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Dynamics and surface segregation during GSMBE of $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ on the Si(0 0 1) surface

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Abstract

This paper reports on the study of the growth dynamics of Si and SiGe containing a small fraction of carbon from the hydrides of Si, Ge and methylsilane. Dynamic changes in the growth rate across heterojunctions show that the presence of carbon on the (0 0 1) surface of Si or SiGe supresses growth rate and the carbon concentration could not be changed abruptly at an interface due to the surface segregation of carbon during growth. Temperature programmed desorption of molecular hydrogen from the Si(0 0 1) surface with various adsorbates shows that the presence of carbon increases the barrier to the desorption of molecular hydrogen and reduces the sticking probability of disilane. Both effects may lead to a reduction in the growth rate but the disilane supply rate (flux) dependence of growth rate on clean and carbon containing Si(0 0 1) surface shows that the primary cause of the growth rate decrease is the reduced sticking probability under the growth conditions used.
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1. Introduction

Incorporation of carbon into the base region of $Si_{1-x}Ge_x$ heterojunction bipolar transistors has been shown to have the benefit of strain compensation [1] and more importantly, the suppression of transient enhanced diffusion(TED) of boron [2]. However, the required carbon concentration exceeds its solubility limit in silicon [3] and a growth process occurring far from thermodynamic equilibrium is necessary in order to avoid carbon clustering. Gas source molecular beam epitaxy (GSMBE), like its chemical vapour deposition counterpart [4,5] is ideally suited to this requirement. Much of the advantage of the technique derives from its low operating temperature and the delivery of carbon using gas precursors which favours substitutional incorporation of carbon and avoids formation of carbon clusters, necessary for the suppression of TED of boron.

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In the work reported here, Si and $Si_{1-x}Ge_x$ films containing small amounts of substitutional carbon ($<1.5\%$) were grown using GSMBE with disilane, germane and methylsilane (MS) precursors. The growth processes are investigated by in-situ techniques including reflection high energy electron diffraction(RHEED) intensity oscillations, temperature programmed desorption (TPD) and ex-situ characterisation by X-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS) measurements.

2. Experimental procedure

The growth facility is a purpose built double ended system based the VG Semicon V80M and its basic configuration has been described previously [6]. The growth chamber is also equipped with a line of sight mass spectrometer (VG Quadrapole SXP300H), associated counting electronics and a multi-channel scaler(MCS) which enables the collection of TPD data using ion counting technique [7]. The temperature of the wafers is measured by a IRCON Series W Infrared Pyrometer, which forms part of the temperature control loop. RHEED measurements were obtained using a VG LEG110 electron gun operating at 15 keV and a k-space data collection system. Layer thicknesses and composition were obtained from ex-situ XRD rocking curve measurements and simulations. The Si and SiGe films and those containing a small fraction of carbon were grown using GSMBE conditions on Si(0 0 1) substrates from disilane, germane and methylsilane (MS) precursors. The substrates were etched by HF/nitric acid cycles followed by standard clean 1 and a final dip in 5% HF. The system pressure under typical growth conditions remains well below 2×10^{-4} mbar.

TPD spectra were recorded using the MCS based electronics during temperature ramps of the substrate under PID controls. The thickness and compositions of the films are measured by ex-situ XRD rocking curves and comparisons with simulations based on dynamic theory of diffraction built into the Philips X'pert software.

3. Experimental results

The growth mode of carbon containing films is very sensitive to the substrate temperature and MS flux. At temperatures much above 550°C and/or high MS fluxes, 3D nucleation occurs and RHEED patterns show typical transmission diffraction features associated with the formation of 3D islands on the surface. At temperatures of 550°C or below, the growth generally proceeds in a layer by layer mode through 2D nucleation and 2D island coalescence, evident from the presence of RHEED intensity oscillations. Fig. 1 shows the RHEED pattern obtained from the surface of a 1μm $Si_{0.898}Ge_{0.1}C_{0.002}$ film grown on a strain relaxed SiGe virtual substrate. They indicate that the surface has good long range order and exhibits

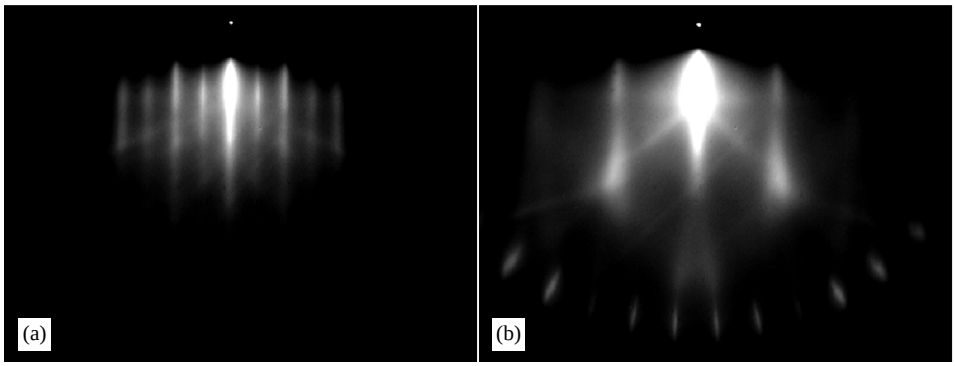


Fig. 1. Diffraction patterns from the surface of a 1μm $Si_{0.898}Ge_{0.1}C_{0.002}$ film grown at 520°C. (a) [1 1 0] azimuth (b) [0 1 0] azimuth.

