Interfacial Studies in Semiconductor Heterostructures by X-Ray Diffraction Techniques

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INTERFACIAL STUDIES IN SEMICONDUCTOR HETEROSTRUCTURES
BY X-RAY DIFFRACTION TECHNIQUES

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Abstract

X-ray radiation is a non-destructive probe well suited to assess structural perfection of semiconductor material. Three techniques are used to study the interfacial roughness, period fluctuations and annealing-induced interdiffusion in various superlattice structures. Reflectivity of long period Si/Si₁₋ₓGeₓ multiple quantum wells reveals an asymmetry oriented along the direction of miscut in the interface roughness with the Si₁₋ₓGeₓ to Si interfaces being about twice as rough (0.5 versus 0.3 nm) as the Si to Si₁₋ₓGeₓ interfaces. For Si-Si₀₆₅Ge₀₃₅ multiple quantum wells, diffuse scattering is minimal for a growth temperature of 550°C and increases substantially at very low (250°C) or high (750°C) growth temperatures. In (SiₓGe₁₋ₓ)₁₀₀ short period superlattices, the X-ray reflectivity data are consistent with interfacial mixing over about two monolayers and thickness fluctuations of about 5% vertically in the structures. For superlattices grown on vicinal surfaces, the roughness spectrum is correlated with the surface miscut orientation. Double-crystal X-ray diffraction using symmetrical and asymmetrical reflections has been used to study epitaxial lattice distortion and strain relaxation in InGaAs/GaAs heterostructures grown on (100) on-orientation and 2° off (100) GaAs surfaces. It is shown that thick InGaAs films retain an appreciable fraction of their initial strain and that their crystal lattice is triclinically distorted. The magnitude of the deformation is larger when growth is carried out on a vicinal surface.

Key Words: X-rays, reflectometry, double-crystal diffraction, interface, superlattice, strain, triclinic distortion.

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Introduction

X-ray scattering techniques have been used extensively to characterize semiconductor materials. In particular, double crystal diffraction is now commonly used to probe the structural properties of heterostructures. It has become a standard non-destructive tool for determining thickness and strain distributions in multilayer media. Applications of double crystal diffraction and related techniques to low dimensional structures have been the object of several recent reviews (Fewster, 1989, 1992, 1993; Baribeau and Houghton, 1991; Tanner and Bowen, 1993).

As novel concepts for electronic or photonic devices often call for growth of structures with very small vertical dimensions, it has become of paramount importance to characterize and understand properties of semiconductor interfaces. In that regard, conventional double crystal diffraction is somewhat limited due to a lack of sensitivity (interface imperfection shows up mostly at large wave vector transfer where the signal is very weak). Furthermore, the strong strain and composition dependence of that technique renders accurate modeling of interfaces very difficult. X-ray reflectivity is an alternative approach particularly suited to the study of interface problems in artificially layered materials (Croce and Nélot, 1976; Pieuch and Nélot, 1990; Russell, 1990; Miceli, 1993). Specular X-ray reflectivity is extremely sensitive to the material density distribution in the vicinity of a solid surface and morphological features at the interfaces, but not sensitive to crystal strain and defects. Modeling of the specular reflectivity is thus a powerful means for determining the thickness, density and roughness of thin films. X-ray reflectivity can also be advantageously used to investigate diffusion phenomena in multilayer periodic structures (Greer and Spaepen, 1985; Baribeau et al., 1990a,b; Baribeau, 1993a).

The behavior of electrons in field-effect transistors and other devices with critical interfaces is expected to depend not only on the magnitude, but also on the characteristic length scale of the interfacial roughness (Noda
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Figure 1. (400) double-crystal diffraction rocking scans from three 10 period Si/Si$_{1-x}$Ge$_x$ superlattices grown at 620°C (a), 400°C (b) and 250°C (c). Each curve is shifted vertically by one decade for clarity. Structural data for the samples are given in Table 1.

et al., 1991). In that regard, radial scans out of the plane of incidence and off-specular reflectivity are powerful methods for determining the lateral wavelength of the interface corrugation and its degree of correlation from interface to interface (Savage et al., 1991; Miceli, 1993; Headrick and Baribeau, 1993a,b). The scaling behavior of the interfacial width is another question of current interest (Vicsek, 1989; Villain, 1991) that can be addressed by low angle X-ray scattering (You et al., 1993).

The nature of the substrate plays a crucial role in determining the properties of an epitaxial layer. Growth on strain-relaxed buffers, for example (Tuppen et al., 1991), is being explored as a means to circumvent the restrictions of a critical thickness for coherent growth in strained layer epitaxy and to hence change the strain distribution in multilayers (Fitzgerald et al., 1991). Recent progress in semiconductor growth technology has also demonstrated the importance of use of vicinal surfaces for better control of morphology and interfacial phenomena in epitaxial growth of dissimilar materials (Kroemer et al., 1989) or fabrication of novel low dimensional structures (Petroff et al., 1989). In lattice matched and strained layered systems, growth on a misoriented substrate can result in a lattice tilt and complex deformation of the epitaxial layer crystal unit cell (Neuman et al., 1983; Auvray et al., 1989; Maigné et al., 1994a,b). Study of these lattice distortions is possible by double crystal diffraction but requires measurements of several asymmetric reflections in different scattering geometry.

