Growth of Si$_{1-x}$Ge$_x$(011) on Si(011)16×2 by gas-source molecular beam epitaxy: Growth kinetics, Ge incorporation, and surface phase transitions

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(Received 8 June 1998; accepted for publication 1 October 1998)

Single crystal Si$_{1-x}$Ge$_x$(011) layers with $x \leq 0.35$ have been grown on double-domain Si(011)16×2 surfaces from Si$_2$H$_6$/Ge$_2$H$_6$ mixtures at temperatures $T_s = 400$–950 °C. D$_2$ temperature programmed desorption was used to show that the structure of the Si(011)16×2 surface unit cell, more correctly written as $\frac{17}{2}1$ since the unit cell vectors are nonorthogonal, is composed of 16 adatoms and eight π-bonded dimers with a dangling bond density half that of the 1×1 surface. Si$_{1-x}$Ge$_x$(011) overlayers are “16×2” when $x < x_c(T_s)$ and “2×8” with $x > x_c(T_s)$. The value of $x_c$ decreases from $0.10$ at $T_s = 475$ °C to $0.08$ at $550$ °C to $0.06$ at $650$ °C. Both the “2×8” and “16×2” Si$_{1-x}$Ge$_x$(011) surface reconstructions gradually and reversibly transform to 1×1 at $T_s$ between 650 and 725 °C. Film growth kinetics exhibit three distinct regimes. At low temperatures ($T_s \leq 500$ °C), the film deposition rate $R_{SiGe}$ decreases exponentially with $1/T_s$ in a surface-reaction-limited growth mode for which the rate-limiting step is hydrogen desorption from Si and Ge monohydride phases. $R_{SiGe}$ becomes essentially constant with $T_s$ in the intermediate impingement-flux-limited range, $T_s = 500$–650 °C. At $T_s > 650$ °C, $R_{SiGe}$ increases again with $T_s$ due initially ($T_s = 650–725$ °C) to an increase in the steady-state dangling bond coverage as the surface reaction-limited growth mode transforms to 1×1. The continued increase in $R_{SiGe}$ at even higher $T_s$ is associated with strain-induced roughening. Ge/Si ratios in as-deposited films are linearly proportional to the incident Ge$_2$H$_6$/Si$_2$H$_6$ flux ratio $J_{GeH_6}/J_{SiH_6}$ and nearly independent of $T_s$ indicating that the reactive sticking probabilities of Si$_2$H$_6$ and Ge$_2$H$_6$ have very similar temperature dependencies. $R_{SiGe}(J_{GeH_6}/J_{SiH_6}, T_s)$ in both the surface-reaction-limited and flux-limited regimes is well described by a simple kinetic model incorporating second-order dissociative chemisorption and second-order hydrogen desorption as rate-limiting steps.

I. INTRODUCTION

Gas-source molecular beam epitaxy (GS-MBE) has been shown to provide several advantages over solid-source MBE for the growth of Si and Si$_{1-x}$Ge$_x$ alloys. These include: elimination of hot crucibles and the change in deposition rate associated with charge depletion, higher sample throughput, better conformal coverage, better lateral film thickness uniformity, and the potential for selective epitaxy on patterned substrates. While initial GS-MBE experiments were carried out using SiH$_4$ and GeH$_4$, more recent results have demonstrated that the use of Si$_2$H$_6$ and Ge$_2$H$_6$ as precursors for Si and Ge growth yields reactive sticking probabilities up to two orders of magnitude higher. This is primarily due to the ease of cleaving IV–IV, compared to IV–H, bonds. Predictive models of the growth rates of GS-MBE Si$_x$Ge$_{1-x}$ and Si$_{1-x}$Ge$_x$ on Si(001) as functions of incident fluxes and deposition temperatures have been developed based upon dissociative chemisorption of the dihydride molecules followed by a series of surface decomposition reactions with the final step being hydrogen desorption from Si and/or Ge monohydride. The models exhibit very good agreement with experimental results. In the case of Si$_{1-x}$Ge$_x$(001) growth, Ge segregation as a function of steady-state hydrogen coverage is also accounted for. The Si$_{1-x}$Ge$_x$/Si(001) system offers potential benefits over Si$_{1-x}$Ge$_x$/Si(001) for certain types of device applications. Strained Si$_{1-x}$Ge$_x$/Si(001) heterostructures have additional degrees of freedom for band gap engineering: the maximum film/substrate conduction-band offset is predicted to be substantially larger, the optical band gap decreases more rapidly with increasing $x$, and optical selection rules allow hole–intersubband transitions to be excited by light polarized parallel to Si$_{1-x}$Ge$_x$/Si(001) multiple quantum well layers. The Si$_{1-x}$Ge$_x$/Si(001) system also exhibits novel dislocation structures and highly asymmetric in-plane strain relaxation. While $a/2(110)$ misfit dislocation glide is allowed on all {111} planes along all {110} interfacial directions in Si$_{1-x}$Ge$_x$/Si(001) heterostructures, they are constrained to glide only on $\{1\bar11\}$ and $\{111\}$ planes and only along one $\{110\}$ in-plane direction, [1 1 0], in Si$_{1-x}$Ge$_x$/Si(001). Another striking difference between Si$_{1-x}$Ge$_x$(001) and Si$_{1-x}$Ge$_x$(001), which has a significant effect on film growth

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kinetics and mechanistic rate limitations during gas-source film growth, is the higher complexity of the Si$_{1-x}$Ge$_x$(011) surface unit cell. Initial reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) studies of the Si(011) surface revealed a variety of reconstructions, including 2\(\times\)1, 4\(\times\)5, 5\(\times\)1, 7\(\times\)1, 9\(\times\)1, "\(\chi\)", and faceted structures.\(^{6,8}\) However, subsequent LEED and Auger electron spectroscopy (AES) results by Ichinokawa et al.\(^{10}\) demonstrated that all are due to Ni contamination and that the clean Si(011) surface has a complex reconstruction which they termed "16\(\times\)2." Yamamoto et al.\(^{11}\) confirmed the Ni-induced reconstructions and reported a "16-structure" for the clean surface.

Based upon an analysis of LEED results, Ampo et al.\(^{12}\) proposed that the Si(011) clean-surface reconstruction is "16\(\times\)2" with a unit cell composed of upper and lower terraces of equal widths and separated by single-atom-height steps along the [2 \(\bar{1}\) 1] direction. Miura et al.\(^{13}\) demonstrated that the Si(001) surface structure, while labeled "16\(\times\)2" based upon observed diffraction pattern periodicities, actually has a [\(\bar{1} 2 \bar{1}\)] reconstruction. This was verified by van Loenen et al.\(^{14}\) using scanning tunneling microscopy (STM). The detailed atomic configurations on the upper and lower terraces were, however, still unknown. Proposed configurations include structures in which the surface atoms form dimers and trimers,\(^{15}\) adatoms,\(^{16,17}\) or adatoms and dimers.\(^{18-20}\) Recently, Kim et al.\(^{21}\) used temperature programmed desorption (TPD) to show that the Si(011) surface unit cell is composed of adatoms and dimers.

