rate of Si on a MS adsorbed surface was found to be at a significantly lower value (0.020 ML/s) compared to that of the homoepitaxial growth of Si (0.056 ML/s) from the same disilane flux. As growth continued, the growth rate gradually increased back to the homoepitaxial growth rate over approximately 40 ML. In contrast to this, the initial growth rate during the growth of $Si_{1-y}C_y$ on a clean Si(0 0 1) surface is that of homoepitaxial growth but this is seen to gradually decrease and saturate at a lower value. It is clear the presence of MS or its pyrolysis reaction products can have a strong influence on the growth rate of Si. The gradual changes in growth rate during deposition in the presence of surface carbon confirm that the surface carbon concentration cannot be changed instantaneously and this is direct evidence of carbon surface segregation. In the growth of $Si_{1-x}Ge_x$ the segregation of Ge has been widely reported [7] and competition in this segregation process with surfactants has also been demonstrated. It is thus reasonable to postulate that during the growth of $Si_{1-x-y}Ge_xC_y$ carbon surface segregation will occur in competition with that of germanium. The effect of carbon on $Si_{0.8915-y}Ge_{0.1085}C_y$ growth was measured and a reduction in the growth rate was observed. This was measured from XRD on quantum well structures grown at 520 °C since RHEED oscillations are problematic even on $Si_{1-x}Ge_x$ surfaces. As the carbon concentration in the film increases the reduction in growth rate ranges from 12% for a bulk C concentration of 0.44% upto a change of 36% for a C concentration of 1.45%.

Under GSMBE conditions it is well known that the growth of Si from disilane is controlled by surface hydrogen which has a passivating effect against the adsorption of hydrides [8,9]. To investigate the effect of MS on Si or $Si_{1-x}Ge_x$ growth, it is essential to study the adsorption of MS and its effect on hydrogen desorption and disilane adsorption. A clean Si surface is first passivated by a full monohydride coverage produced by

the adsorption of disilane at 400 °C. The surface is further dosed with 1500 L of MS at the same temperature and then raised to 550 °C. The RHEED oscillations recorded during subsequent Si growth exhibit the same growth rate as Si homoepitaxy. TPD measurement of hydrogen desorption from a surface prepared in an identical way also shows exactly the same spectra as those of a monohydride covered Si surface. In comparison with the RHEED results it can be concluded that the hydrogen passivation of Si surfaces is also effective against MS adsorption as expected.

TPD spectra of molecular hydrogen desorption from various surfaces at a ramp rate of 0.5 °C/s are shown in Fig. 2. The effect of carbon on hydrogen desorption is clear by observing changes in peak position. The surface used for spectra (a) is a Si surface with a full monohydride coverage [9] produced by 3000 L disilane adsorption at 400 °C. For spectra (b) a Si surface with 15,000 L MS adsorption at 400 °C was used. A comparison between spectra (a) and (b) shows that the peak of hydrogen desorption flux shifts to a slightly higher temperature under the influence of carbon produced by the pyrolysis of MS. There is also a small increase in the hydrogen coverage associated with the shift and can be explained by the stronger C–H bond and the presence of CH_x species where $x > 2$.

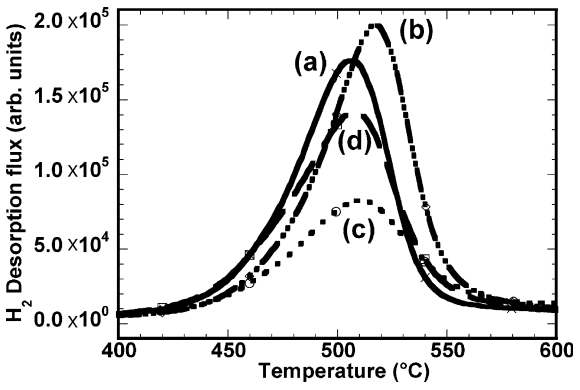


Fig. 2. Molecular hydrogen TPD spectra obtained from (a) a fully saturated monohydride surface (b) after 15,000 L of MS adsorption at 400 °C (c) after 1000 L adsorption of disilane on the surface produced after TPD for (b) and (d) after 100,000 L adsorption of disilane also on the surface produced after TPD for (b).