In this paper, we address some of the questions discussed above. First, X-ray reflectivity and double crystal diffraction techniques are applied to the study of various Si/Si$_{1-x}$Ge$_x$ heterostructures including thick (15 nm periodicity) Si/Si$_{1-x}$Ge$_x$ multiple quantum wells and very thin ($S_{m,Ge_{1-y}}$) atomic layer superlattices. In particular, specular reflectivity is used to estimate the superlattice perfection (i.e., period fluctuation) and the roughness of the interfaces in these structures. Next, offset θ-2θ and transverse reflectivity scans are performed to determine the lateral wavelength of this roughness and study its evolution from interface to interface. The influence of thermal annealing on the interfaces is also examined.

Figure 2. Experimental (full lines) and theoretical (dotted lines) X-ray reflectivity curves from the samples of Figure 1 presented in the same order. Fitting parameters are given in Table 1. Here and throughout $c^* = 2\pi/c$, where c is the lattice constant in the growth direction.
X-ray studies of semiconductor heterostructures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth Temp (°C)</th>
<th>( t_{\text{SiGe}} ) (± 0.1 nm)</th>
<th>( t_{\text{Si}} ) (± 0.1 nm)</th>
<th>( \sigma_{\text{SiGe-Si}} ) (± 0.05 nm)</th>
<th>( \sigma_{\text{Si-SiGe}} ) (± 0.05 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1480</td>
<td>250 ± 50</td>
<td>4.8</td>
<td>11.3</td>
<td>0.2 to 2.2</td>
<td>0.3 to 2.4</td>
</tr>
<tr>
<td>Si1481</td>
<td>400 ± 50</td>
<td>4.8</td>
<td>11.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Si1481A</td>
<td>400 ± 50</td>
<td>5.3</td>
<td>10.8</td>
<td>0.55</td>
<td>0.3</td>
</tr>
<tr>
<td>Si1487</td>
<td>620 ± 25</td>
<td>5.0</td>
<td>10.8</td>
<td>1.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*After annealing for 20 seconds at 750°C.

Finally, we focus our attention on the semiconductor substrate and investigate, using double crystal diffraction, the influence of substrate misorientation on the structural properties and relaxation behavior of thick InGaAs/GaAs heterostructures.

Materials and Methods

Epitaxial growth

The Si-Ge epitaxial layers were produced in a VG Semicon V80 molecular beam epitaxy system using a growth methodology described elsewhere (Baribeau et al., 1988, 1989). The \( \text{Si}_{1-x}\text{Ge}_x \) multiple quantum wells were grown on nominal (100) Si (residual misorientation about 0.2° approximately along [001]) in a temperature range of 250-750°C and at a growth rate of about 0.4 nm/s. The \( \text{(Si}_{m}\text{Ge}_{n})_p \) superlattices (m, n < 12) were grown on (100) Si wafers or on wafers vicinal to the (100) orientation (4° off toward [001] and 4-6° off toward [011]) at a temperature between 325 and 400°C and at a growth rate of approximately 0.04 nm/s. The superlattices were deposited on an approximately 150 nm thick epitaxial Si buffer layer and were protected with an approximately 5 nm Si cap. The wafer temperature during growth was measured by infrared pyrometry (above 400°C) or by extrapolation of pyrometric temperature calibration curves (below 400°C).

InGaAs/GaAs heterostructures were grown by low pressure metal organic vapor deposition using arsine, trimethylgallium and trimethylindium (Roth et al., 1989). The growth temperature was kept constant at 625°C. Using growth calibration curves, the layer thickness was varied between 20 nm and 3 µm and the Indium composition was varied between \( x = 0.05 \) and \( x = 0.23 \). Epitaxial layers were deposited on (100) GaAs nominal wafers and on vicinal wafers with a 2° miscut angle towards [001].

X-ray measurements

X-ray reflectometry was performed with a Philips 1820 3θ-2θ vertical goniometer using a 2.5 kW generator and Cu k\( \alpha \) radiation. A divergence slit of 0.25° was used and the instrumental 2θ resolution was estimated ca. 0.02°, with a background signal corresponding to a reflectivity of about \( 5 \times 10^{-7} \). Samples of dimension ca. 2 cm × 2 cm were investigated to reduce instrumental effects at very small incidence angles. At low angle of incidence, the angular resolution of the diffractometer determines a parallel wave vector transfer resolution \( \Delta Q_x \) of the order of \( 1-2 \times 10^{-2} \text{ nm}^{-1} \). The low resolution measurement is thus only sensitive to roughness on spatial frequencies less than the coherent length of \( \sim \pi/\Delta Q_x \). Specular reflectivity curves were analyzed using a recursive formalism (Parratt, 1954) which includes a Debye-Waller modeling of the interface roughness (Croce and Névot, 1976). Fits to experiment were calculated using Philips GIXA simulation software which includes a fit optimization algorithm (Press and Teukolsky, 1991).

