Hydrogen Induced Si Surface Segregation on Ge-Covered Si(001)

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Using Fourier transform infrared-attenuated total reflectance spectroscopy in conjunction with hydrogen adsorption to probe surface layer composition, we observe a reversible place exchange between Ge and Si on Ge-covered Si(001) when the surface is dosed with atomic H at elevated temperatures. First-principles calculations confirm a thermodynamic driving force for this place exchange. To explain the intriguing kinetics of the place exchange, which shows no time dependence, we propose a dimer-vacancy diffusion-assisted mechanism limited by vacancy interactions. [S0031-9007(98)07429-8]

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In vapor deposition of thin films the growth front will always exhibit some degree of roughness. Roughness can be caused by kinetic limitations, e.g., by limited mobility and hence inability to reach equilibrium positions before being buried by other atoms. When multiple atomic components are involved, energetics additionally play a role in broadening the growth front because one component, the one that lowers surface free energy, generally prefers to reside on surface sites. In heteroepitaxy (the growth of one material on a different one) it is difficult to create an abrupt interface, even in the absence of significant kinetic roughening, when covering the component that segregates to the surface.

Control of interfacial structure, morphology, and composition is a significant issue [1]. The heteroepitaxy of SiGe on Si has, in this regard, received much recent attention, because the resultant structures could potentially lead to devices with unique electronic and optoelectronic properties based on the Si device fabrication paradigm [2]. During Si_xGe_{1-x} growth, Ge preferentially segregates to the surface because the Ge dangling-bond energy is lower than that of Si. This segregation makes it difficult to create an abrupt Si/SiGe interface [3–6].

Extensive studies [3–9] have shown that surface H (as well as other surfactants [10]) effectively suppresses Ge segregation during SiGe epitaxy. Suppression of Ge segregation to the surface has been observed in chemical vapor deposition (CVD) [4,5] and gas-source molecular beam epitaxy (MBE) [7,8], in which H is provided from the precursor molecules, and in solid-source MBE when atomic H is supplied by dosing [9]. It has been speculated that the suppression of Ge segregation may be caused by a thermodynamic effect, the saturation of Si or Ge dangling bonds by H to reduce the difference in Ge and Si surface free energy and hence the driving force for segregation [5] and/or by a kinetic effect, a decrease in the surface diffusion of Si and Ge (H acting as blocking sites) [4,9]. No quantitative information is, however, available on how the segregation energy and kinetic barriers for Ge surface segregation will change in the presence of H.

In this Letter, we demonstrate that surface H in fact induces Si surface segregation rather than suppressing Ge surface segregation in a growth front consisting of Si, Ge, and H. The exchange between Ge and Si in the top layer is reversible by adsorbing or desorbing H. We present first-principles calculations that give quantitative values of segregation energies and show that there is indeed a thermodynamic driving force for H induced Si surface segregation. We also deduce from temperature- and time-dependent measurements that the amount of Si surface segregation is kinetically limited. We propose an atomistic model explaining these observations.

In order to determine the composition of the outer layer of the SiGe system dynamically and *in situ,* we have combined Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy and hydrogen tagging of surface species. The SiGe system is ideally suited for this type of analysis because both Si-H and Ge-H bonds are easily identifiable with FTIR-ATR spectroscopy.

The experiments were performed in a custom UHV-CVD system containing a differentially pumped reflection high-energy electron diffraction (RHEED) system that allows real-time structural analysis during growth. *In situ* FTIR-ATR is performed with several adaptations to the sample and the FTIR optical interface. The ATR prism is fabricated by cutting a double-side-polished 3 in. Si wafer into a 2.6 in. long slice and polishing its two ends into 45° bevels. UHV-CVD growth is subsequently performed on this slice. Infrared (IR) radiation enters and leaves the reactor through BaF_2 windows and enters and leaves the beveled faces of the sample at normal incidence. The beam undergoes approximately 100 reflections inside the wafer. Because the input beam is focused on the bevel with an f/5 lens, the beam undergoes little divergence inside the wafer. Therefore, no lateral guiding is needed.

The surfaces of the wafer prism are prepared using an IMEC clean [11] followed by dry oxidation (growing a 60 nm SiO_2 layer) and a final 5 min dip into a 10% HF/H_2O solution to create a H-passivated surface. The prism is immediately introduced into the reactor and a Si buffer layer is deposited at 650 °C substrate temperature using SiH_4 to produce a smooth (2×1) reconstructed surface. The temperature is then reduced to 525 °C, and

~1.3 monolayer (ML) Ge is deposited using 2.1% GeH_4 in H_2. The coverage is determined from RHEED observations of the onset of the $(2 \times N)$ reconstruction at ~0.8 ML [12]. The $(2 \times N)$ reconstruction consists of lines of dimer vacancies separated by $N - 1$ dimers, where N is typically between $N = 8$ and $N = 14$, depending on the Ge coverage [13] and hence the surface stress. We monitor the change of surface composition with FTIR after dosing the sample surface with atomic H supplied by dissociating molecular H_2 using a resistively heated tungsten filament.

