A study of $Si_{1-y}C_y/Si_{1-x-y}$ Ge_x C_y growth: C segregation and hydrogen desorption

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Abstract. Gas source molecular beam epitaxy (GSMBE) was used to grow $Si_{1-y}C_y(001)$ and $Si_{1-x-y}Ge_xC_y(001)$ layers using methylsilane (CH_3SiH_3), disilane (Si_2H_6) and germane (GeH_4). During the production of $Si/Si_{1-y}C_y$ carbon was found to effect the rate of growth. This was observed by a decrease in the period of intensity oscillations of reflection high energy electron diffraction (RHEED). A decrease in growth rate was also observed in the presence of carbon by performing *ex-situ* X-ray diffraction (XRD) layer thickness measurements. XRD can also give a measure of the amount of interstitial carbon in the grown layers. Gradual changes in the growth rate during growth of $Si/Si_{1-y}C_y$ and $Si_{1-y}C_y/Si$ heterojunctions was considered indicative of carbon segregation. A study of the precise effect carbon has on H_2 desorption and disilane adsorption was performed using temperature programmed desorption (TPD). By studying the steady state hydrogen coverage during growth the relative importance of the disilane sticking probability to hydrogen desorption rate is discussed.

1. Introduction

In the production of many semiconductor devices heat treatments are used to activate implanted dopants or grow dry oxides. This activation of dopants can also have a have a detrimental side effect on device performance since the dopants diffuse into regions where they can cause a reduction in the collector current enhancement in heterojunction bipolar transistors [1]. The diffusion of boron is thought to proceed by an interstitial mechanism. Substitutional carbon is found to block this diffusion [2] and this is postulated to be due to the removal of silicon self intersitials. However incorporating carbon into the silicon crystal is problematic since 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) or Gas Source MBE (GSMBE). Reports of $Si_{1-y}C_y(001)$ film growth exceeding the equilibrium soluble limit are widely spread. In the work of Mocuta *et al* [3] $Si_{1-y}C_y(001)$ was grown with y ranging from 0.5% to 1.16% which was found to depend on the substrate

temperature during growth. The growth rate was found to decrease with increasing y over the temperature range 550°C to 650°C and they 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.

This paper reports on a temperature programme desorption (TPD) study of the effect of carbon on the Si(001) surface on both the adsorption of disilane and the desorption of hydrogen. X-ray diffraction (XRD) measurements were performed *ex-situ* to measure the thickness of grown layers however reflection high energy electron diffraction (RHEED) intensity oscillations were also used *in-situ* to probe the steady state growth of $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$. The technique of TPD uses a mass spectrometer to record the desorption flux of adsorbed surface species as a function of substrate temperature. The kinetics governing the desorption process and the temperature ramp rate govern the temperature at which the maximum rate of desorption occurs. By using the same ramp rate for all measurements the effect of different surface species can be directly measured by observing any change in the position of the maximum rate of desorption. For hydrogen adsorbed from methylsilane on a silicon (001) surface the peak rate of desorption is observed to increase to a higher temperature. For hydrogen adsorbed from disilane on a hydrogen free surface previously exposed to methylsilane the area of the peak, and hence hydrogen coverage, is seen to diminish in respect to adsorption under the same conditions on a carbon free surface. RHEED intensity oscillations were recorded during steady state growth from methylsilane and disilane on clean Si(001) They were also recorded during the adsorption of disilane on a carbon contaminated surface. In both cases the growth rate is seen to vary gradually during deposition and this is direct evidence for the segregation of carbon during growth.

Experimental Procedure

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]. The 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 chamber is also equipped with a line of sight mass spectrometer (VG Quadrupole SXP300), associated counting electronics and a multi-channel scaler which enables the collection of temperature programmed desorption data using ion counting techniques [5]. The Reflection High Energy Electron Diffraction (RHEED) measurements were obtained using a VG LEG110 electron gun operating at 15keV and a k-space data collection system. 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 beam equivalent pressure (BEP) of methylsilane used during the growth ranged from 5.0×10^{-7} mbar to 5.0×10^{-5} mbar and that for disilane ranged from 5.0×10^{-5} mbar to 2.0×10^{-4} mbar with the total system pressure remaining below 5.0×10^{-4} mbar.

