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Epitaxial growth mode and silicon/silicon–germanium heterointerfaces

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Silicon–germanium/silicon ($Si_{1-x}Ge_x/Si$, $x<0.50$) multiple quantum wells (MQWs) have been grown on (0 0 1) Si substrates by gas source molecular beam epitaxy (GSMBE) using disilane (Si_2H_6) and germane (GeH_4) as source gases. Their structural properties have been evaluated by X-ray diffraction (XRD), rocking curve techniques and transmission electron microscopy (TEM). For the substrate temperatures used in this work (450 °C to 520 °C) the Si growth rate is limited by hydrogen desorption kinetics, whereas the growth of SiGe is limited primarily by the arrival rate of the source gases onto the Si substrates. XRD analysis of the structures indicates a significant well plus barrier period variation of approximately 5–10%, attributed to fluctuations in the substrate temperature during growth, since these cause significant variations in the growth rate of the Si barriers. For $x<0.30$ we find nearly ideal Si/SiGe interfaces as determined from a comparison of the XRD data with dynamical simulations of the 0 0 4 X-ray reflectivity, although TEM micrographs indicate that the $x=0.30$ samples exhibit undulations in the first SiGe/Si interface of the structures. For $x=0.50$ such undulations occur throughout the MQW structure; the undulation amplitude decreases with decreasing growth temperature but the period remains unchanged. The observed improvement in the SiGe/Si interface planarity at lower growth temperatures is attributed to a reduction in the surface diffusion of Si and Ge with decreasing growth temperature.

1. Introduction

Abrupt heterointerfaces between silicon (Si) and compressively strained silicon–germanium (SiGe) are of paramount importance in the realization of novel heterostructure device concepts in this material system. Smeared Si/SiGe heterointerfaces could introduce undesirable interfacial built-in electric fields in electronic devices where charge transport occurs perpendicular to them; thickness variations, occurring during growth along a single quantum well, could significantly broaden quantized states in devices whose operation is based on quantum confinement effects. Examples of such devices are heterojunction bipolar transistors (HBTs) [1], resonant tunnelling diodes (RTDs) [2], *n* and *p* channel modulation-doped field effect transistors (MODFETs) [3, 4] and infrared detectors [5].

Gas source epitaxial deposition techniques, such as atmospheric pressure chemical vapour deposition (APCVD) [6], low pressure chemical vapour deposition (LPCVD) [7], ultrahigh vacuum chemical vapour deposition (UHV/CVD) [8] and gas source molecular beam epitaxy (GSMBE) [9], have all been used to realize device-quality Si/SiGe heterostructures with abrupt interfaces. In these growth techniques, the use of hydride gas sources and their subsequent dissociative adsorption is thought to form an adsorbed layer of hydrogen (H) in the form of a surface monohydride during growth of Si and SiGe. This is believed to lower the surface energy and has the effect of enhancing two-dimensional growth of the alloy and reducing Ge segregation at the growth front [10, 11]. At high Ge compositions and/or high growth temperatures, however, the interplay between strain and growth kinetics can produce local elastic relaxation in SiGe films via the formation of undulations in the growth front, undulations which are highly deleterious for the realization of Si/SiGe heterostructure devices.

This work presents results from the growth and characterization of $Si/Si_{1-x}Ge_x/Si$ multiple quantum well structures ($x < 0.50$) grown by GSMBE at low temperatures (460 °C $< T_s <$ 520 °C). The structural integrity of the interfaces has been examined by X-ray diffraction (XRD) rocking curve measurements and transmission electron microscopy (TEM) studies.

2. Experimental details

The structures examined in this work have been grown by GSMBE using disilane (Si_2H_6) and germane (GeH_4) as hydride sources. Details of the deposition system have been reported elsewhere [12]. The MQW samples were grown on high resistivity boron (B) doped (1 0 0) Si substrates which were chemically cleaned by a technique leaving an H passivated (1 0 0)

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Si surface prior to loading in the deposition chamber [13]. A homoepitaxial buffer layer of approximately 100 nm is grown at 750 °C prior to deposition of the MQWs. For $x < 0.30$ the samples consist of 10 periods of $Si_{1-x}Ge_x$/Si well/barrier structures grown at approximately 520 °C. For $x = 0.50$, five periods of $Si_{0.50}Ge_{0.50}$/Si well/barrier layers were grown at 460 °C and 500 °C. Typical growth rates at these temperatures are, 0.2–0.1 nm min^{-1} for Si and ≈ 1.5 nm min^{-1} for SiGe, although this value depends on the Ge content of the SiGe well. A 2 min growth interruption at each heterointerface was used to reduce the partial pressure of unwanted precursor species in the growth chamber. During these interruptions the base pressure reached about 10^{-10} torr (13.3 nPa), there is no evidence of carbon (C) or oxygen (O) incorporation at these heterointerfaces during the growth interruptions as determined from SIMS measurements. The Ge compositions in the wells are adjusted by controlling the partial pressure of GeH_4 in the chamber while keeping the Si_2H_6 pressure constant.