High resolution reflectivity measurements were performed at the dipole beam line, F3, using 0.11 nm radiation from the Cornell High Energy Synchrotron Source (CHESS). A (111) Si crystal was used to analyze the reflected beam with an acceptance angle ca. 7.6 arcsec. This allowed us to obtain diffuse scattering intensities within \( \Delta Q_x \sim 10^{-3} \text{ nm}^{-1} \), and the experiment is thus sensitive to roughness with spatial frequency ranging from a few nanometers (determined by the reflectance cut-off effects at grazing incidence) to several micrometers.

Double crystal diffraction (400 rocking curves; +,- geometry) of the \( \text{Si}_{1-x}\text{Ge}_x \) multiple quantum wells was performed on a BEDE 150 instrument using Cu K\( \alpha \) radiation and a (100) Si first crystal. Experimental rocking curves were simulated by dynamical calculation of diffraction (Takagi, 1962; Taupin, 1964). The known nonlinear variation of lattice parameter with Germanium content (Dismukes et al., 1964) was considered in the calculation. Double crystal X-ray rocking curves from InGaAs/GaAs heterostructures were recorded using a Rigaku diffractometer using Cu K\( \alpha \) radiation from a rotating anode source and with a GaAs monochromator crystal. Symmetrical and asymmetrical rocking curves were recorded in either (+,-) or (-,+ ) geometry.
X-Ray Characterization of Si-Ge Heterostructures

Thick Si/Si$_{1-x}$Ge$_x$ multiple quantum wells

In order to investigate the influence of growth temperature on the structural and interfacial properties of Si/Si$_{1-x}$Ge$_x$ heterostructures, a series of multiple quantum well structures were grown in the temperature range $250 \pm 50^\circ C < T < 750 \pm 25^\circ C$. The structures investigated here consist nominally of a 10 period superlattice with $x = 0.35$ and with the Si and Si$_{1-x}$Ge$_x$ layer thicknesses $t_{Si}$ and $t_{SiGe}$ of 10 and 5 nm, respectively. Figure 1 compares the (400) rocking curves from three superlattice structures grown at 250, 400 and 620°C. All the curves exhibit the usual satellite peaks due to the structure periodicity. The sample grown at the intermediate temperature exhibits well-defined satellites with strong thickness fringes arising from the finite dimensions of the superlattice. The satellites in the sample grown at 250°C are somewhat broadened and the thickness fringes are not resolved, indicating poor interfacial quality or, alternatively, presence of microstructural defects. For the sample grown at 620°C, we observe sharp satellites but the lower intensity of high negative order peaks and the weakening of the thickness fringes suggest that the interfaces are not as sharp as in the sample grown at 400°C. Note also that the satellites exhibit no significant shift or broadening, indicating that no appreciable strain relaxation has occurred at 620°C. More pronounced broadening was observed in similar structures grown at 650 and 750°C (not shown).

The amount of information that can be extracted from conventional double-crystal diffraction is somewhat limited in the case of defective or non-ideal superlattice structures (Barnett et al., 1991; Baribeau, 1993b; Baribeau et al., 1993). Further insight on the structural properties of the above superlattices can be obtained by X-ray reflectometry; Figure 2 compares the X-ray reflectivity curves from the same samples. The dotted lines in Figure 2 are simulations obtained using the structural parameters listed in Table 1.

Substantial differences can be seen in these curves. At the intermediate temperature, the reflectivity exhibits fairly sharp satellite peaks whose intensity is modulated due to an approximate 2:1 thickness ratio between the Si
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and Si$_{1-x}$Ge$_x$ layers. For this sample, best fit of the profile is obtained assuming that the roughness at the two different interfaces is different. The simulation suggests that the Si$_{1-x}$Ge$_x$ to Si interfaces are about twice as rough (0.5 nm versus 0.3 nm) as the Si to Si$_{1-x}$Ge$_x$ interfaces. This is in agreement with an earlier study (Hudson et al., 1992), although the magnitude of the roughness found here is about half that reported previously. Calculations using uniform roughness or rougher Si to Si$_{1-x}$Ge$_x$ interfaces consistently resulted in poorer agreement with experiment. The broadening of the Si$_{1-x}$Ge$_x$ to Si interface is probably related to Ge surface segregation in Si-Ge heterostructures as has been reported by several authors (Zalm et al., 1989; Jesson et al., 1991, 1992; Fujita et al., 1991; Grutzmacher et al.; 1993; Lu et al., 1994). The broadening or loss of definition of the high order satellites is explained by a random fluctuation of ca. 5% about the average periodicity across the superlattice (Baribeau, 1993b; Baribeau et al., 1993).