The effect of carbon on the disilane sticking probability can be observed by observing changes in the total hydrogen coverage which is proportional to the area of the TPD peak. Since at low substrate temperatures disilane is found to decay sequentially with all the associated hydrogen remaining on the surface [9] the TPD peak area is directly proportional to the amount of silicon or carbon deposited. Spectra (c) is from a surface produced after the TPD for spectra (b) followed by 1000 L of disilane adsorption at 400 °C. Spectra (d) is also from the surface produced after the TPD for spectra (b) but followed by a much larger dose of disilane adsorption (100,000 L) at 400 °C. Spectra (a), (c) and (d) indicate significant differences in the total hydrogen coverage due to the presence of carbon from a previous MS adsorption/TPD cycle. The disilane dose used is sufficient to produce a saturated monohydride coverage on a clean Si(0 0 1) surface, however, the hydrogen coverage derived from spectra (c) and (d) obtained from disilane adsorption on a surface with carbon, is clearly far from saturation and is strongly dependent on the disilane dosage. The sticking probability is obviously dramatically reduced in the presence of carbon.

The mechanism of the reduction in growth rate of $Si_{1-y}C_y$ or $Si_{1-x-y}Ge_xC_y$ compared to that of Si and $Si_{1-x}Ge_x$ can now be considered in terms of these experimental findings. A reduction or enhancement of the GSMBE Si growth rate due to the incorporation of Ge [10] or As [11] are well known. The former is attributed to the modification of hydrogen desorption kinetics whereas the latter occurs through adsorption site passivation by As [11]. The TPD results in Fig. 2 show that the hydrogen desorption kinetics are modified by the presence of carbon. This is unlikely to be the main mechanism by which the growth rate is reduced since the shift in the desorption peak is even smaller for lower carbon concentrations (compare TPD spectra (c) and (d) with that for saturated MS adsorption in spectra (b)). It is possible that the large carbon population on the surface due to surface segregation may also passivate the sites against adsorption of disilane in a similar fashion to arsenic.

However, the gradual increase in hydrogen coverage with greater disilane doses shown in

spectra (c) and (d) suggests that hydrogen is able to move onto carbon sites. This may occur as a result of the adsorption of disilane at carbon sites or as a result of surface migration of hydrogen. If the former is true, then it appears that the sticking probability of disilane on surfaces with carbon is much reduced and suggests that the disilane adsorption kinetics differ significantly from that on the clean Si(0 0 1) surface [8–10]. In order to distinguish these two possibilities, TPD data were obtained from a surface produced under similar conditions to spectra (c) but with an increased disilane adsorption temperature of 425 °C. The hydrogen coverage remained the same as spectra (c). These findings are therefore consistent with a reduced disilane sticking probability on carbon containing Si(0 0 1) surfaces.

TPD clearly demonstrates the effect of carbon on both the disilane sticking probability and the desorption rate of hydrogen. However, RHEED can be used to distinguish between these two effects. Under steady state growth the surface hydrogen coverage (θ) is determined by: $Jk_a(1-\theta)^2 = k_d\theta$ [9]. For a given incident flux (J) of disilane a reduction in the desorption rate constant (k_d) would result in an increase in θ whereas reducing the sticking probability has the opposite effect on θ. TPD shows that carbon reduces k_d therefore a study of θ, and hence the ratio k_d/k_a, would highlight the relative importance of k_a in controlling θ. Since the growth rate is always proportional to $k_d\theta$, RHEED oscillations can be used to directly probe the steady state hydrogen coverage as a function of disilane flux on the two different surfaces. Growth rates were measured at 550 °C for growth from a disilane BEP of 2.0×10^{-4} and 5.0×10^{-5} mbar on both clean Si(0 0 1) and $Si_{1-y}C_y$(0 0 1). For this incident disilane flux ratio of 4:1 the growth rate ratio on clean Si(0 0 1) is found to be 1.3 however for $Si_{1-y}C_y$(0 0 1) the ratio is 1.5. It is therefore clear that the steady state hydrogen coverage is lower on $Si_{1-y}C_y$(0 0 1) than on Si(0 0 1) and this is a result of a dominant low sticking probability k_a. Therefore the reduction in growth rate on a carbon contaminated surface with a low steady state hydrogen coverage is primarily caused by a reduction in the sticking probability of disilane.