Figure 1 shows a series of FTIR spectra demonstrating that H induces Si surface segregation and that the place exchange between Si and Ge in the surface layer and lower layers is reversible. The original $(2 \times N)$ Ge-terminated Si(001) surface is first cooled to room temperature and dosed to saturation coverage with H. The main features of the FTIR spectrum shown in Fig. 1(*a*) are two strong peaks at 1980 and 2000 cm^{-1}, which are both associated with Ge-H stretch vibrations [14,15], reflecting the dominant Ge surface termination. But the surface is not completely covered by Ge; the small peak at 2100 cm^{-1} associated with the Si-H stretch [16] indicates a trace of Si left on the surface and/or exposed in lower layers at defect sites (e.g., voids).

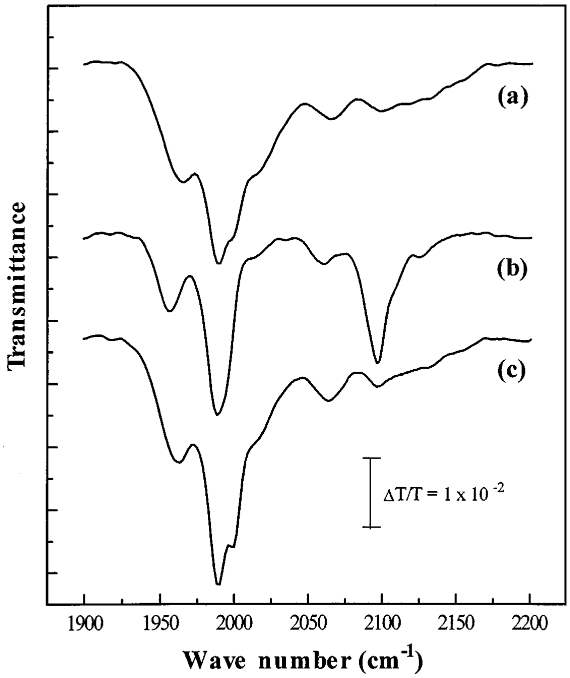

FIG. 1. FTIR-ATR spectra of Si(001) initially covered with ~1.3 ML Ge and exhibiting a $(2 \times N)$ reconstruction. (*a*) After H dosing at room temperature. The surface shows a large peak associated with the Ge-H stretch vibration and only a small Si-H stretch peak (at 2100 cm^{-1}). (*b*) After H dosing at 330 °C followed by dosing at room temperature to saturate all dangling bonds. A large Si-H stretch peak appears. (*c*) After annealing the surface of (*b*) to 550 °C, quenching in vacuum, and dosing with H at room temperature. The Si-H stretch peak disappears.

After obtaining this base line for the starting surface, we raise the temperature to 330 °C, dose again with H, cool the sample to room temperature, and dose a third time with H to ensure that the surface dangling bonds are saturated. Figure 1(*b*) shows the resultant FTIR spectrum. The Si-H peak at 2100 cm^{-1} increases substantially while the Ge-H peak decreases, indicating a large increase in the amount of Si in the surface layer.

This reaction is reversible. Starting with a H-covered surface of Fig. 1(*b*), we heat the sample to 550 °C to desorb the H completely, quench the surface to room temperature, and redose it. Figure 1(*c*) shows that the surface returns to its original state, shown in Fig. 1(*a*). We can repeat the cycle from Fig. 1(*a*) to Fig. 1(*c*) many times. This reversibility precludes H etching of Ge. We conclude that Si and Ge exchange places in the outermost layers under the influence of H. RHEED shows that the $(2 \times N)$ reconstruction is preserved with the same value of N during elevated-temperature H dosing, but with a reduced intensity, suggesting increasing disorder in the vacancy lines.