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 to 550°C . The RHEED patterns displayed features indicative of good long range order with half order features indicating a $(2\times1)+(1\times2)$ reconstruction. The two dimensional layer by layer mode was inferred from RHEED intensity oscillations since they could be easily

observed [6]. During growth at higher substrate temperatures or higher methylsilane fluxes, transmission features in RHEED patterns were observed indicating three dimensional growth. Therefore, annealing a methylsilane exposed surface to temperatures above 650 °C was avoided.

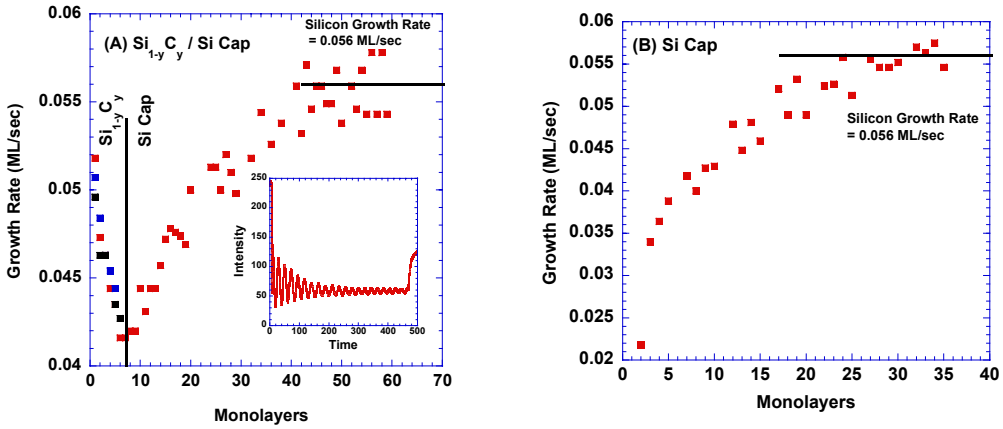


Figure 1: (A) Growth rate variation during growth of $Si_{1-y}C_y$ on a clean Si(001) surface followed by a Si capping layer. (B) Si growth rate variation on a methylsilane adsorbed Si(001) surface. The insert shows the RHEED intensity oscillations from which the results for (A) were obtained.

The growth rate, as measured from the period of RHEED intensity oscillations, was recorded during the growth of Si from disilane on various starting surfaces. The measured growth rates are given in Figure 1 as a function of the number of monolyaers deposited. Figure 1A shows the growth rate measured from RHEED oscillations during the growth of $Si_{1-y}C_y$ from disilane (BEP=1.0×10^{-4} mbar) combined with methylsilane (BEP=1.0×10^{5} mbar) at 550°C on a clean Si(001) starting surface. The methylsilane flux was removed after approximately 7 monolayers (ML) where growth continued purely from disilane. The insert shows RHEED intensity oscillations recorded in the case (A). In the case (B) the growth was from disilane with a beam equivalent pressure (BEP) of 1.0×10^{-4} mbar and a substrate temperature of 550°C on a surface previously dosed with 1500 Langmuirs (L) of methylsilane at 400°C.

For the results given in figure 1A the intitial growth rate during the growth of $Si_{1-y}C_y$ on a clean Si(001) surface is that of homoepitaxial growth but this is seen to gradually decrease and saturate at a lower value. In contrast to this the intitial growth rate of Si on a methylsilane adsorbed surface (figure 1B) was found to be at a significantly lower value (0.020 ML/sec) compared to that of the homoepitaxial growth of Si (0.056 ML/sec) from the same disilane flux. As growth continued, the growth rate gradually increased back to the homoeptiaxial growth rate over approximately 40 monolayers. It is clear the presence of methylsilane or its pyrolysis reaction products can have a strong influence on the growth rate of Si. Figure 1 gives clear evidence 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 therefore possible that during the growth of $Si_{1-x-y}Ge_xC_y$ carbon surface segregation will occur in competition with that of germanium.