For the superlattice grown at 250°C, the reflectivity shows a sharp decay with angle of incidence. This is direct evidence of a larger interface roughness. Good fit to experiment is obtained by allowing the interfacial roughness to increase linearly from ca. 0.2 nm at the substrate/superlattice interface to ca. 2.5 nm at the top surface. From simple statistical mechanics arguments, fluctuations of the incident atomic beams should result (assuming no surface diffusion) in a coarsening of the growth front that should scale as the square root of the thickness $t$ (Villain, 1991). Attempts to fit the data with a roughness $\sigma$ obeying a power law of the form $\sigma = t^{\beta}$ ($\beta < 1/2$) did not provide good agreement. A value of $\beta$ approaching unity as found here has been associated to grooved or textured surfaces (Tang et al., 1990; Johnson et al., 1994) and may indicate the onset of polycrystalline growth or poor epitaxial growth at 250°C.

For higher growth temperature (620°C), the experimental reflectivity exhibits sharp but weak satellite peaks. This suggests that the structure has a well defined periodicity but that the mass contrast between the two layers in the superlattice period is small. The experimental reflectivity can be qualitatively reproduced by increasing considerably (see Table 1) the roughness at the Si$_{1-x}$Ge$_x$ to Si interface. This would be consistent with the observation of an undulation of the Si$_{1-x}$Ge$_x$ to Si interface of wavelength of about 100 nm and amplitude of 2 nm in similar superlattices grown at 580°C (Kuan and Iyer, 1991; Phang et al., 1993). Such waviness over a length scale comparable to the X-ray coherence length would result in an apparent broadening of the composition profile at the interface, consistent with the modeling. This result emphasizes the importance of not only the strain relaxation, but also of the intermixing and growth morphology problems for high temperature growth of Si-Si$_{1-x}$Ge$_x$ heterostructures. More information about the in-plane structure of the roughness can be obtained from X-ray reflectivity rocking scans (see below).

The double crystal rocking curve from the superlattice grown at 400°C is next analyzed in light of the X-ray reflectivity results. Figure 3 displays two dynamical simulations of the experimental data obtained using the thickness values determined from the reflectivity study, and calculated assuming two different composition profiles at the Si$_{1-x}$Ge$_x$ to Si interface. It is found that modeling with perfectly abrupt interfaces results in a relatively poor fit to experiment, especially for the high negative orders satellite reflections. A closer fit to experiment is obtained when the Si$_{1-x}$Ge$_x$ to Si interface is graded exponentially over a distance of 2 nm (see inset, Figure 3). Although detailed modeling of the interfaces is difficult in double-crystal diffraction, this result is consistent with a 0.5 nm interfacial broadening and supports the idea of asymmetrical interfaces in these superlattices.

The effect of annealing on the Si$_{1-x}$Ge$_x$/Si multiple quantum wells was also examined. Figure 4 shows reflectivity curves from the superlattice grown at 400°C before and after annealing for 20 seconds at 750°C. The data show that annealing results in a small damping of the high order satellites and in a substantial change in the modulation intensity envelope. The first observation indicates some loss of interface sharpness while the second is consistent with a change in the Si to Si$_{1-x}$Ge$_x$ layers thickness ratio. The latter may appear somewhat surprising considering the mildness of the heat treatment, but is explained by the strong composition dependence of the Ge diffusion coefficient of Ge in Si$_{1-x}$Ge$_x$ as a function of Ge composition (McVay and DuCharme, 1974; Schorer et al., 1991; Baribeau, 1993a; Hamberger et al., 1993). The diffusion of Ge in pure Si being extremely slow, the Si$_{1-x}$Ge$_x$ distribution profile is expected to broaden gradually in a way in which the maximum Ge concentration in the layer is reduced through a thickening process that leaves relatively sharp Si-Si$_{1-x}$Ge$_x$ boundaries. Good fit (see Figure 4 and Table 1) of the reflectivity curve after annealing is obtained by simply increasing the alloy layer thickness by 0.4 nm while keeping the period length constant and leaving the interface roughness relatively unchanged. This result again shows that besides strain relaxation, intermixing is another phenomenon that may restrict the thermal budget for processing Si-Si$_{1-x}$Ge$_x$ heterostructures.