Ichinokawa et al.\(^{10}\) found, based upon LEED results, that the "16\(\times\)2" surface reconstruction undergoes a gradual and reversible transition to 1\(\times\)1 during high temperature annealing. The transition temperature, as determined by LEED and RHEED investigations, was reported as 760 °C by both Yamamoto et al.\(^{11}\) and Shimaoka.\(^{22}\) In a later article, Yamamoto et al.\(^{23}\) observed, using STM, that the "16\(\times\)2" to 1\(\times\)1 transformation starts at 710 °C and is complete at 770 °C.

Much less data are available on the surface structure of Si$_{1-x}$Ge$_x$(011), and local atomic configurations are completely unknown. Miura et al.\(^{13}\) used LEED and AES to show that depositing Ge, with coverages \(\theta_{Ge}\) up to 4.1 ML, on Si(011) and post-annealing for one minute at 650 °C results in Ge/Si intermixing which in turn gives rise to several reversible temperature-dependent surface phase transitions upon subsequent heating. The "16\(\times\)2" reconstruction was obtained with \(\theta_{Ge} < 0.3\) ML and \(T < 720°C\), a [\(\bar{1} 3 \bar{1}\)] reconstruction at 0.3 < \(\theta_{Ge}\) < 0.7 ML with \(T < 640°C\), and a [\(\bar{3} 1\)] reconstruction at 0.8 ML < \(\theta_{Ge}\) < 4.1 ML with \(T < 620°C\). At higher temperatures, all three reconstructions transformed to 1\(\times\)1. Butz and Lüth\(^{24}\) used STM to investigate the surface structure of Si$_{1-x}$Ge$_x$ films grown by solid-source MBE. Si$_{1-x}$Ge$_x$ layers with \(x \leq 0.06\) had surface terraces of width 3.9 nm, with step edges along [\(\bar{1} 1 \bar{3}\)] and [\(\bar{1} \bar{1} \bar{3}\)], while the terraces of films with \(x \approx 0.10\) were only 1.9 nm wide with step edges along [\(\bar{1} 1 \bar{2}\)].

There are no detailed studies in the literature on the growth kinetics of Si or Si$_{1-x}$Ge$_x$ deposited on Si(011) by gas-source techniques. Liu et al.\(^{7}\) reported the deposition of Si$_{1-x}$Ge$_x$(011) films by rapid-thermal chemical vapor deposition from SiCl$_2$H$_2$ and GeH$_4$ at \(T_s = 625°C\) and found that, compared to deposition on Si(001) substrates, the 011 film growth rate \(R_{SiGe}\) was a factor of two to three times lower although the Ge content \(x\) was similar. Both \(R_{SiGe}\) and \(x\) increased with increasing GeH$_4$ flow rates.

In this article, we present the results of an investigation of composition- and temperature-dependent surface phase transitions and their role in controlling the kinetics of Si$_{1-x}$Ge$_x$(011) growth by GS-MBE from SiH$_4$ and GeH$_4$. All films were deposited on Si(011) at \(T_s = 400–950°C\) with dihydride precursor fluxes \(J_{SiH_4} = 2.2 \times 10^{16} cm^{-2} s^{-1}\) and \(J_{GeH_4} = 0–7.8 \times 10^{14} cm^{-2} s^{-1}\). D$_2$ TPD analyses reveal that the unit cell of the Si(011) 16\(\times\)2 reconstructed surface consists of 16 adatoms and eight \(\pi\)-bonded dimers with a maximum dangling bond density which is only half that of the 1\(\times\)1 structure. RHEED and LEED results show that the Si(011) 16\(\times\)2 surface gradually transforms to a bulk terminated 1\(\times\)1 structure over a temperature range between 700 and 725 °C. Si$_{1-x}$Ge$_x$(011) films grown on Si(011) at temperatures below the 1\(\times\)1 transition have the "16\(\times\)2" surface reconstruction at low Ge concentrations but transform to a "2\(\times\)8" reconstruction at a critical concentration \(x_c\) which ranges from \(\approx 0.10\) at \(T_s = 475°C\) to 0.06 at \(T_s = 650°C\). Both the "16\(\times\)2" and "2\(\times\)8" Si$_{1-x}$Ge$_x$(011) surface reconstructions also transform reversibly to 1\(\times\)1. The transformation temperature range varies from \(\approx 700–725°C\) at low Ge concentrations to 650–725°C for Si$_{0.65}$Ge$_{0.35}$.

For a given \(J_{GeH_4}/J_{SiH_4}\) flux ratio, Si$_{1-x}$Ge$_x$(011) growth kinetics are characterized by three primary temperature regimes. At low temperatures, growth proceeds in a surface-reaction-limited mode in which the rate-limiting step is hydrogen desorption from the monohydride phase and \(\log(R_{SiGe}) \propto 1/T_s\). In the intermediate temperature range, film growth is limited by the flux impingement rate and is essentially independent of \(T_s\). At higher temperatures, \(R_{SiGe}\) increases again as the Si$_{1-x}$Ge$_x$ surface reconstruction gradually transforms to 1\(\times\)1 with a higher surface dangling bond density. \(R_{SiGe}(J_{GeH_4}/J_{SiH_4}, T_s)\) results in the surface-reaction and flux-limited regimes are well described by a simple kinetic model incorporating second-order dissociative chemisorption and hydrogen desorption as rate-limiting steps.

II. EXPERIMENTAL PROCEDURE

All films were grown in a multichamber ultra-high-vacuum system (described in detail in Refs. 2 and 25) evacuated using a combination of ion and turbomolecular pumps to provide a base pressure of 5 \times 10^{-11} Torr. The GS-MBE system contains a film growth chamber equipped with an in situ RHEED apparatus. A sample transfer chamber connects to an analytical chamber with provisions for TPD, LEED, AES, and electron energy loss spectroscopy (EELS).

The film growth experiments were carried out at temperatures \(T_s = 400–950°C\) using a Si$_2$H$_6$ flux \(J_{SiH_4} = 2.2 \times 10^{16} cm^{-2} s^{-1}\) and Ge$_2$H$_6$ fluxes \(J_{GeH_4} = 0–7.8 \times 10^{14} cm^{-2} s^{-1}\). During deposition, the Si$_2$H$_6$ and Ge$_2$H$_6$ molecular
beams are delivered to the substrate through individual, directed tubular dosers located 3 cm from the substrate at an angle of 45°. The dosers are coupled to feedback-controlled constant-pressure reservoirs in which pressures are separately monitored using capacitance manometers. Valve sequencing, gas flows, and substrate temperature are all computer controlled.

The substrates used in these experiments were $13 \times 3 \text{cm}^2$ plates cleaved from 0.38-mm-thick $n$-type (resistivity $=0.5-2.0 \ \Omega \ \text{cm}$) Si(011) wafers with a miscut of 0.36° along [772]. Initial cleaning consisted of degreasing by successive rinses in trichloroethane, acetone, propanol, and deionized DI water followed by four consecutive oxidation/etch cycles composed of a 2 min dip in an oxidizing solution of $6:1:1 \ \text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{O}_2$, a 30 s rinse in DI water, a 20 s etch in dilute (2%) HF, and a final 30 s rinse in fresh DI water. The substrates were then blown dry in ultra-high-purity N$_2$, exposed to a UV ozone treatment in which they were irradiated from a low-pressure Hg lamp ($15 \ \text{mW cm}^2$) for 30 min in air to remove C-containing species, and introduced into the deposition system. The substrates were heated by direct current to $600 \ ^\circ \text{C}$ and degassed for 5 h, then rapidly heated at $100 \ ^\circ \text{C s}^{-1}$ to $1100 \ ^\circ \text{C}$ for 1 min to remove the oxide. Temperatures were calibrated using chrome-alumel thermocouples and an optical pyrometer. RHEED patterns from substrates subjected to this procedure were sharp "$16\times2"", as described in the following section. No residual C or O was detected by AES.