XRD was peformed *ex-situ* on $Si_{0.8915-y}Ge_{0.1085}\ C_y$ and $Si_{0.8915}Ge_{0.1085}$ quantum well structures grown at 520°C. A reduction in the growth rate was observed in the presence of carbon. 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%.

The growth of Si from disilane has been widely reported to be controlled by surface hydrogen which has a passivating effect against the further adsorption of hydrides [8, 9]. Some simple experiments were performed to investigate what effect hydrogen has on limiting methysilane 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 methylsilane 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. Both the RHEED and TPD results show that the hydrogen terminated Si(001) surfaces is effectively passivated against methylsilane adsorption.

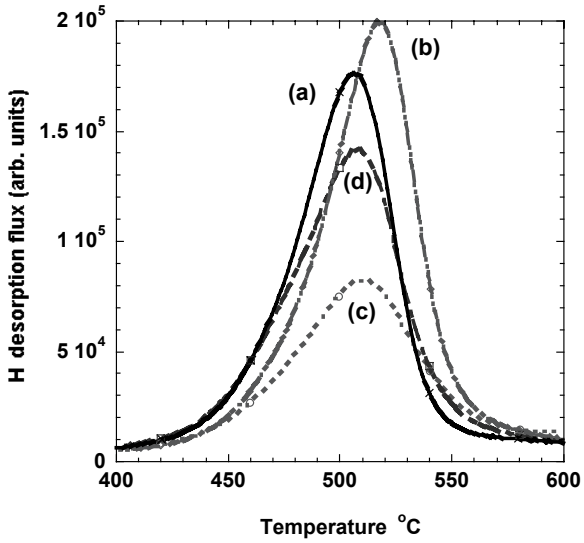


Figure 2: Molecular hydrogen TPD spectra obtained from (a) a fully saturated monohydride surface (b) after 15,000L of methylsilane adsorption at 400°C (c) after 1,000L adsdorption of disilane on the surface produced after TPD for (b) and (d) after 100,000L adsopriton of disilane also on the surface produced after TPD for (b).

The effect of carbon on hydrogen desorption can be studied by observing changes in the temperature at which the peak rate of desorption occurs. TPD spectra of molecular hydrogen desorption from various surfaces at a ramp rate of 0.5°C/s are shown in Figure 2. 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 methylsilane adsorption at 400°C was used. The peak rate of hydrogen

desorption shifts to a slightly higher temperature between spectra (a) and (b). 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_2 and larger species.

At low substrate temperatures disilane is found to decay sequentially with all the associated hydrogen remaining on the surface [9]. In this case the TPD peak area is directly proportional to the amount of silicon deposited. Therefore, the effect of carbon on the disilane sticking probability can be studied by observing changes in the total hydrogen coverage. In figure 2 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 methylsilane adsorption/TPD cycle. The disilane dose used is sufficient to produce a saturated monohydride coverage on a clean Si(001) 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 TPD results in Figure 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 small. A reduction or enhancement of the GSMBE Si growth rate due to the incorporation of Ge[10] or As[11] is well known. The former is attributed to the modification of hydrogen desorption kinetics whereas the latter occurs through adsorption site passivation by As[11]. 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(001) surface [8, 9, 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(001) surfaces.