Figure 5 shows a comparison of X-ray reflectivity rocking scans for three different growth temperatures. The data show a sharp specular peak in each case and...
broad diffuse components. The intensity of the specular component is influenced by interface smearing (interdiffusion) and also by roughness, while the diffuse scattering is related to roughness only. It can be characterized by an interface width, \( \sigma \), and in-plane longitudinal correlation length, \( \xi_x \). The three scans are taken along the direction of miscut (0.2° approximately towards [001]) in order to emphasize any asymmetry related to interface step structures. Scans are through the 5th order satellite peak so that vertically correlated roughness dominates the diffuse scattering. In general, we see two distinct types of diffuse scattering: a compact asymmetric component with peaks at about \( \pm 5 \, \mu m^{-1} \), and a much broader symmetric component with a peak at \( Q_x = 0 \). The azimuthal direction of the asymmetry is oriented along the direction of miscut on all samples measured so far and is due to a one-dimensional corrugation of the interface (Headrick and Baribeau, 1993a,b). The line-shape often resembles that of a staircase structure, although the "step" height is probably a few nanometers, rather than a single (or double) monolayer step. This structure is propagated through the entire thickness of the multilayer and does not appear to vary in a systematic way as a function of growth temperature. Presence of large steps (and small terraces) is conceivable since it is known that formation of double layer steps on Si surfaces vicinal to (100) requires high temperature annealing treatments (Bringans et al., 1986; Saloner et al., 1987). However, the absence of strong asymmetry for the 250°C growth suggests that the step propagation is inhibited for growth at low temperature. In contrast, the broader symmetric component exhibits systematic variations with the superlattice growth temperature, and hence, is thought to be intrinsic to the superlattice film growth. It is related to roughness with a lateral wavelength \( < 0.1 \, \mu m \) on all \( Si_{1-x}Ge_x/Si \) samples measured so far. In Figure 6, we plot the intensity of the broad diffuse component and the specular component at the 5th order peak as a function of growth temperature. At the lowest growth temperature of 250°C, the high diffuse scattering is indicative of large amplitude roughness. From the width of the diffuse scattering component of Figure 5, we estimate that \( \xi_x \) on the order of 100 nm at 250°C. The sample grown at 400°C exhibits a sharp reduction in the broad component of diffuse scattering and an increase in the specular component, indicating sharper interfaces at least with respect to the short lateral wavelength roughness. At still higher growth temperatures, the specular component drops sharply and the diffuse scattering increases, indicating the presence of roughness or vertically correlated interface undulations (Kuan and Iyer, 1991). Scans along \( Q_z \) through diffuse
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Figure 7. Experimental (full lines) and theoretical (dotted lines) X-ray reflectivity curves from a 20 period Si$_7$Ge$_3$ atomic layer superlattice. The calculation in the lower trace was obtained assuming constant periodicity throughout the superlattices. The upper trace calculation was obtained by introducing a random variation of the Ge and Si layer thicknesses. The histograms in inset are the thickness distributions used in the calculation.

Figure 8. Experimental (full lines) and theoretical (dotted lines) X-ray reflectivity curves from a 20 period Si$_7$Ge$_3$ atomic layer superlattice. The calculation in the lower and upper traces were obtained by introducing a random variation of the Ge and Si layer thicknesses according to the corresponding histograms in inset.

scattering (not shown) are significantly broadened relative to the specular component for growth at 620 and 750°C indicating reduced vertical correlation of the roughness (Baribeau et al., 1995).

To summarize this section on Si$_{1-x}$Ge$_x$/Si multiple quantum wells, we discuss general conclusions about the influence of growth temperature on interface roughness. The Si$_{1-x}$Ge$_x$ growth surface is rougher than the Si surface over a broad range of growth temperatures (400 - 750°C). This effect has been observed before (Xie et al., 1993; Kuan and Iyer, 1989) and is believed to be driven by compressive strain in the Si$_{1-x}$Ge$_x$ growing film. Subsequent overgrowth of a silicon layer actually smooths out the growth front while the roughness of the Si to Si$_{1-x}$Ge$_x$ interface remains nearly constant over this range of growth temperatures. The roughness of the Si$_{1-x}$Ge$_x$ to Si interface generally increases with increasing growth temperature, consistent with a kinetically limited, strain-driven model for the roughness. For each sample, the amplitude of the roughness is nearly constant over the thickness of the heterostructure other than a smooth/rough alternating pattern. Ge surface segregation also possibly contributes to the loss of chemical abruptness at the Si$_{1-x}$Ge$_x$ to Si interfaces.

Growth in the low temperature regime (250°C) is characterized by rapidly increasing roughness as growth proceeds in contrast to the higher temperature growth discussed above. An unusual feature of this is that it is highly vertically correlated, so that features on the growth front continuously increase in amplitude. This behavior has also been observed by high resolution TEM (Eaglesham, private communication). The amplitude as a function of time is characterized by $\sigma \propto t^\beta$, where $\beta$ is found to be $\sim 1$. In the case of randomly deposited atoms, $\beta = 0.5$, so the observed roughening is faster than a random deposition and may indicate the onset of polycrystalline growth.

Below, we discuss reflectivity results for a similar system, (Si$_m$Ge$_n$)$_p$ short-period superlattices on 4° miscut (100) Si.

(Si$_m$Ge$_n$)$_p$ atomic layer superlattices

(Si$_m$Ge$_n$)$_p$ short-period superlattices are another type of heterostructures that have stimulated considerable interest recently (Pearsall, 1989; Presting et al., 1992). These structures are made of very thin (few monolayers) alternating layers of pure Si and Ge and are attractive because they constitute a novel class of man-made semiconductor materials to which optoelectronic properties can be tailored by a judicious choice of the layer thickness and strain distribution (Froyen et al., 1987). In
particular, direct band gap character has been predicted for certain strain/thickness combinations, although unambiguous observation of direct gap behavior is yet to be reported (Noël et al., 1992). Besides their technological relevance, these superlattices are interesting model systems to investigate interface properties at the atomic level (Lockwood et al., 1993; Baribeau et al., 1994).