TPD experiments were carried out in the analytical chamber which is equipped with a differentially pumped quadrupole mass spectrometer. As-deposited samples were heated to $200 \ ^\circ \text{C}$ and exposed to atomic deuterium until saturation coverage. (Additional experiments involving H$_2$ TPD as well as flash heating followed by D$_2$ TPD were carried out to show that all H was removed by this procedure, even for the lowest growth temperatures used. In situ AES results also established that the Ge coverage remained constant during the deuterium site exchange process.) Deuterium, rather than hydrogen, was used in order to reduce the background signal and obtain greater sensitivity. D$_2$ was delivered through a doser identical to that described above with a hot W filament near the outlet to crack the gas. The samples were placed 2 mm from the 5-mm-diameter hole in the skimmer cone of the mass spectrometer and heated by direct current at a linear rate $\xi = 5 \ ^\circ \text{C s}^{-1}$.

Si$_{1-x}$Ge$_x$ film thicknesses and alloy compositions were determined by Rutherford backscattering spectrometry (RBS). The RBS probe beam consisted of 2 MeV He$^+$ ions incident at $15^\circ$ to the sample normal with the detector set at a $150^\circ$ scattering angle. Backscattering spectra were analyzed using the RUMP simulation program. The reported film compositions are accurate to within 2 at. %.

Cross-sectional transmission electron microscopy (XTEM) examinations were carried out using a Philips CM12 microscope operated at 120 kV. Specimens were prepared by gluing two samples film-to-film and then cutting a
vertical section which was thinned by mechanical grinding to a thickness of \approx 25 \mu m. Final thinning to electron transparency was done by Ar\(^+\) ion milling. The incident beam angle and energy were progressively reduced from 15° to 11° and from 5 to 3.5 keV, respectively, in order to minimize radiation damage artifacts and to obtain samples with uniform thickness distributions.

III. EXPERIMENTAL RESULTS

A. Si(011)\(^{16\times2}\) and 1\(\times\)1 surface reconstructions

The RHEED pattern shown in Fig. 1(a) was obtained along the [1\(\bar{1}\)1] azimuth of a clean Si(011) surface. It is composed of well-defined diffraction spots, rather than streaks, with sharp Kikuchi lines and essentially equi-intense fundamental and partial-order reflections indicating an atomically smooth surface with relatively large terraces. The pattern consists of curved rows with 15 partial-order reflections between the fundamental reflections in the zero-order Laue zone \(L_0\) and the corresponding reflections in the first-order Laue zone \(L_1\). (See, for example, the set of partial-order reflections between the specular Bragg reflection labeled 00 in \(L_0\) and the 11 in \(L_1\).) The rows along the growth direction are curved because the incident beam is in the [1\(\bar{1}\)1] direction while the sides of the reciprocal space unit cell are oriented along [100] and [\(\bar{1}\)\(\bar{1}\)1]. Within each Laue zone arc, there are half-order reflections between every set of fundamental Bragg spots.

Based upon the overall symmetry, this surface reconstruction was originally designated \(^{16\times2}\)\(^{-10}\) even though in the Wood’s surface notation\(^{28}\) scheme, \(16\times2\) implies that the vectors defining the surface unit cell are orthogonal, which is clearly not the case here. The symmetry is more clearly seen in the reciprocal space map in Fig. 1(b) in which arcs of the \(L_0\) and \(L_1\) Ewald spheres are labeled together with the incident electron beam direction. The reconstruction is \(^{17\times1\}2}\) with real-space unit cell vectors \(\mathbf{a}_r=17\mathbf{a}+\mathbf{b}\) and \(\mathbf{b}_r=2\mathbf{a}+2\mathbf{b}\). \(\mathbf{a}^*\) and \(\mathbf{b}^*\) in Figs. 1(b) and 1(d) are the unit vectors along the edges of the reciprocal-space unit cell defined by \(\mathbf{a}_s^*=(\mathbf{a}^*+\mathbf{b}^*)/16\) and \(\mathbf{b}_s^*=(-\mathbf{a}^*+17\mathbf{b}^*)/32\). Figures 1(c) and 1(d) are the corresponding experimentally observed (using an electron energy of 42.8 eV) and simulated Si(011)\(^{16\times2}\) LEED patterns. These results confirm the \(^{17\times1\}2}\) reconstruction and show, in addition, that the surface consists of a double-domain structure in which the two sets of domains are rotated by 73°. The two-domain nature of the \(^{16\times2}\) reconstruction is not observed in the RHEED patterns since the unit cell is nonorthogonal. Thus, only one domain is visible for a given RHEED azimuth.

Our RHEED and LEED observations show that the Si(011) surface reconstruction gradually transforms from \(^{16\times2}\) to \(1\times1\), in agreement with previously published results\(^{10,11,22,23}\) at \(T_s\) between 700 and 725°C. RHEED patterns obtained at temperatures within this range exhibit a continuous decrease in the intensity of the partial order reflections with increasing \(T_s\). Figure 2 is a typical RHEED pattern obtained along the [1\(\bar{1}\)1] azimuth of a \(1\times1\) reconstructed Si(011) surface at \(T_s=750°\)C. The reflections are still sharp and distinct but there is a much higher diffuse scattering intensity due primarily to the Debye–Wallor effect. The \(^{16\times2}\) to \(1\times1\) transition was found to be reversible upon sample cooling.

[FIG. 2. RHEED pattern obtained along the [1\(\bar{1}\)1] azimuth of a 750 °C Si(011) \(1\times1\) surface.]

[FIG. 3. (a) \(D_2\) TPD spectra from Si(011) surfaces with relative deuterium coverages \(\theta/D_{\text{sat}}=1.0, 0.97, 0.78, 0.55, 0.40, \) and 0.08. \(\theta/D_{\text{sat}}\) is the saturation coverage. (b) Fitted (solid and dashed lines) and measured (open circles) \(D_2\) TPD spectra from a Si(011) sample with \(\theta/D_{\text{sat}}=1.0\). \(\beta_2\) corresponds to the dideuteride phase, \(\beta_1^*\) to the adatom monodeuteride phase, and \(\beta_1\) to the surface-atom monodeuteride phase. The linear heating rate in all experiments was \(\xi=5°\) C s\(^{-1}\).]
TPD was used to probe atomic positions within the Si(011) surface.\textsuperscript{21} Figure 3(a) is a typical set of D$_2$ TPD spectra from Si(011) surfaces dosed for successively longer times. The upper curve corresponds to saturation coverage $\theta_{D_{sat}}$. The spectra are very similar to those we obtained from Si(111)\textsuperscript{21} and consist of a low temperature desorption peak centered at 430 $^\circ$C and a high temperature feature at 550 $^\circ$C. The primary difference between the Si(011) and Si(111) TPD spectra is that the high-temperature Si(011) feature contains a more obvious shoulder peak, split in this case by 30 $^\circ$C and centered at 520 $^\circ$C.