It is clear that two effects are responsible for the observed growth rate decrease in the presence of carbon on the Si(001) surface: 1) a decrease in the hydrogen desorption rate and 2) and decrease in the disilane sticking probability. To probe the relative importance of these two effects a final growth study was performed where the flux dependence of the period of RHEED oscillations was studied. The reasoning for performing such an experiment is as follows. The growth rate from a disilane flux (J) is always given by $GR= 2\ J\ k_a(1-\theta)^2$ where θ is the hydrogen coverage and k_a is the sticking probability. Under steady state growth θ is determined by $6\ J\ k_a(1-\theta)^2 = 2\ k_d\theta$ [9] where k_d is the desorption rate constant, solving this gives:

$$\theta = [2+\alpha\text{-SQRT}(\alpha\text{^}2 + 4\ \alpha)]/2 \qquad [1]$$

where $\alpha = k_d/(3\ J\ k_a)$. We can see that the flux dependence of the growth rate for the different surfaces will give an indication of the relative magnitude of the relation k_d/k_a. The effect of k_d/k_a on the dependence of growth rate with incident flux is illustrated for a purely theoretical case in figure 3. It is not necessary to perform an exhaustive RHEED intensity oscillation growth rate study as it is possible to compare the ratio of the growth rates for both the clean and carbon contaminated surface at two different fluxes. This trend is illustrated for incident fluxes of 8ML/sec and 2ML/sec in figure 3.

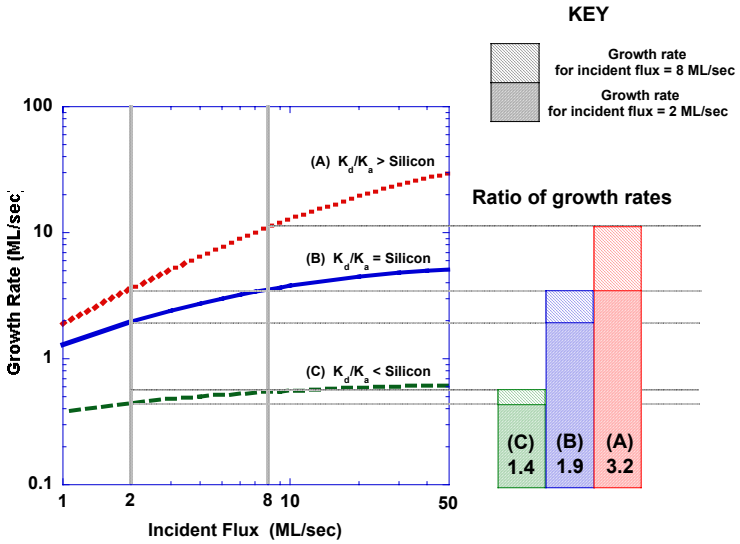


Figure 3: The theoretical growth rate dependence on flux and desorption rate constant to sticking probability ratio k_d/k_a. For case (A) k_d/k_a is larger than that for silicon (B) and the ratio of growth rates for a ratio of incident fluxes 4 is calculated to be larger than that for silicon. The opposite is true if k_d/k_a is smaller than that for silicon (C).

Growth rates were measured at 550°C for growth from a disilane BEP of 2.0×10^{-4}mbar and 5.0×10^{-5}mbar on both clean Si(001) and $Si_{1-y}C_y$(001). For this incident disilane flux ratio of 4:1 the growth rate ratio on clean Si(001) is found to be 1.3 however for $Si_{1-y}C_y$(001) the ratio is 1.5. The ratio k_d/k_a is therefore greater for $Si_{1-y}C_y$(001) (case A in figure 3) than it is for Si(001). TPD shows that k_d has decreased in the presence of carbon and therefore a reduction in the ratio k_d/k_a must be due to a dominant low sticking probability k_a. Therefore the reduction in growth rate on a carbon contaminated surface is primarily caused by a reduction in the sticking probability of disilane.

Conclusion

Carbon is isoelectronic with Si and Ge. On the (001) surface, diamond, Si and Ge all have surface reconstructions produced by the formation of dimers [11]. It is, perhaps, surprising to observe the large difference in sticking probability of disilane on Si(001) and $Si_{1-y}C_{y(001)}$ 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(001) surface containing some carbon compared to a clean surface. A reduced growth rate is then observed.

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