Nominal thicknesses of SiGe wells and Si barriers were chosen so that for the growth temperatures used each SiGe quantum well would be coherently strained relative to Si [14] and the total thickness of the MQW structure would not exceed the critical thickness for plastic relaxation via the formation of misfit dislocations. These design criteria allowed the realization of metastable coherently strained MQW structures.

XRD rocking curves were obtained in a Philips high resolution X-ray diffractometer with a four-reflection Ge 2 2 0 monochromator and $CuK\alpha_1$ radiation. Low resolution TEM micrographs were obtained in a 200 keV Jeol 2000FX electron microscope, and high resolution images (not shown in this paper) were recorded in a 200 keV JEM 2010 microscope.

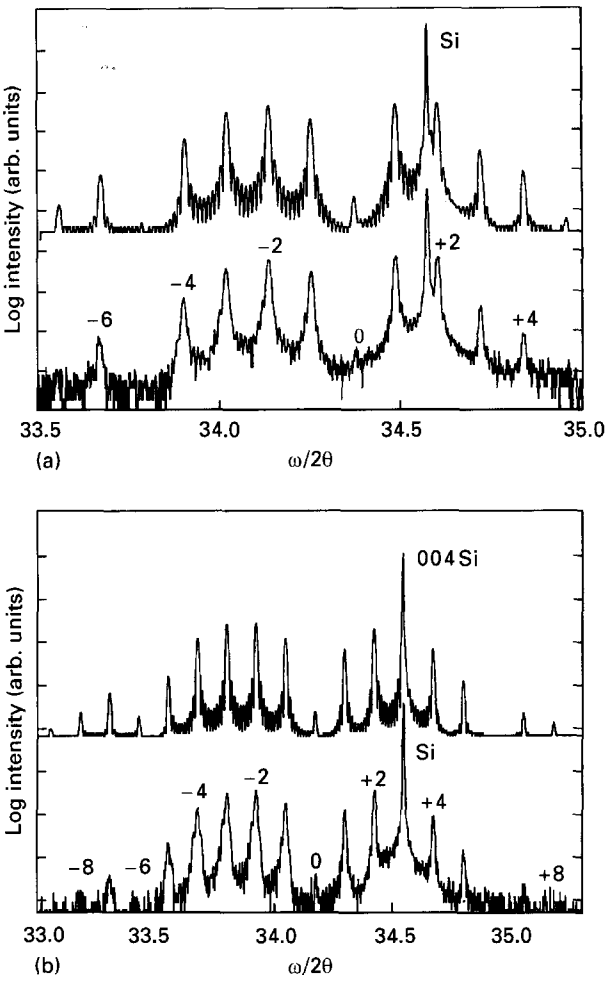

Figure 1 Double-crystal X-ray diffraction (XRD) rocking curves for the 10 period $Si_{1-x}Ge_x$/Si multiple quantum well structures with nominal compositions (a) $x = 0.20$ and (b) $x = 0.30$. Good agreement between the experimental (lower) and simulated (upper) curves is obtained in terms of the zeroth-order and satellite peak intensities and widths. Pendellösung fringes due to interference effects can be observed in both structures. These results suggest abrupt $Si_{1-x}Ge_x$/Si interfaces with negligible composition variation within the MQW structure. The experimental XRD rocking curves exhibit a slight broadening of the higher-order satellites, indicating a well plus barrier period variation in the growth direction of the order of 5–10%. Data: (a) 19 nm $Si_{0.80}Ge_{0.20}$, 27 nm Si, $T_S = 520$ °C; (b) 15 nm $Si_{0.72}Ge_{0.28}$, 28 nm Si, $T_S = 520$ °C.