The Si(111)7×7 surface reconstruction has the dimer/adatom/stacking-fault structure in which Si adatoms have three backbonds to surface atoms. At low coverages on Si(111)7×7, deuterium adsors on the single dangling bonds of adatoms and rest atoms (first layer atoms not bonded to adatoms) giving rise to a high-temperature monodeuteride feature. Detailed analyses have shown that the two second-order Si(111)7×7 monohydride components are separated by ≈10 $^\circ$C, with the higher temperature peak at 530 $^\circ$C attributed to hydrogen desorption from rest atoms.\textsuperscript{29} The Si(111) dideuteride peak at 430 $^\circ$C is first observed at higher coverages as hydrogen begins to insert into adatom backbonds. Dihydride-bonded adatoms form disordered islands in which the majority species are SiH$_2$ with some isolated SiH$_3$.\textsuperscript{30}

The position of the low-temperature peak in the Si(011) TPD spectra is almost identical to that obtained from Si(111),\textsuperscript{21} but the splitting in the high-temperature feature is, as noted above, larger in the (011) spectra. We have fit the data using standard Polanyi–Wigner analyses.\textsuperscript{5} Best fits were obtained using, as in the case of Si(111)7×7, one low temperature and two high temperature second-order desorption peaks while ignoring the small peak near 375 $^\circ$C which we attribute to D$_2$ desorption from trideuteride species. An example is shown in Fig. 3(b) for a sample exposed to saturation deuterium coverage. The low temperature dideuteride peak is labeled $\beta_2$ and the two monodeuteride peaks are $\beta_1^+$ and $\beta_1^-$. Frequency factors $\nu$ and desorption activation energies $E_a$ are $1 \times 10^{15}$ s$^{-1}$ and 2.22±0.02 eV for $\beta_1^+$, and $2 \times 10^{15}$ s$^{-1}$ and 2.68±0.02 eV for $\beta_1^-$. In contrast to our Si(011) results, Si(001) TPD data is best fit using only two peaks: a low-temperature dideuteride peak centered at 405 $^\circ$C and a high temperature monodeuteride peak at 515 $^\circ$C.\textsuperscript{31} While $\beta_2$ desorption from Si(001) is second order, $\beta_1$ follows first order kinetics due to $\pi$-bonding-induced pairing of dangling bonds on single dimers. However, the pairing mechanism is not expected to be important on the more open Si(011) surface. This is consistent with the observed second-order Si(011) $\beta_1$ desorption kinetics.

The bulk-terminated Si(011) surface consists of zigzag in-plane rows of atoms along [011] as shown in Fig. 4(a). Each surface atom has one dangling bond at an angle of 36° with respect to the surface normal. Previously suggested atomic models for the reconstructed Si(011) surface include dimers and trimers,\textsuperscript{15} adatoms,\textsuperscript{16,17} and adatoms plus dimers\textsuperscript{18–20} as the building blocks. The existence of a Si(011) $\beta_2$ TPD peak at the same temperature as the $\beta_2$ peak in Si(111) spectra,\textsuperscript{21} together with the fact that bulk-terminated (011) surface atoms have only one dangling bond, argues strongly in favor of the presence of adatoms on the reconstructed surface and against the dimer/trimer model. By analogy with the Si(111) case, we propose that Si adatom backbonds are broken to form dideuteride species during deuterium adsorption on Si(011).

After desorbing the dideuteride $\beta_2$ phase, the remaining deuterium on the Si(011) surface is present as a monodeuteride. However, the TPD spectra clearly show that the high-temperature desorption feature is composed of two peaks, $\beta_1^+$ and $\beta_1^-$, indicating the presence of two types of monodeuterides. The Si(011) surface structure which is most consistent with our TPD results is the adatom/dimer model shown schematically in Fig. 4(b). A similar adatom/dimer foundation has been proposed for Ge(011) based upon STM observations.\textsuperscript{32} Both the Si adatoms, giving rise to the $\beta_1^+$ peak, and the surface atoms, $\beta_1^-$, have three backbonds and one dangling bond.

For Si(111), the difference in D$_2$ desorption energies from the two monohydride phases, for which the Si–H bond directions on both adatoms and rest atoms are normal to the surface, is only 0.04 eV.\textsuperscript{29} Based upon the Si(011) surface structure model in Fig. 4(b), in which the adatom Si–H bond direction is close to normal but the surface Si–H bond is far from normal, a larger splitting in the monodeuteride desorption peaks would be expected. This is consistent with our experimental results, where the difference in Si(011) $\beta_1^+$ and $\beta_1^-$ activation energies is 0.13 eV.

The [1/2 1/2] Si(011) primitive unit cell is shown in Fig. 4. It contains 16 adatom monodeuteride species plus an additional 16 surface atom monodeuteride species generated by the D-induced breaking of the $\pi$-bonded dimers. This results in 32 dangling bonds per unit cell, compared to 64 on the unreconstructed surface. Therefore, the maximum dangling bond coverage for this surface is 0.5 ML.
B. Si$_{1-x}$Ge$_x$(011) surface reconstructions

Si$_{1-x}$Ge$_x$ layers were grown on Si(011) at temperatures $T_s=400$–950 °C using a Si$_2$H$_6$ flux $J_{Si_2H_6}=2.2\times10^{16}$ cm$^{-2}$s$^{-1}$ and Ge$_2$H$_6$ fluxes $J_{Ge_2H_6}=0.78\times10^{14}$ cm$^{-2}$s$^{-1}$. Film thicknesses and Ge concentrations ranged from 5 to 8500 Å and 0 to 35 at. %, respectively. Si$_{1-x}$Ge$_x$(011) surface reconstructions were determined using in situ RHEED and LEED. Below a temperature-dependent critical Ge concentration $x_c$, the surface reconstruction of Si$_{1-x}$Ge$_x$ is "16 ×2", identical to that of the substrate. At Ge fractions above $x_c(T_s)$, the reconstruction transforms to "2×8". $x_c$ varies from 0.10 at $T_s=475$ °C to 0.06 at $T_s=650$ °C and is not a function of film thickness. For Si$_{1-x}$Ge$_x$ films with $x > x_c$, the "2×8" reconstruction is obtained immediately upon initiating deposition.

Figure 5(a) is a typical "2×8" RHEED pattern obtained along the [111] azimuth, in this case from a Si$_{0.78}$Ge$_{0.22}$ layer grown at $T_s=650$ °C. There are seven partial-order reflections between the 00 specular reflection and the 12 and 12 fundamental reflections along the zero-order Laue zone $L_0$. The half-order reflections lie along the $L_{1/2}$ zone.

Our RHEED observations show that the Si$_{1-x}$Ge$_x$(011) surface, like Si(011), transforms to a 1×1 reconstruction at temperatures between 650 and 725 °C. Figure 5(b) is a 1×1 RHEED pattern obtained at 800 °C along the [111] azimuth of the Si$_{0.78}$Ge$_{0.22}$(011) layer corresponding to Fig. 5(a). This pattern is identical to those obtained from Si(011)×1. The transformation between the two "16×2" and "2×8" surface reconstructions and the 1×1 is completely reversible with temperature.