a symmetry corresponding to that of a $(2 \times 1) + (1 \times 2)$ reconstruction, similar to those of the Si (0 0 1) surface. With a beam equivalent pressure (BEP) of MS ranging from 5×10^{-7} to 5×10^{-5} mbar, the carbon concentration in the growing film can be controlled between 0.1% and 1.5% for growth in the temperature range between 500 and 550°C while maintaining the layer by layer growth mode. To avoid the formation of 3D nucleation centres, annealing of surfaces exposed to MS to high temperatures is therefore avoided and TPD measurements involving surfaces exposed to MS were limited to below 650°C.

Dynamic changes in the growth rate of Si capping layers on MS adsorbed Si(0 0 1) surface and during growth of a $Si_{1-y}C_y$ quantum well structure were measured by RHEED intensity oscillation technique and are illustrated in Fig. 2. Fig. 2a shows the growth rate variation during the Si cap layer growth on MS adsorbed surface and Fig. 2b shows the changes of growth rate during the growth of a $Si_{1-y}C_y$ quantum well followed by Si cap layer growth. The growth rate varies slowly across the heterointerface and the growth rate of silicon on a carbon containing surface, either the during the growth of $Si_{1-y}C_y$ or a Si cap layer on MS adsorbed surface, is reduced compared to the Si homoepitaxy growth rate under the same disilane flux (BEP $= 1 \times 10^{-4}$ mbar) at 550°C. The presence of MS or its pyrolysis reaction

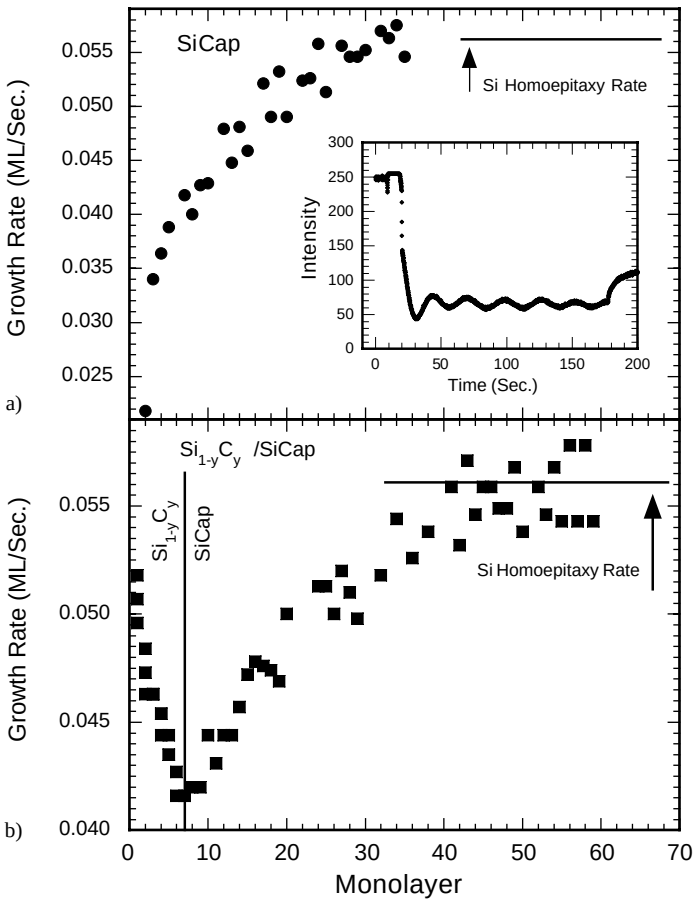


Fig. 2. Si growth rate variation on (a) MS adsorbed Si(0 0 1) surface and (b) during growth of $Si_{1-y}C_y$ at temperature of 550°C. Insert shows typical RHEED intensity oscillations from which the results are obtained.

products on the Si(0 0 1) surface clearly have a strong influence on the growth rate of Si. This is also true for the growth of $Si_{1-x-y}Ge_xC_y$. A reduction in the growth rate of $Si_{0.89-y}Ge_{0.11}C_y$, as the carbon concentration in the film increased, was observed from XRD measurements on quantum well structures grown at 520°C. This ranged from 12% for a bulk C concentration of 0.44% up to a change of 36% for a C concentration of 1.45%.