3. Results

Fig. 1a and b show the XRD 0 0 4 reflectivity for MQW structures with $x = 0.20$ and $x = 0.30$, respectively. Relative to the (0 0 1) Si substrate, these SiGe films experience a 0.8% and 1.2% misfit strain, respectively. The compositions and thicknesses indicated have been determined from full dynamical simulations of the 0 0 4 reflectivity profiles shown as the upper trace in each figure. In these simulations, the dependence of the $Si_{1-x}Ge_x$ lattice constant on composition includes bowing parameters to account for slight deviations from Vegard's law [15]. We find good agreement between the experimental data and the simulated profiles with negligible satellite broadening and good definition of Pendellössung fringes originating from the interference effects in such periodic structures. Furthermore, narrow zeroth-order satellites are obtained which are indicative of negligible composition variations in the SiGe quantum wells. Good satellite intensity matching is also obtained, which points to highly abrupt Si/SiGe interfaces. In addition, the results indicate almost complete coherency of the MQW structures with the 0 0 1 Si substrates. A slight asymmetric broadening of higher-order satellites is evident and is attributed to variations in the well plus barrier period of the order of 5% [16]. This probably arises from substrate temperature variations during growth of the Si barriers since this takes place in the kinetically limited regime, where there is a strong dependence of growth rate on temperature. Conversely, alloy growth occurs under supply-limited conditions where there is only a weak temperature dependence of the growth rate.

The results for the $x = 0.50$ samples (2% misfit strain) grown at 500 °C and 460 °C are shown in Fig. 2a and b, respectively. The dynamical simulation of the 0 0 4 reflectivity for the sample grown at 500 °C includes a linear Ge gradient at the SiGe/Si interface. Uniform Ge compositions within and between wells are deduced from the narrow zeroth-order peaks observed, and such narrow peaks also indicate good coherency of the structures to the (0 0 1) Si substrates. The intensity match between the simulated

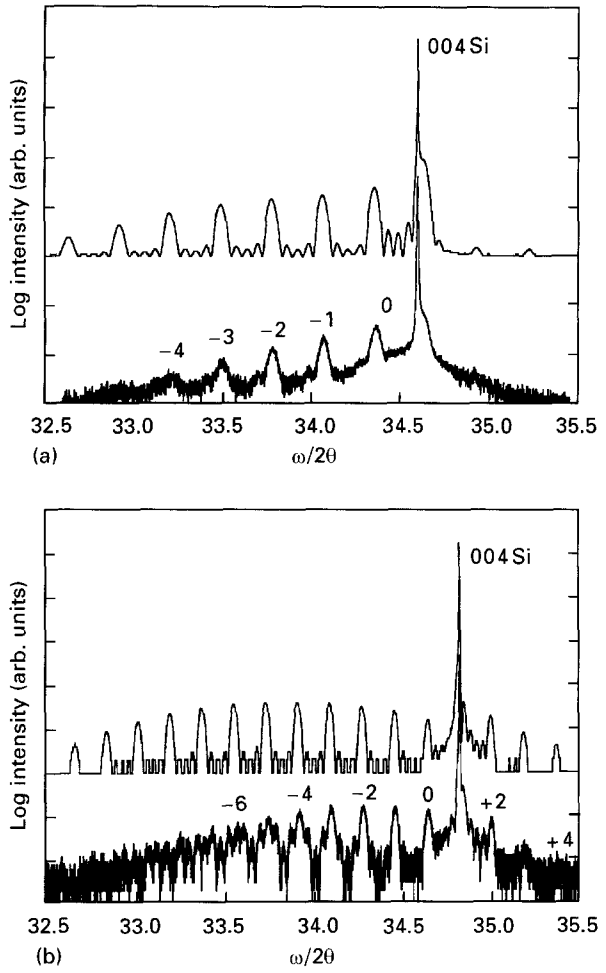

Figure 2 Double-crystal X-ray diffraction (XRD) rocking curves for the 5 period $Si_{0.5}Ge_{0.5}$/Si multiple quantum well structures grown at (a) 500 °C and (b) 460 °C. Poor intensity matching for high-order satellites between the experimental (lower) and simulated (upper) curves indicate severe interface grading at the interfaces as determined by XRD. Pendellösung fringes due to interference effects can only be observed for the structure grown at 460 °C, indicating a higher degree of periodicity in this sample. Broadening of the higher-order satellites also indicates a well plus barrier period variation in the growth direction of the order of 5–10%. Data: (a) 2 nm $Si_{0.50}Ge_{0.50}$, 3 nm linear grading, 13.5 nm Si, T_S = 500 °C; (b) 4.3 nm $Si_{0.49}Ge_{0.51}$, T_S = 460 °C, 25.3 nm Si, T_S = 520 °C.