To assess whether the above observation is thermodynamically feasible, we calculate the surface energy difference of Si(001) surfaces containing 1 ML of Ge either as the top layer or as the second layer, using an *ab initio* pseudopotential plane-wave method. We consider both the clean and the monohydride-terminated surfaces. We model the clean surface, with $p(2 \times 2)$ reconstruction [17], with a 56-atom supercell of a slab containing 14 atomic layers and the monohydride surface, with (2×1) reconstruction, with a 32-atom supercell containing 16 layers. The same plane-wave cutoff energy of 20 Ry and the equivalent special k-points Brillouin-zone sampling are used for both types of surfaces to facilitate comparison [17]. The energy of the clean Ge-terminated surface is 210 meV/atom lower than that of the clean Si-terminated surface (with Ge in the second layer). With H adsorbed on the surface, however, the energy of the Ge-H-bond-terminated surface is 30 meV/atoms higher than that of Si-H-bond-terminated surface. Because the bonding between Si and H is stronger than that between Ge and H, the presence of H makes a Si-H termination of the surface energetically preferred to a Ge-H termination. The calculated energy differences indicate an approximate equilibrium concentration (simply using the Boltzmann factor), at room temperature, of surface Ge of 99.97% for the clean surface and 24% for the H-terminated surface. The equilibrium concentrations of Si and Ge in the surface would become more equal with increasing temperature, i.e., the equilibrium Ge concentration would decrease in the clean surface but increase in the H-terminated surface toward 50%, as the temperature increases.

We have examined the influence of substrate temperature and the length of time of H dosing on surface composition. Si(001) with a coverage of ~1.3 ML Ge and exhibiting a strong $(2 \times N)$ pattern is dosed with H for

120 sec at a series of temperatures, quenched, and measured at room temperature with FTIR. Representative FTIR-ATR spectra are shown in Fig. 2. The strength of the Ge-H peak decreases continuously with increasing temperature, while the strength of the Si-H peak intensity increases. Above 320 °C, the Si-H signal begins to drop, due to H desorption. Both eventually vanish due to the complete desorption of H from the surface [11,15,18,19].

The observations do not support the thermodynamic model presented above. The rise in the Si signal and drop in the Ge signal with increasing temperature indicate that, despite the existence of a thermodynamic driving force, the H induced Si surface segregation is controlled by kinetics. The first-principles calculations predict, for thermodynamic equilibrium at room temperature, a Ge concentration lower than the Si concentration in the H-terminated surface layer. From entropic considerations (i.e., the Boltzmann factor), the Ge concentration should increase with increasing temperature. Figure 2 shows the reverse trend. Hence there must be a driven Si surface segregation that reaches a higher state of completion at higher temperature, i.e., the system is farthest from equilibrium at low temperature but never reaches equilibrium, even at the highest dosing temperature. Hydrogen desorption complicates the picture at high temperatures, but cannot explain the initial increase of the Si-H signal. Desorption of hydrogen in the monohydride bonding configuration from both Si and Ge should be negligible below 320 °C [18].

From measurements of dosing the surface with H at a given temperature for different times, we determine that the reaction saturates very quickly. For example, dosing at 250 °C for 5 and 600 sec produces spectra that are essentially identical to the spectra obtained after a 120 sec dose. Despite the rapid saturation, the place exchange is incomplete, as demonstrated by the kinetic limitations implied from the temperature behavior.

We propose a plausible atomistic model that is consistent with all of the observations. The exchange reaction has a measurable extent already at a rather low temperature (~250 °C), implying a kinetic process with a barrier lower than that for breaking Si-Ge bonds, for which the rate would be much lower than observed. We therefore postulate that the reaction cannot proceed everywhere in the surface but only in regions in which defects can lower the exchange barrier. On clean Si(001), a surface dimer can exchange positions with two subsurface atoms through the migration of a dimer vacancy [20], through a concerted motion of several atoms without bond breaking. A similar exchange can occur here, except that now surface dimers are made of Ge and they are bonded to H, as schematically depicted in Fig. 3(a). The addition of H biases the random migration of a dimer vacancy in the direction to bring the buried Si to the surface, producing a rapid growth of the Si-H stretch signal, as is observed. It may also lower the kinetic barrier, a question that we are currently investigating. A higher density of vacancies should produce more surface Si in unit time; also the farther a vacancy can meander in unit time the more surface Si it can create.

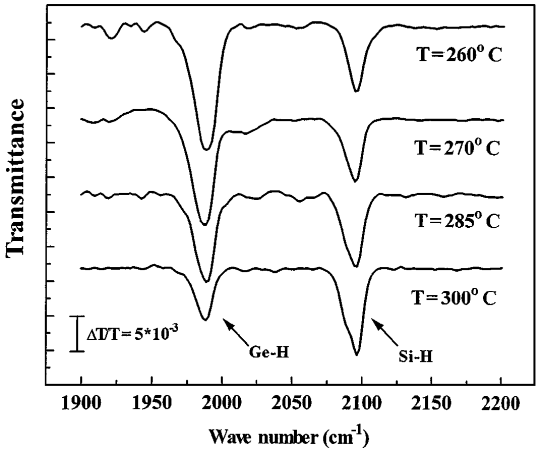

FIG. 2. FTIR-ATR spectra of Ge-terminated Si(001) after dosing with H for 120 sec at several temperatures.