Figure 6 is a surface reconstruction phase map, plotted as a function of $x$ and $T_s$, for Si$_{1-x}$Ge$_x$(011) films grown on Si(011)"16×2" at $T_s=400$–950 °C.

While there are no published STM data on the atomic structure of the Si$_{1-x}$Ge$_x$(011)"2×8" surface, insight can be gained from TPD measurements. Figure 7 is a typical D$_2$ TPD spectrum from a Si$_{0.8}$Ge$_{0.2}$(011)"2×8" layer grown at $T_s=650$ °C. Si(011)"16×2" and Ge(011)×8×10 TPD spectra are also shown for comparison. The primary spectral feature shifts to lower temperature, from 550 °C (the $\beta_1$ monodeuteride peak) for Si(011)"16×2" to 330 °C for Si$_{0.8}$Ge$_{0.2}$(011)"2×8". In fact, the alloy TPD peak occurs quite close to the position of the $\alpha$ monodeuteride peak, at

FIG. 5. RHEED patterns from a Si$_{0.78}$Ge$_{0.22}$(011) layer grown at $T_s=650$ °C. The patterns were obtained along the [111] azimuth and are indexed as (a) "2×8" at 300 °C and (b) 1×1 at 800 °C.

FIG. 6. A surface reconstruction phase map, plotted as a function of $x$ and $T_s$, for Si$_{1-x}$Ge$_x$(011) films grown on Si(011)"16×2" at $T_s=400$–950 °C.

FIG. 7. A D$_2$ TPD spectrum from a GS-MBE Si$_{0.8}$Ge$_{0.2}$(011)"2×8" layer grown at $T_s=650$ °C. Si(011)"16×2" and Ge(011)×8×10 TPD spectra are also shown for comparison. The linear heating rate in all experiments was $\zeta=5$ °C s$^{-1}$.
FIG. 8. GS-MBE Si$_{1-x}$Ge$_x$(011) growth rates $R_{\text{SiGe}}$ from Si$_2$H$_6$/Ge$_2$H$_6$ mixtures as a function of temperature $T_s$. Incident precursor fluxes were $J_{\text{SiH}_6}=2.2\times10^{16}$ cm$^{-2}$ s$^{-1}$ with $J_{\text{GeH}_6}=6.0\times10^{14}$ and $7.8\times10^{14}$ cm$^{-2}$ s$^{-1}$.  

300 °C, from Ge(011)$c\times8\times10$. This is completely analogous to TPD results from the Si$_{1-x}$Ge$_x$/Si(001) system$^{3,4}$ where the very rapid decrease in the position of the monodeuteride TPD peak with increasing alloy composition is due to strong Ge surface segregation.$^5$ Thus, we assign the 330 °C TPD peak, labelled $\alpha$, from the Si$_{0.8}$Ge$_{0.2}$(011)$''2\times8''$ layer to D$_2$ desorption from the Ge monodeuteride phase and the high-temperature shoulder near 400 °C, labeled $\beta_1$, to D$_2$ desorption from the Si monodeuteride phase.

The observed decrease in Si–D surface binding energy, and the corresponding increase in the Ge–D binding energy with Si$_{1-x}$Ge$_x$(011) alloy formation is, as in the case of Si$_{1-x}$Ge$_x$(001),$^{3,4}$ due to long-range electronic interactions which reflect the effect of Ge (Si) alloying on the Si (Ge) band structure. Furthermore, again in analogy with GS-MBE Si$_{1-x}$Ge$_x$(001),$^{3,4}$ a comparison of integrated Si$_{1-x}$Ge$_x$(011) $\alpha$ and $\beta_1$ TPD peak intensities as a function of bulk alloy composition reveals that $\theta_{\text{Ge}}$ increases much faster than $x$ indicating the presence of strong Ge surface segregation during Si$_{1-x}$Ge$_x$(011) film growth.

C. Si$_{1-x}$Ge$_x$(011) film growth kinetics

A plot of GS-MBE Si$_{1-x}$Ge$_x$(011) film deposition rates $R_{\text{SiGe}}$ as a function of $1/T_s$ is shown in Fig. 8 for films grown with a Si$_2$H$_6$ flux $J_{\text{SiH}_6}$ of $2.2\times10^{16}$ cm$^{-2}$ s$^{-1}$ and Ge$_2$H$_6$ fluxes $J_{\text{GeH}_6}$ of either $6.0\times10^{14}$ or $7.8\times10^{14}$ cm$^{-2}$ s$^{-1}$. At $T_s=650^\circ C$, these fluxes correspond to film compositions within the $''2\times8''$ surface reconstruction regime. For deposition temperatures between $=650$ and 725 °C, the surface reconstruction is two phase, $''2\times8''$+$1\times1$, during growth with the $1\times1$ fraction increasing to 100% at $T_s=725$ °C. Upon cooling, however, the surface reconstruction returns to pure $''2\times8''$. At all growth temperatures, increasing $J_{\text{GeH}_6}$ from 6.0 to $7.8\times10^{14}$ cm$^{-2}$ s$^{-1}$ results in an approximately proportional increase in $R_{\text{SiGe}}$. The Ge fraction $x$ in alloy layers grown with $J_{\text{GeH}_6}=6.0\times10^{14}$ cm$^{-2}$ s$^{-1}$ is $0.20\pm0.03$ while $x=0.31\pm0.02$ with $J_{\text{GeH}_6}=7.8\times10^{14}$ cm$^{-2}$ s$^{-1}$, independent of temperature.

Overall film growth rates $R_{\text{SiGe}}$ in these experiments range from 0.004 $\mu$m h$^{-1}$ at $T_s=400$ °C to 0.238 $\mu$m h$^{-1}$ at 950 °C and are characterized by three primary temperature regimes. With $T_s\le500^\circ C$, $R_{\text{SiGe}}$ increases exponentially with decreasing $1/T_s$, the signature of surface-reaction-limited growth. $R_{\text{SiGe}}$ for Si$_{1-x}$Ge$_x$(011) in this mode is nearly a factor of four lower than reported Si$_{1-x}$Ge$_x$(001) growth rates for layers deposited using the same precursor fluxes.$^3$ In the second regime, $T_s=500–650^\circ C$, $R_{\text{SiGe}}$ is essentially independent of $1/T_s$, characteristic of impingement-flux-limited growth. Here, $R_{\text{SiGe}}$ is nearly an order of magnitude lower than equivalent Si$_{1-x}$Ge$_x$(001) growth rates.$^3$ In addition, the transition between the surface-
reaction and impingement-flux-limited regimes occurs at 500 °C, compared to 600 °C for Si$_1-x$Ge$_x$(001). Unlike the Si$_1-x$Ge$_x$(001) case, however, $R_{SiGe}$ for Si$_1-x$Ge$_x$(011) increases again with a further increase in $T_s$. At temperatures between 650 and 725 °C, this is due to a gradual change in the surface reconstruction to 1×1, with an accompanying increase in the dangling bond density. The continued increase in $R_{SiGe}$ at even higher growth temperatures is associated with strain-induced surface roughening as demonstrated by preliminary atomic force microscopy and XTEM investigations. We have previously reported a similar increase in the GS-MBE growth rate of Ge on Ge(001) from Ge$_2$H$_6$ due to surface roughening. The enhanced deposition rate was shown to result from a combination of an increased reactive site density together with a higher digermane reactive sticking probability on the facets.