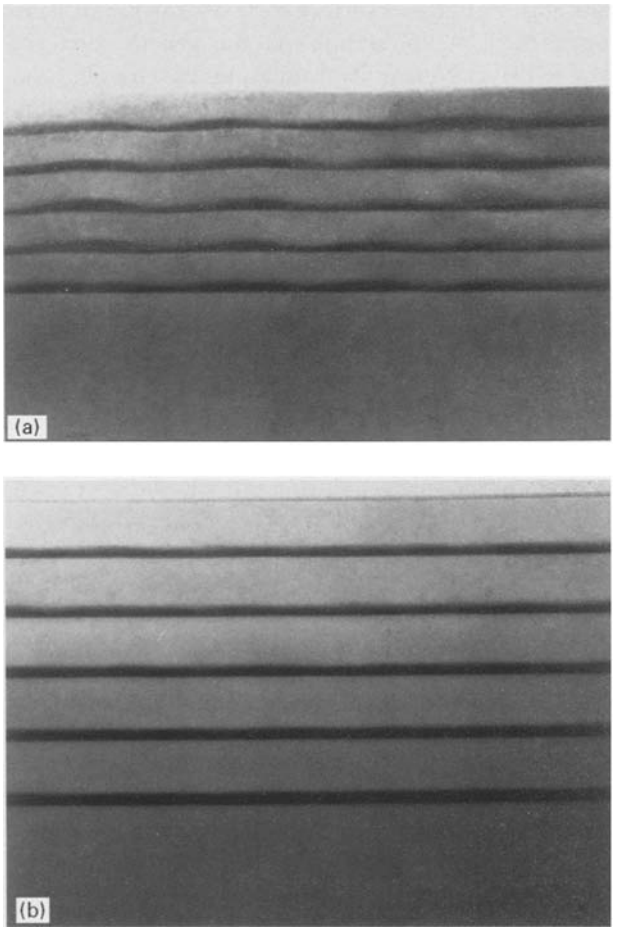

Figure 3 Cross-section transmission electron micrographs (TEM) of the 5 period $Si_{0.50}Ge_{0.50}$/Si multiple quantum well structures grown at (a) 500 °C and (b) 460 °C. Surface undulations at the SiGe/Si interface are clearly observable throughout the structure; (a) has undulation period and amplitude 2 nm and 55 nm, respectively, (b) 1 nm and 50 nm.

and experimental XRD curves of the high-order satellites, however, is quite poor and it is an indication of severe grading at the interfaces as detected by XRD. Furthermore, the sample grown at 500 °C does not exhibit Pendellösung fringes between satellites, indicating a poorer degree of periodicity compared with the sample grown at 460 °C, where clear Pendellösung fringes are measured. As for $x \leq 0.30$ samples, an asymmetric broadening of the higher-order satellites indicates a variation in the well plus barrier period in these samples of the order of 10%, and again is attributed to fluctuations in the growth temperature during growth of the Si barriers.

TEM micrographs confirm the periodic nature of the structures and the thicknesses determined by XRD. Fig. 3a and b show the cross-section TEM micrographs of the MQW structures with $x = 0.50$ grown at 500 °C and 460 °C, respectively. They indicate that the SiGe/Si interfaces exhibit a lateral interface undulation whose peak-to-valley amplitude and peak-to-peak period depend on growth temperature. For the structure grown at 500 °C the amplitude is 2 nm, whereas for the structure grown at 460 °C the amplitude is 1 nm. The period of this undulating growth front appears unaffected by growth temperature, however, and is approximately 55 nm. Although it is possible to include these TEM observations in the simulation of the XRD reflectivity curves, to obtain an improved fitting (top trace of Fig. 2a) by including an interfacial gradient at the SiGe/Si interface, the analysis is further complicated by the possibility of lateral modulation of the strain field via elastic deformation at the peaks of the undulating SiGe films [17]. The Si/SiGe interfaces, however, are planar relative to their SiGe/Si counterparts and indicate the planarizing nature of Si when grown on an undulating SiGe surface. For the $x = 0.30$ sample, TEM micrographs indicated the onset of surface undulation formation at the SiGe/Si interface only in the first quantum well of the structure.

4. Discussion

In describing the development of surface undulations at the SiGe/Si interface in the $x = 0.30$ and $x = 0.50$ films, it is necessary to consider the effects of strain, surface diffusion currents, solid phase reactions and

monolayer or bilayer surface steps. Pidduck *et al.* have modelled such undulations in the general case for strained layer epitaxy by estimating the overall excess volume strain energy, including a sinusoidally varying interfacial strain field, as well as the change in surface free energy resulting from the increase in surface area from these undulations [17]. They found their period to be inversely proportional to the square of the strain in the epitaxial film. The data extracted from our TEM studies has a good fit to their model. A more detailed model [18] has been proposed in which gradients in the surface chemical potential, including a surface free energy term and an elastic energy term, lead to atomic drift velocities that produce a rate of change of the surface profile. For example, an initial local strain modulation during growth of the strained film provides sufficient gradient in the surface chemical potential for surface diffusion currents to be established.