What, however, can cause the place exchange to saturate before completion? Although a large number of vacancies are available on a Ge-covered Si(001) surface, their positions are confined to vacancy lines [12]. An attractive force between vacancies on neighboring dimer rows (effectively, a line tension tending to keep the dimer vacancy line straight) and a repulsive force between vacancies on the same dimer rows [12] (effectively keeping the dimer vacancy rows equally spaced) limit the motion of an individual vacancy. We propose that the extent of the H induced Si surface segregation is controlled by the extent of meandering of vacancy lines. In the clean surface a vacancy that has moved one space along the dimer row in either direction [see Fig. 3(b)]

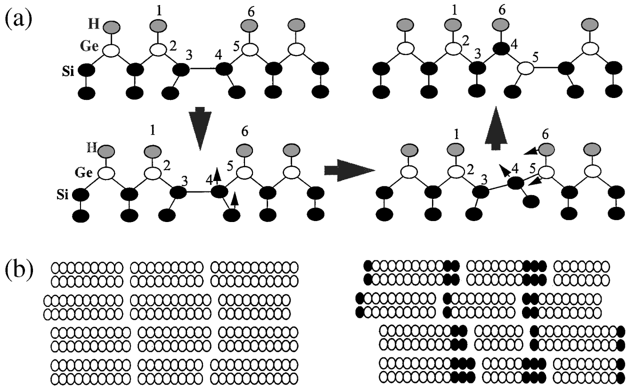

FIG. 3. Atomistic models of the proposed place exchange mechanism and structure. (a) Dimer-vacancy diffusion-assisted Si-Ge place exchange reaction. When a vacancy moves one step, two Si atoms are brought to the surface. (b) A top view of the $(2 \times N)$ reconstructed surface before and after Si segregates to the surface at the vacancy lines. The dimer rows run horizontally; Si, occupying surface sites in the vicinity of the vacancy lines, produces a striped phase (vertical dark bands).

thereafter has a greater probability to move back, because of the vacancy line tension and long-range repulsion between vacancies. However, with H on the surface, vacancy motion produces Si/Ge place exchange. Once Si has been brought to the surface, the vacancy now sees a barrier for returning, despite the fact that the line tension and long range repulsion likely still exist. A vacancy, once committed, would tend to continue to move in the same direction, bringing up a line of Si dimers. On average, then, H tends to drive the vacancies farther away from their mean positions with increasing temperature to bring up more Si, leading to the increased Si-H stretch signal at higher temperature. At a given fixed temperature, because the barrier for diffusion is low, vacancies quickly reach their maximum deviations from their mean positions because of the confinement potential of other vacancies. The consequence of this vacancy-diffusion-assisted mechanism is the formation, at each vacancy line, of a ragged striped domain of Si in the top layer. Their width saturates quickly with time but grows with increasing temperature. The ultimate size of the domains increases with increasing annealing temperature but is limited by domain-wall interactions at a given temperature. The mechanism is consistent with RHEED observations, which show that the vacancy lines are preserved but meander more when H is adsorbed at higher temperature. Vacancy-vacancy repulsion and line tension will lead to the concerted motion of vacancy lines and the eventful formation of high-energy domain walls between domains where vacancies are migrating in opposite directions. This type of kinetic behavior has previously been observed for domain coarsening in the O on W(110) system [21].

In summary, we have shown that H dosing combined with FTIR-ATR spectroscopy can be used as a semiquantitative surface composition probe for Ge on Si. We demonstrate that H induces a reversible Si/Ge place exchange reaction on Ge-terminated Si(001) at temperatures above 250 °C. We show by first-principles calculations that there is a thermodynamic driving force for this place exchange reaction. Nevertheless, the reaction is largely dominated by kinetics, with an intriguing behavior: The extent of the reaction increases with increasing temperature but saturates quickly with time at a given temperature. A mechanism that involves formation of striped Si-rich domains associated with the motion of vacancies away from their positions in the vacancy line of the clean surface explains the results. The vacancy lines themselves are quite straight in the clean surface, suggesting that the Si stripes may also be quite straight. If this is so, the exchange mechanism demonstrated here could form the basis of a self-organizing nanolithography, as Si and Ge behave differently to chemical reaction, e.g., oxide or silicide formation or metal organic deposition. We are presently investigating this potential.

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