Figures 9(a)–9(c) are plots of $R_{SiGe}$ as a function of the incident flux ratio $J_{GeH_2}/J_{SiH_6}$ during Si$_1-x$Ge$_x$(011) film growth at $T_s=475$, 550, and 650 °C, respectively. At $T_s=475$ °C, $R_{SiGe}$ increases from 0.001 to 0.029 $\mu$m$^{-1}$ as $J_{GeH_2}/J_{SiH_6}$ is increased from 0.004 to 0.35. The “16×2” to “2×8” phase transition, which occurs over the flux ratio range $J_{GeH_2}/J_{SiH_6}=0.008–0.012$ ($x_c=0.087–0.120$) has no apparent effect on $R_{SiGe}$. Since $T_s=475$ °C is well within the surface-reaction-limited regime, this indicates that the hydrogen desorption energy is less dependent on the “16×2” to “2×8” phase transition than on changes in the Ge film concentration. This can be understood from the fact that adatoms are major building blocks for both surface reconstructions.

The film growth rate increases approximately linearly with $J_{GeH_2}/J_{SiH_6}$ at least initially, at $T_s=550$ °C in the impingement-flux-limited regime where $R_{SiGe}$ ranges from 0.011 $\mu$m$^{-1}$ with $J_{GeH_2}/J_{SiH_6}=0$ to 0.057 $\mu$m$^{-1}$ with $J_{GeH_2}/J_{SiH_6}=0.015$. In this case, though, the surface transformation to “2×8” results first in a decrease in $R_{SiGe}$, after which the growth rate remains nearly constant, with perhaps a slow increase, with increasing $J_{GeH_2}/J_{SiH_6}$. A qualitatively similar behavior is observed at $T_s=650$ °C; $R_{SiGe}$ increases from 0.067 $\mu$m$^{-1}$ at $J_{GeH_2}/J_{SiH_6}=0$ to 0.149 $\mu$m$^{-1}$ at $J_{GeH_2}/J_{SiH_6}=0.008$. Following the surface structural transition to “2×8”, $R_{SiGe}$ decreases to 0.036 $\mu$m$^{-1}$ at $J_{GeH_2}/J_{SiH_6}=0.027$ and increases slowly at higher flux ratios. Thus, in contrast to the surface-reaction-limited growth regime in which $R_{SiGe}$ is not strongly dependent on the surface phase transition due in large part to the high H coverages, $R_{SiGe}$ vs $J_{GeH_2}/J_{SiH_6}$ exhibits an abrupt decrease at the “16×2” to “2×8” transition in the flux-limited regime. However, our TPD results indicate that there is no significant difference in the dangling bond density for the two reconstructions. Thus, the decrease in $R_{SiGe}$ is most likely due to lower precursor reactive sticking probabilities on the “2×8” surface. The flux-limited film growth rate on “2×8” is not nearly as sensitive to increasing flux ratio as the growth rate on “16×2”.

The Ge concentration in as-deposited Si$_1-x$Ge$_x$(011) alloys, also plotted in Figs. 9(a)–9(c), increases linearly with the flux ratio at all three growth temperatures. At $T_s=475$ °C, $x$ ranges from 0.03 to 0.29 as $J_{GeH_2}/J_{SiH_6}$ increases from 0.004 to 0.035. Nearly identical $x$ vs $J_{GeH_2}/J_{SiH_6}$ results were obtained at both $T_s=550$ and 650 °C in the flux-limited regime. This can be better seen in Fig. 10 in which the entire set of film composition versus flux ratio data is plotted together as $x/(1-x)$ vs $J_{GeH_2}/J_{SiH_6}$. The slope was determined by least squares analysis to be $10.77\pm0.35$, significantly higher than the value of 7.7 obtained for Si$_1-x$Ge$_x$(001) grown at $T_s=550$ and 800 °C. This indicates that the ratio of the Ge$_2$H$_6$ to Si$_2$H$_6$ reactive sticking probabilities, while not strongly temperature dependent in either case, is higher for 011 Si$_1-x$Ge$_x$ growth.
The microstructure of fully strained Si$_{1-x}$Ge$_x$(011) films was found, as judged by TEM and XTEM analyses, to be highly perfect. Typical XTEM and high-resolution XTEM (HR-XTEM) results, in this case from a 1010-Å-thick Si$_{0.95}$Ge$_{0.07}$ layer grown at $T_s = 550^\circ$C, are shown in Fig. 11. The bright-field XTEM micrograph in Fig. 11(a), obtained under two-beam diffraction conditions using a 0 2 2 diffraction vector near the [ 1 1 1] zone axis, is essentially featureless with the exception of the lattice-mismatch strain contrast which is clearly visible at the interface. There is no evidence of extended defects and the film surface is flat to within the resolution of the micrograph. The 1 1 1 selected-area diffraction pattern shown as an insert in Fig. 11(a) consists of single-crystal reflections with uniform symmetric intensities. Figure 11(b) is a 1 1 0 HR-XTEM image showing 1 1 1 lattice fringes which are continuous across the film/substrate interface.

IV. DISCUSSION

The results in Sec. III A show that the surface structure of Si(011) is complex and temperature dependent. This is of direct consequence for epitaxial Si$_{1-x}$Ge$_x$ growth on Si(011) since it results in the surface dangling bond density, and hence the number of available reaction sites and therefore the film deposition rate, changing dramatically with surface reconstruction. Based upon a combination of RHEED and LEED observations, we have shown that the low-temperature Si(011)“1 6 2” surface reconstruction gradually and reversibly changes to 1 1 1 over the temperature range of 700–725 °C. From our D$_2$ TPD experiments combined with previous STM results, 2 the [ 1 7 1 ] surface unit cell consists of 1 6 adatoms and eight π-bonded dimers giving rise to 32 dangling bonds. Thus, compared to the bulk-terminated 1 1 1 surface, the “1 6 2” reconstruction has a maximum dangling bond coverage of 0.5 ML.

We have shown that at low Ge concentrations, the surface reconstruction of epitaxial Si$_{1-x}$Ge$_x$(011) is like that of the substrate, “1 6 2”. However, for alloy films with $x$ above a critical temperature-dependent value $x_c$, the reconstruction converts to “2 8 8”. $x_c$ for the “1 6 2” to “2 8 8” transition decreases continuously from 0.10 at $T_s = 475^\circ$C to 0.06 at 650°C. As in the case of Si(011), the surface reconstruction of Si$_{1-x}$Ge$_x$(011), irrespective of whether “1 6 2” or “2 8 8” initially, gradually and reversibly transforms to 1 1 1 over the temperature range between 650 and 725 °C. A summary of observed Si$_{1-x}$Ge$_x$(011) surface reconstruction as a function of alloy composition and temperature is plotted in the form of a surface structure phase map in Fig. 6.

From an analysis of our TPD results, we deduced in Sec. III B that the “2 8 8” reconstruction occurs at high Ge coverages generated by strong surface segregation during film growth. Further, the TPD results in Fig. 7 are consistent with a surface structure in which adatoms are a fundamental building block. However, a determination of local atomic positions in the surface unit cell will require additional TPD investigations combined with STM.