TPD spectra of molecular hydrogen from the (0 0 1) surface with various adsorbates were examined to identify the cause of growth rate reduction. Fig. 3 shows the molecular hydrogen TPD spectra obtained at a ramp rate of 0.5°/s. The spectra correspond to (a) clean Si(0 0 1) surface followed by adsorption of 1000 Langmuirs(L) of disilane at 400°C, (b) Si(0 0 1) surface adsorbed with 15,000 L of MS at 400°C, (c) after further 1000 L disilane adsorption at 400°C on a surface following the recording of (b) and finally (d) after further 100,000 L disilane adsorption at 400°C on the surface following the recording of (b). Given that the hydrogen desorption at 400°C is negligible, the amount of hydrogen measured in the TPD process reflects the amount of hydride adsorbed [8]. The results show that the H_2 desorption kinetics are slightly modified but the most striking effect is the reduction of the disilane sticking coefficient on the carbon containing

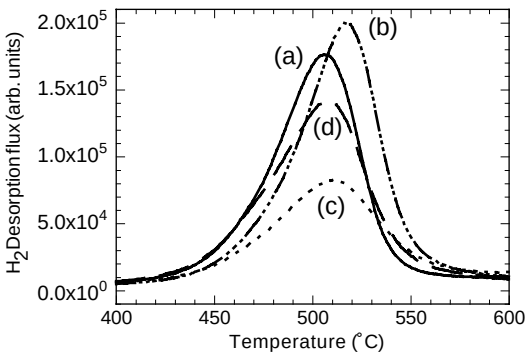


Fig. 3. Molecular hydrogen TPD spectra obtained from (a) fully saturated mono-hydride surface, (b) after 15,000 L of MS adsorption at 400°C, (c) after 1000 L adsorption of disilane on surface produced by TPD in (b) and (d) after 100,000 L adsorption of disilane on surface produced by TPD in (b).

surface compared d to the clean surface. This is seen as the main mechanism for the reduction in growth rate.

The gradual change in growth rate across the heterointerface shown in Fig. 2 indicates that the carbon surface concentration could not be changed instantaneously by the introduction or removal of the MS flux. Initial SIMS measurements of the carbon concentration across $Si_{1-y}C_y$ quantum well also indicate that the leading edge (at the Si to $Si_{1-y}C_y$ interface) is more shallow compared to the trailing edge (at the $Si_{1-y}C_y$ to Si interface). Even taking into account of any effects due to SIMS measurements, the $Si_{1-y}C_y$ to Si interface is sharper than the Si to $Si_{1-y}C_y$ interface. Given the sequence of layer growth, the carbon is incorporated into the Si cap layer as a result of C surface segregation during cap layer growth. Together with the RHEED measurements, they provide direct evidences of the surface segregation of carbon during growth.

4. Discussion

Using GSMBE operating at relatively low substrate temperatures, $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ with good long range order can be grown. The measurement of dynamic changes in growth rate reveal two issues, the reduction in growth rate compared with growth without carbon on the surface and the surface segregation of carbon.

The reduction of growth rate [9] could have arisen from two causes, the reduction of the rate of desorption of molecular hydrogen (pyrolysis reaction product) and the reduction in the sticking probability of disilane (pyrolysis reaction reactant). The TPD measurements suggest that both processes are affected by presence of carbon or a MS pyrolysis product. While the TPD results show a reduction in the sticking coefficient of disilane is the likely cause, the evidence does not allow a distinction between the two. However, the changes in these two process produces quite different results on the surface hydrogen coverage based on the hydrogen coverage rate equation model of growth from disilane [10]. For a given incident flux

of disilane and substrate temperature, a reduction in hydrogen desorption rate would increase the hydrogen coverage as well as reducing the growth rate. A reduction in disilane sticking probability, on the other hand, reduces the hydrogen coverage as well as the growth rate. A measurement of hydrogen surface coverage can then be used to identified the main cause of growth rate reduction. This can be inferred from the flux dependence of Si growth rate on clean and carbon containing surfaces. For a given increase in the disilane incident flux at a substrate temperature of 550°C, the increase in growth rate on carbon containing Si(0 0 1) surface is more pronounced compared to the clean surface. Applying the same rate equation model, one can infer that the hydrogen coverage on the carbon containing surface is lower and hence the main cause of growth rate reduction is the reduction of the disilane sticking probability.

A clear consequence of carbon surface segregation is the smearing of the heterointerface. The small temperature window for 2D growth restricts the range of growth conditions available for studying the segregation behaviour. The appropriate techniques would be the application of RHEED intensity oscillations and a modelling approach [11,12] in conjunction with ex-situ SIMS measurements. This area remains to be explored.

Acknowledgements

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