An undulating surface profile develops where the increase in surface free energy is compensated by a reduction in the elastic energy term. Provided that relaxation by plastic deformation via the formation of misfit dislocations does not occur, this reduction in the elastic energy term induces Ge surface diffusion towards elastically relaxed crests, producing a Ge enrichment at the crests of the undulations. Upon growth of Si barriers on the SiGe wells, the reduction in the elastic energy term would result in preferential surface diffusion of Si towards the strained valleys where the in-plane lattice constant of the film is coherent with the (0 0 1) Si substrate. Such Si surface diffusion currents would then have a planarizing effect on the growth front, observed in the TEM micrographs of Fig. 3a and b, further reducing gradients in the surface chemical potential by lowering the surface free energy term.

Undulations at the growth front of strained SiGe require an initial modulation of the local strain field, which in turn modifies the surface chemical potential and causes the development of surface diffusion currents. Although heterogeneous sources may be responsible for modifying the surface chemical potential, preferential ordering during alloy formation and/or the presence of monolayer or bilayer steps could also act as active sources for the development of undulations. Ohshima *et al.* have observed undulations during the growth of Ge on (0 0 1) Si with characteristic {8 1 1} facets and attributed their formation to alloy ordering with a double periodicity in a ⟨1 1 1⟩ direction induced during early stages of growth [19]. Molecular dynamic simulations performed by Xie *et al.* have shown a reduction of the step free energy for growth under compressive strain, producing the observed surface roughening for SiGe films with strains exceeding 1.4% [20].

Since surface diffusion is a kinetically driven process, a reduction in substrate temperature and/or the use of surfactants would inhibit surface transport, producing a flatter SiGe growth front [21]. It is well known that the growth of Si and SiGe alloys by GSMBE is strongly influenced by the existence of adsorbed hydrogen – as mono-, di- or trihydride species – formed by the dissociative adsorption of Si_2H_6 and GeH_4 on the (0 0 1) Si surface [22]. Gates and Kulkarni have determined the temperature dependence of H surface coverage on (0 0 1) Si from Si_2H_6 using direct-recoil time-of-flight measurements [23]. For Si_2H_6 fluxes comparable to those used in the experiments reported here ($\approx 10^{15}\,cm^{-2}s^{-1}$), they found an H surface coverage at 500 °C that exceeded one H atom per surface Si atom. This adsorbed hydrogen acts to block sites for the dissociative adsorption of disilane, so the film growth rate is limited by the desorption of surface hydrogen.

Surface hydrogen acts as a surfactant, decreasing the Gibbs heat of segregation of Ge; this allows GSMBE to create more abrupt interfaces than SSMBE, its solid source counterpart [11]. Hydrogen, then, may inhibit surface transport, producing flatter SiGe/Si interfaces. However, temperature-programmed desorption experiments from deuterated Ge-covered and clean (0 0 1) Si surfaces have shown that, for a given growth temperature, the hydrogen surface coverage is inversely proportional to the Ge concentration [24]. It is therefore apparent that, with increasing Ge content in compressively strained SiGe films grown on (0 0 1) Si substrates, there exists an intricate relationship between strain, surface diffusion currents, solid phase reactions and monolayer or bilayer surface steps, which are responsible for the development of surface undulations at the SiGe/Si growth front.

5. Conclusions

We have used GSMBE to grow $Si_{1-x}Ge_x$/Si ($x < 0.50$) MQWs in the temperature range 460–520 °C and characterized their structural properties by X-ray diffraction (XRD) and transmission electron microscopy (TEM). For $x < 0.30$ we find nearly ideal Si/SiGe interfaces as determined from a comparison of the XRD data with dynamical simulations of the 0 0 4 X-ray reflectivity, although TEM micrographs indicate that the $x = 0.30$ samples exhibit undulations in the first SiGe/Si interface of the structures. For $x = 0.50$ such undulations occur throughout the MQW structure; with decreasing growth temperature, the undulation amplitude decreases whereas its period remains unchanged. The observed improvement in the SiGe/Si interface planarity at lower growth temperatures is attributed to a reduction in the surface diffusion of Si and Ge with decreasing growth temperature.

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