4. Conclusion

A great deal of research has been carried out on the $Si_{1-x-y}Ge_xC_y$ system [11] and the techniques for growing good quality material are well refined. The incorporation of carbon from the growing surface into the crystal is also well characterised and has been modelled successfully. However the actual mechanism of adsorption of the gas precursors to the surface has not been fully elucidated. Although several groups have studied the decomposition of methylsilane on Si(0 0 1) and $Si_{1-x}Ge_x$(0 0 1) [12,13], to our knowledge, measurements during steady state growth have not been performed and carbon segregation has not been observed in real time.

The effect of carbon on the growth rate has been studied and by measuring the flux dependence we have shown that the overall growth rate is dominated by a reduction in the sticking probability of disilane and not the reduced hydrogen desorption rate constant shown in TPD. This result is interesting since carbon is isoelectronic with Si and Ge and on the (0 0 1) surface, diamond, Si and Ge all have surface reconstructions produced by the formation of dimers [14]. It is therefore surprising to observe the large difference in sticking probability of disilane on Si(0 0 1) and $Si_{1-y}C_y$(0 0 1) surfaces. The electronic structure of mixed dimers or C–C dimers on Si must be sufficiently different from those of the elemental semiconductor/insulator. The origin of this may lie in the large strain present on the surface given the substantial difference in the Si–Si and Si–C bond lengths. This could then explain the difference in adsorption mechanisms at Si and C sites, in particular the disilane precursor state leading to dissociation/pyrolysis. The resultant effect is a much reduced sticking probability of disilane on the Si(0 0 1) surface containing some carbon compared to a clean surface. A reduced growth rate is then observed.

Acknowledgements

The work reported here is funded by engineering and physical sciences research council UK under grant no. GR/R03808.

References

[1] E.J. Prinz, P.M. Garone, P.V. Schwartz, X. Xiao, J.C. Strum, IEEE Electron. Dev. 12 (2) (1991) 42.
[2] H.J. Osten, B. Heinemann, D. Knoll, G. Lippert, H. Rucker, J. Vac. Sci. Technol. B 16 (1998) 1750.
[3] A.C. Mocuta, D.W. Greve, J. Appl. Phys. 85 (2) (1999) 1240.
[4] J. Zhang, A. Marinopoulou, J. Hartung, E.C. Lightowlers, N. Anwar, G. Parry, M.H. Xie, X.D. Wu, B.A. Joyce, J. Vac. Sci. Technol. A 12 (1994) 1139.
[5] H. Nakazawa, M. Suemitsu, Appl. Surf. Sci. 130–132 (1998) 298.
[6] S.M. Mokler, W.K. Liu, N. Ohtani, B.A. Joyce, Appl. Phys. Lett. 59 (1991) 3419.
[7] F.C. Zhang, J. Singh, P.K. Bhattacharya, J. Vac. Sci. Technol. B 14 (1996) 2378.
[8] F. Hirose, J. Cryst. Growth 179 (1997) 108.
[9] R.W. Price, E.S. Tok, J. Zhang, Phys. Rev. B 59 (2000) R5292.
[10] E.S. Tok, A.D. Hartell, J. Zhang, Appl. Phys. Lett. 78 (2001) 919.
[11] H.J. Osten, Thin Solid Films 367 (2000) 101.
[12] A. Ichikawa, Y. Hirose, T. Ikeda, T. Noda, M. Fujiu, T. Takatsuka, A. Moriya, M. Sakuraba, T. Matsuura, J. Murota, Thin Solid Films 369 (2000) 167.
[13] M. Shinohara, T. Maehama, M. Niwano, Appl. Surf. Sci. 162–163 (2000) 161.
[14] P. Kruger, J. Pollmann, Phys. Rev. Lett. 74 (1995) 1155.