As was pointed out previously (Baribeau, 1992), conventional double crystal diffraction is not ideally suited to study properties of structures of very short periodcity and very small total thickness. On the other hand, on- and off-specular X-ray reflectivity is a powerful probe for such multilayer structures. In earlier work (Baribeau et al., 1994; Headrick and Baribeau, 1993a,b), interface properties of (Si_{12}Ge_{8})_{50} and (Si_{2}Ge_{12})_{48} superlattices were investigated. In these studies, the interface roughness of these structures was estimated to be about two monolayers. Off-specular reflectivity revealed a strong vertical correlation of this interfacial roughness for growth on (100) Si. Rocking scans were also consistent with a correlation length of ca. 0.3 μm in the plane of growth.

The modification of the band gap in very thin superlattices arises from a folding of the band structure due to the super periodicity of the structure (Gnutzmann and Clausecker, 1974). This concept remains valid to the extent that heterostructures with constant period length and well-defined interfaces can actually be grown. To elucidate these questions, different (Si_{n}Ge_{10})_{p} superlattices were examined by X-ray reflectometry. Figure 7 shows the reflectivity curve from a (Si_{7}Ge_{3})_{20} sample together with calculated curves in which the individual layer thickness is fixed or is allowed to vary. It can be seen that a constant periodicity provides a relatively poor fit of the data whereas an excellent match is obtained when random thickness fluctuations are introduced in the structure. The layer thickness distribution used in the calculation is shown in inset in Figure 7. It should be emphasized that other thickness distributions can provide very good fit to data, as is demonstrated for another similar superlattice in Figure 8. These results, however, suggest that the periodicity in these structures can be controlled to at least a 5% accuracy. From the modeling, the interface roughness is estimated to be about 0.2-0.3 nm in these superlattices but no conclusion about possible asymmetry in the interfaces could be drawn from the analysis.

Figure 9 shows data from a (Si_{7}Ge_{3})_{20} sample grown on a 4° miscut (100) Si substrate towards [011]. High resolution X-ray reflectivity scans can, through the first order Bragg peak, demonstrate a large asymmetry.
in the roughness when the X-ray beam is aligned with the miscut direction. The scans are carried out to large Qx to show the large asymmetry in the short-wavelength roughness. The scan perpendicular to the miscut direction shows a more symmetric line shape with more diffuse scattering at shorter frequencies.

In summary, the X-ray investigation of (SimGen)p, atomic layer superlattices leads us to conclude that there are serious instrumental and physical limitations to growth of such artificially layered structures. Due to fluctuations in the deposition fluxes, it is difficult to maintain a constant (and reproducible) period length in these structures. Possibly due to Ge surface segregation, even use of very low growth temperatures does not allow formation of chemically abrupt interfaces. Although surfactant-assisted growth (Cao et al., 1992; Rioux and Hochst, 1993; Sakamoto et al., 1993) may resolve this problem, earlier studies (Lockwood et al., 1993) have shown that the fast diffusion rate of Ge in Ge-rich Si1-xGex alloys seriously restricts thermal processing of these heterostructures. Finally, X-ray rocking scans revealed that the interfacial roughness is influenced by that of the substrate and that vertical correlation of the roughness is present in these structures. Although the idea of band gap engineering using atomic layer superlattices may be quite appealing, practical realization of these structures remains a technological challenge.

### Residual Strain and Triclinic Deformation of Relaxed Epitaxial Layers

In lattice mismatched systems, the growth of strain-free, defect-free buffer layers could lead, if successful, to the development of new optoelectronic applications. However, a major obstacle seems to be the presence of residual strain, even for thick layers, which makes difficult the prediction of the in-plane lattice parameter of the surface hosting the device structure. The measurement of the residual strain and hence its reduction through different growth procedures can be achieved using double-crystal diffractometry.

Symmetrical (400) reflections are commonly used to measure the lattice parameter, c, in the growth direction. The peak spacing between the epitaxial layer and substrate has, however, a tilt component which results from an inclination of the (100) epitaxial layer planes with respect to the (100) substrate planes. In order to cancel the contribution from this tilt, two (400) rocking curves, corresponding to two different values of the azimuth angle (180° apart), have to be measured. This procedure is straightforward and has been described in details elsewhere (Pasek et al., 1991). It must be pointed out that the variation of the (400) peak spacing as a function of the azimuth can be interpreted only by an inclination of the (100) planes. If the epitaxial layer unit cell is assumed to have retained its tetragonal symmetry, the epitaxial tilt then corresponds to a rigid body rotation of the structure with respect to the underlying substrate.