The experimental results in Fig. 8 show that GS-MBE Si$_{1-x}$Ge$_x$(011) growth kinetics at $T_s = 650^\circ$C are similar to those of Si$_{1-x}$Ge$_x$(001) 3 in that the film deposition rate is characterized by a low-temperature surface-reaction-limited growth mode followed by a higher-temperature impingement-flux-limited regime. For the dihydride fluxes used in the present experiments, the surface reconstruction of all films in this temperature range is “2 8 8”. At growth temperatures above 650 °C, additional Si$_{1-x}$Ge$_x$(011) growth regimes emerge due to the gradual surface phase transition to 1 1 1 at $T_s = 650–725$ °C and, at even higher temperatures, to strain-induced surface roughening. In the following discussion, we will focus primarily on the surface-reaction and flux-limited modes assuming, as in the case of Si$_{1-x}$Ge$_x$(001), 3 that growth in these regimes can be described by a superposition of previously developed models for GS-MBE Si 1 and Ge 2 from Si$_2$H$_6$ and Ge$_2$H$_6$, respectively.

$R(J,T_s)$ results for Si(001) 1 and Ge(001) 2 GS-MBE are well described by a model, containing no fitting parameters, in which dissociative chemisorption of the dihydride precursor is followed by a series of fast surface decomposition reactions and H$_2$ desorption from the surface monohydride phase. This leads to the following growth rate equation describing both GS-MBE Si(001) and Ge(001),

$$R = \frac{2SJ\theta_{db}^2}{N}.$$

where $S$ is the zero-coverage reactive dihydride sticking probability, $\theta_{db}$ is the steady-state dangling bond coverage, and $N$ is the bulk Si or Ge atom number density. Precursor reactive sticking probabilities have been measured in the flux-limited growth regime for Si$_2$H$_6$ on Si(001) 1 and for Ge$_2$H$_6$ on Ge(001). 2 The temperature dependencies of $S_{Si2H6}$ and $S_{Ge2H6}$ over the temperature range used in the film growth experiments in Refs. 1 and 2 were small and could be safely ignored. More recently, the reactive sticking probabilities of Si$_2$H$_6$ on Ge(001) and Ge$_2$H$_6$ on Si(001) have also been determined. 3

From the above discussion, GS-MBE Si$_{1-x}$Ge$_x$ growth rates can be expressed as

$$R_{SiGe} = \frac{2\theta_{Si}f_{db, Si}^2}{N_{SiGe}}(J_{Si2H6}S_{Si2H6}^{Si} + J_{Ge2H6}S_{Ge2H6}^{Si})$$

$$+ \frac{2\theta_{Ge}f_{db, Ge}^2}{N_{SiGe}}(J_{Si2H6}S_{Si2H6}^{Ge} + J_{Ge2H6}S_{Ge2H6}^{Ge}),$$

where $f_{db, Si}$ and $f_{db, Ge}$ are Si and Ge surface dangling bond site fractions and $S_{Si2H6}^{Si}$ is the reactive sticking probability of the B precursor molecule on A sites. The steady-state Ge surface coverage $\theta_{Ge}$ during growth depends upon the bulk film composition together with Ge surface segregation kinetics for which the segregation enthalpy is a function of hydrogen coverage which is itself temperature-dependent. 4 We have shown by TPD that hydrogen desorption from the surface monohydride phase on Si$_{1-x}$Ge$_x$(001) is second order 4 and we expect the same kinetic order for Si$_{1-x}$Ge$_x$(011) where desorption from adatom sites will be limited by the rate of bimolecular recombination. Thus, the Si (Ge) dangling bond fractions $f_{db}$ can be written as

$$f_{db, Si} = \frac{1}{2}J_{Si2H6}S_{Si2H6}^{Si}$$

$$f_{db, Ge} = \frac{1}{2}J_{Ge2H6}S_{Ge2H6}^{Ge}.$$
\[ f_{db, SiGe} = \left[ 1 + \sqrt{\frac{2J_{Si_2H_6(Ge_2H_6)_{Si_2H_6(Ge_2H_6)}}{N_s \nu_s \exp \left( \frac{-E_{d, SiGe}}{kT_s} \right)}} \right]^{-1} \]

in which \( N_s \) is the surface site number density, \( 9.6 \times 10^{14} \) cm\(^{-2}\) for Si(001) and \( 8.8 \times 10^{14} \) cm\(^{-2}\) for Ge(001)], \( \nu_s \) is a pre-exponential factor, and \( E_{d, SiGe} \) is the hydrogen desorption activation energy which is a function of Ge surface coverage.\(^4\)

Unlike the \( Si_{1-x}Ge_x(001) \) system, for which detailed quantitative information is available,\(^1-3\) little is known about individual reactive sticking probabilities and Ge surface segregation rates during GS-MBE of \( Si_{1-x}Ge_x(011) \). Thus, to proceed, we make some simplifications and assumptions for the purpose of performing calculations. The \( Si_{1-x}Ge_x(011) \) \( R_{SiGe} \) vs \( 1/T_s \) plot in Fig. 8 correspond to alloy compositions \( x = 0.20 \) for films grown with \( J_{GeH_6} = 6.0 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\) and 0.31 with \( J_{GeH_6} = 7.8 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\). In the analogous case of \( Si_{1-x}Ge_x(001) \) growth over this composition range in the surface-reaction and flux-limited modes, \( \theta_{Ge} \) varies only over a relatively narrow range. For example, \( \theta_{Ge} \) ranges from 0.70 ML at \( T_s = 525 \) °C to 0.82 ML at 800 °C to 0.76 ML at 950 °C with \( x = 0.18 \).\(^4\) This is due to competing effects. The experiments are carried out in the equilibrium segregation regime in which increasing \( T_s \) results in a decrease in \( \theta_{Ge} \). However, this is partially compensated by the fact that the hydrogen coverage also decreases with \( T_s \), thereby increasing the negative segregation enthalpy.\(^4\)

If \( \theta_{Ge} \) does not vary greatly, we can express the \( SiH_6 \) and \( GeH_6 \) reactive sticking probabilities as average values \( S_{SiH_6} \) and \( S_{GeH_6} \). This allows Eq. (3) to be simplified and rewritten for an average dangling bond formation \( f_{db} \) as

\[ f_{db} = \left[ 1 + \sqrt{\frac{2J_{Si_2H_6(Ge_2H_6)_{Si_2H_6(Ge_2H_6)}}{N_s \nu_s \exp \left( \frac{-E_{d, SiGe}}{kT_s} \right)}} \right]^{-1} \]

\( E_{d, SiGe} \) in Eq. (4) is the average hydrogen desorption energy. Equation (2) can now be expressed in a more usable form,

\[ R_{SiGe} = \left[ \frac{2J_{Si_2H_6(Ge_2H_6)_{Si_2H_6(Ge_2H_6)}}}{N_s \nu_s \exp \left( \frac{-E_{d, SiGe}}{kT_s} \right)} \right] \]

Similarly, the steady-state composition of GS-MBE \( Si_{1-x}Ge_x(011) \) can be approximated as

\[ x = \frac{S_{SiGe}J_{GeH_6}}{S_{SiH_6}J_{SiH_6}} \]

Equation (6) predicts that the film composition ratio is linearly related to the flux ratio in agreement with the results in Fig. 10. From the slope of the experimental data, \( S_{SiGe}/S_{SiH_6} = 10.77 \). \( R_{SiGe} \) has no significant growth temperature dependence over the range \( T_s = 475-650 \) °C. Moreover, the plot of \( x/(1-x) \) vs \( J_{GeH_6}/J_{SiH_6} \) in Fig. 10 is continuous with little change in slope for three growth temperatures, indicating that \( S_{SiGe}/S_{SiH_6} \) remains approximately constant across the “16×2” to “2×8” phase transition.

At the high-temperature end of the flux-limited growth regime, \( f_{db} \) approaches unity and individual values for \( S_{SiH_6} \) and \( S_{GeH_6} \) can be estimated by combining the result that \( S_{SiGe}/S_{SiH_6} = 10.77 \) with Eq. (5) and the measured \( R_{SiGe} \) results in Fig. 8. This yields \( S_{SiGe}/S_{SiH_6} = 1.0 \times 10^{-3} \) and \( S_{GeH_6}/S_{SiH_6} = 10.8 \times 10^{-3} \) with \( J_{GeH_6} = 6.0 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\). Increasing \( J_{GeH_6} \) to \( 7.8 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\) gives \( S_{SiGe}/S_{SiH_6} = 1.2 \times 10^{-3} \) and \( S_{GeH_6}/S_{SiH_6} = 12.9 \times 10^{-3} \). Using these values for the average reactive sticking probabilities, we fit the GS-MBE \( R_{SiGe} \) vs \( 1/T_s \) results over the surface-reaction and flux-limited regimes. The only free parameters are \( \nu_s \) and \( E_{d, SiGe} \). Best fits were obtained with \( \nu_s = 5 \times 10^{14} \) s\(^{-1}\) and \( E_{d, SiGe} = 2.22 \) and 2.20 eV with \( J_{GeH_6} = 6.0 \times 10^{14} \) and \( 7.8 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\), respectively. We used the same pre-exponential factor as reported previously for \( Si_{1-x}Ge_x(001) \) since we showed in Sec. III A that \( \nu_s \) values obtained from Si(001) and Si(011) TPD spectra were nearly identical. The fits were found to be very sensitive to the values chosen for \( E_{d, SiGe} \) with the goodness of fit decreasing rapidly if \( E_{d, SiGe} \) is changed by more than 0.01 eV. As an additional test, we used our best-fit \( \nu_s \) and \( E_{d, SiGe} \) values to calculate peak temperatures \( T_p \) and peak shapes for the high-temperature \( Si_{1-x}Ge_x(011) \) TPD features. The results were found to be in very good agreement with measured spectra. In the case of \( SiH_6Ge_{0.2} \) growth, for example, we calculate \( T_p = 404 \) °C while in Fig. 7, \( T_p \) is \( = 400 \) °C. The agreement provides additional confidence in the validity of the growth model.

The calculated and experimental curves in Fig. 12 exhibit quite good agreement. The results show that \( E_{d, SiGe} \) decreases with increasing \( J_{GeH_6} \), and, hence, increasing Ge concentration in the alloy layer. This is consistent with our previous \( Si_{1-x}Ge_x(001) \) results showing that the hydrogen...
desorption energy decreases with increasing $\theta_{Ge}$ due primarily to a weakening of Si–H bonds through long-range electronic interactions.  

Unlike the Si$_{1-x}$Ge$_x$(001) case, however, Fig. 8 shows that Si$_{1-x}$Ge$_x$(011) growth rates increase again at higher deposition temperatures in the flux-limited regime. This is due to an increase in the surface dangling bond density as the surface structure gradually changes from a “2×8” reconstruction to bulk-terminated 1×1 over the temperature range between ≈650 and 725 °C. Indeed, the results show that $R_{SiGe}$ increases sharply over this growth temperature range. As $T_s$ is increased still further, $R_{SiGe}$ continues to increase. This, we propose, is associated with surface roughening. Initial atomic force microscopy investigations show that strong strain-induced roughening, already detectable as increased diffuse scattering in RHEED patterns from Si$_{1-x}$Ge$_x$(011), becomes significant at $T_s \geq 725$ °C.

V. CONCLUSIONS

TPD was used to show that the Si(001)‘‘16×2’’ reconstructed unit cell is composed of 16 adatoms and eight π-bonded dimers, resulting in a maximum dangling bond coverage of 0.5 ML. The surface reconstruction of Si$_{1-x}$Ge$_x$(001) overlayers grown on Si(001) remains ‘‘16 ×2’’ at low Ge concentrations but transforms to ‘‘2×8’’ at a critical x value which decreases from ≈0.10 at $T_s = 475$ °C to 0.06 at $T_s = 650$ °C. At even higher temperatures, both Si(001) and Si$_{1-x}$Ge$_x$(011) surfaces gradually and reversibly transform to 1×1. The transformation is complete at ≈725 °C. We showed, based upon analyses of TPD results, that the ‘‘2×8’’ surface occurs at high Ge coverages generated by strong surface segregation during film growth. Further, the TPD results are consistent with a surface structure in which Si and Ge adatoms are fundamental components in the ‘‘2×8’’ reconstruction.

GS-MBE Si$_{1-x}$Ge$_x$(001) growth kinetics in the surface-reaction and flux-limited regimes are well described by a model in which dissociative chemisorption of the dihydride precursors is followed by a series of surface decomposition reactions and second-order H$_2$ desorption. In the surface-reaction-limited regime ($T_s \leq 500$ °C), $R_{SiGe}$ decreases exponentially with 1/$T_s$ and is rate-limited by H$_2$ desorption from the adatom and surface atom monohydride phases but is not affected by the ‘‘16×2’’ to ‘‘2×8’’ surface transformation. At $T_s = 500–650$ °C, in the impingement-flux-limited regime, $R_{SiGe}$ is limited by precursor reactive sticking probabilities which are essentially independent of $T_s$. In this growth mode, $R_{SiGe}$ increases linearly with $J_{GeH_2}/J_{SiH_2}$ but at a higher rate for growth on the ‘‘16×2’’ than the ‘‘2×8’’ surface reconstruction. The ratio of the Ge$_2$H$_6$ to Si$_2$H$_6$ reactive sticking probabilities was found to be constant, 10.77, at $T_s = 475–650$ °C. Thus, $x/(1-x)$ increases linearly with increasing $J_{GeH_2}/J_{SiH_2}$ in both the surface-reaction-limited and impingement-flux-limited regimes. At higher growth temperatures, $R_{SiGe}$ once again increases with increasing $T_s$. Initially, at $T_s = 650–725$ °C, this is due to a gradual change in the surface reconstruction to 1×1 with a corresponding increase in the maximum dangling bond density from 0.5 to 1.0 ML. The continued increase in $R_{SiGe}$ at even higher $T_s$ is associated with strain-induced surface roughening.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Office of Naval Research under a contract administered by Dr. Larry Cooper, the U.S. Department of Energy Division of Materials Sciences under Award DEFG02-ER9645439, and the Semiconductor Research Corporation. P. Desjardins is partially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We also appreciate the use of the Center for Microanalysis of Materials at the University of Illinois, which is partially supported by the U.S. Department of Energy.

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