Residual strain measurements require also the determination of the lattice parameter, a, parallel to the interface. This is done by recording {hkl} reflections such as the (511) or (422). In these cases, the incident beam can be diffracted by four equivalent sets of planes corresponding to four orthogonal values of the azimuth angle. The peak spacing between the epitaxial layer and the substrate peak is then a function of the alloy composition, the state of strain in the epitaxial layer as well as the epitaxial tilt. The value of the in-plane lattice parameter and hence, the residual strain, ε, can be easily obtained from the average of the four asymmetrical peak spacing (Wie et al., 1988).

Such a procedure has been used to study the residual strain in InGaAs/GaAs heterostructures. The residual strain as well as the In composition are listed for the samples under investigation in Table 2. The data can be better compared by introducing a relaxation coefficient for each layer, defined by R = (1-ε/β), where β is the lattice mismatch. The variation of R as a function of a normalized epitaxial layer thickness t = h/he is presented in Figure 10. Here h_e is the critical layer thickness. The expression for the critical thickness used in the present work is:

$$h_e = (b/4\pi f)[(1-\nu)/2(1+\nu)][\ln(ah_e/b) + 1]$$  (1)

with the core parameter, a, taken equal to 0.4 nm and, b, the magnitude of the Burger's vector for the 60° type

<table>
<thead>
<tr>
<th>Sample</th>
<th>t (nm)</th>
<th>In Content (degree)</th>
<th>ρ</th>
<th>h_e (nm)</th>
<th>ε/β</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0.192</td>
<td>&lt;0.5</td>
<td>9.3</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0.223</td>
<td>2</td>
<td>7.7</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>0.227</td>
<td>&lt;0.5</td>
<td>7.5</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>0.222</td>
<td>2</td>
<td>7.8</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>0.235</td>
<td>&lt;0.5</td>
<td>7.2</td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>0.195</td>
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<td>9.1</td>
<td>1.07</td>
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<td>7</td>
<td>3000</td>
<td>0.06</td>
<td>2</td>
<td>37.2</td>
<td>0.06</td>
</tr>
<tr>
<td>8</td>
<td>3000</td>
<td>0.108</td>
<td>2</td>
<td>18.6</td>
<td>0.11</td>
</tr>
<tr>
<td>9</td>
<td>3000</td>
<td>0.158</td>
<td>2</td>
<td>11.8</td>
<td>0.16</td>
</tr>
</tbody>
</table>

X-ray studies of semiconductor heterostructures
Figure 11. Four different \{511\} rocking scans from an InGaAs/GaAs heterostructure.

Table 3. Substrate and epilayer Bragg peak spacing for the four different sets of \{511\} planes for a typical InGaAs/GaAs heterostructure grown on a vicinal (100) GaAs substrate. $\Delta_{\text{exp}}$ is the experimental value, $\Delta_1$ is the calculated value including tetragonal distortion and lattice tilt, $\Delta_2$ is calculation including triclinic distortion and lattice tilt.

<table>
<thead>
<tr>
<th>hkl</th>
<th>$\Delta_{\text{exp}}$ (± 10 arcsec)</th>
<th>$\Delta_1$ (arcsec)</th>
<th>$\Delta_2$ (arcsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5\overline{1}</td>
<td>2415</td>
<td>2419</td>
<td>2414</td>
</tr>
<tr>
<td>51\overline{1}</td>
<td>3285</td>
<td>3218</td>
<td>3285</td>
</tr>
<tr>
<td>511</td>
<td>2976</td>
<td>2971</td>
<td>2975</td>
</tr>
<tr>
<td>5\overline{1}</td>
<td>2019</td>
<td>2085</td>
<td>2021</td>
</tr>
</tbody>
</table>

dislocation). The value of $h_c$ for each layer is given in Table 2 and was calculated assuming isotropic elastic constants, a dislocation core radius of 0.4 nm and 60° type dislocations. Similar results have been found by other authors and have been plotted in Figure 10. Results of Dunstan et al. (1991) are in very good agreement with our data, in particular the value of $R$ reached in the plateau is within a few percent of our experimental value. In contrast, the study of Krishnamoorthy et al. (1992) showed a similar trend in the behavior of $\tau$ as a function of $R$, but a substantial residual strain was observed for very thick films. It must be pointed out that, in the three studies, the samples under investigation cover about the same range in composition and layer thickness. In addition, our samples have been grown by metal-organic chemical vapor deposition (MOCVD) at a temperature of 625°C (Roth et al., 1989), while the two other sets of samples have been grown by molecular beam epitaxy at about the same temperature. These experimental data, which can be compared to available models for strain relaxation (Matthews et al., 1970; Mareè et al., 1987; Dodson and Tsao, 1987), show that strain-free buffer layers are difficult to achieve and the magnitude of the residual strain, which does not depend solely upon layer thickness and layer composition, is difficult to predict for a given material system.

Additional information on the structural properties of partially relaxed layers can be obtained by a careful analysis of the individual asymmetrical peak spacing as represented in Figure 11 and summarized in Table 3 for a particular sample. Also indicated in Table 3 are the values of the calculated peak spacing for each \{511\} reflection, expected from a tetragonal unit cell tilted with respect to the substrate (Maigné et al., 1994a,b). The agreement is poor for the \{511\} and \{5\overline{1}1\} reflections. This demonstrates that this particular sample does not
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Table 4. Thickness $t$, nominal substrate misorientation $\rho$, tilt magnitude $\alpha$ and tilt direction $\chi$ measured with respect to the [010] direction. $\beta$, $\gamma$ and $\delta$ are the parameters corresponding to the triclinic distortion described in Figure 12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$t$ (nm)</th>
<th>$\rho$ (degrees)</th>
<th>$\alpha$ (± 10 arcsec)</th>
<th>$\chi$ (± 2°)</th>
<th>$\beta$ (± 0.05°)</th>
<th>$\gamma$ (± 35 arcsec)</th>
<th>$\delta$ (± 10°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>&lt;0.5</td>
<td>152</td>
<td>47</td>
<td>-</td>
<td>83</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>2</td>
<td>218</td>
<td>180</td>
<td>-</td>
<td>190</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>&lt;0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>53</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>2</td>
<td>153</td>
<td>159</td>
<td>-</td>
<td>419</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>&lt;0.5</td>
<td>496</td>
<td>26</td>
<td>-</td>
<td>86</td>
<td>127</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>2</td>
<td>1212</td>
<td>38</td>
<td>0.12</td>
<td>452</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>3000</td>
<td>2</td>
<td>133</td>
<td>18</td>
<td>0.06</td>
<td>54</td>
<td>293</td>
</tr>
<tr>
<td>8</td>
<td>3000</td>
<td>2</td>
<td>370</td>
<td>128</td>
<td>0.12</td>
<td>95</td>
<td>153</td>
</tr>
<tr>
<td>9</td>
<td>3000</td>
<td>2</td>
<td>628</td>
<td>341</td>
<td>0.06</td>
<td>205</td>
<td>319</td>
</tr>
</tbody>
</table>

have a tetragonal symmetry. On the other hand, if a triclinic deformation, as the one described in Figure 12, is assumed, an excellent agreement is reached with the experimental data. The angle $\beta$ is explained by an asymmetry in the dislocation densities along orthogonal $<011>$ in-plane directions, leading to an asymmetry in strain relief. The deformation is also characterized by an angle $\gamma$ which corresponds to the fact that the [100] direction of the epitaxial layer is no longer perpendicular to the (100) planes but makes an angle equal to $\pi/2 - \gamma$. The presence of such a distortion can be interpreted as a balance of the effect of the epitaxial tilt in order to keep the [100] direction of the epitaxial layer parallel to that of the substrate, provided that the two angles are equal and that the direction of the tilt is opposed to that of the distortion. This effect has been observed in AlGaAs layers grown on misoriented GaAs substrates (Lieberich and Levkoff, 1990).

A similar analysis has been performed on the other heterostructures and the results are summarized in Table 4, along with the magnitude and direction of the epitaxial tilt as obtained from the analysis of the (400) rocking curves. It can be seen that thick partially relaxed layers always display a triclinic deformation of their unit cell. However, it was not possible to establish a correlation between the characteristics of the distortion and the characteristics of the tilt, but it can be seen that the magnitude of the angle $\gamma$ depends upon the misorientation of the substrate (see Table 2).

Conclusion

In this work, we have applied X-ray scattering techniques to the study of structural properties of semiconductor heterostructures with special focus on interface formation and phenomena. Glancing incidence X-ray scattering has been used to investigate the nature of the interfacial roughness in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ multiple quantum wells. Significant differences have been found on the magnitude, vertical correlation and characteristic length of the interface corrugation as a function of growth temperatures. In particular, the analysis showed that smoother interfaces are obtained for growth at temperatures between 400-550°C. Growth at both low (250°C) or high temperature (> 620°C) resulted in comparatively poorer interfaces due, respectively, to a coarsening of the growth front and to intermixing and/or long range undulation at the interfaces. Atomic layer ($\text{Si}_{n}\text{Ge}_{m}$)$_p$ superlattices were also examined. These exhibit an interfacial roughness of magnitude comparable to the physical dimensions of the layers. The data analysis revealed vertical thickness fluctuations of the order of 5% that could also be detrimental to the exploitation of electronic effects related to zone folding. Finally, we have presented a study of the relaxation of thick InGaAs epitaxially films on (100) GaAs and vicinal surfaces. Interestingly, we found that substantial residual strain is present in layers with thickness by far exceeding the critical thickness for pseudomorphic growth. The data presented could be helpful for testing or refining current models for strain relaxation. The measurement also showed that thick relaxed epitaxial layers are triclinically distorted. This effect is more pronounced on vicinal surfaces and may have important consequences if these relaxed layers are to be used as host surfaces for subsequent growth of active epitaxial layers in device structures.

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Phys. 5: 426-430.


Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.