Thermodynamically driven Ge/Si place exchange induced by hydrogen on Ge-covered Si(001) surfaces

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(Received 9 July 1999; revised manuscript received 18 October 1999)

Recently, hydrogen induced Si segregation on 1.4 monolayer Ge-covered Si(001) surface has been observed by means of Fourier transform infrared-attenuated total reflectance spectroscopy [E. Rudkevich *et al.*, Phys. Rev. Lett. **81**, 3467 (1998)]. We confirm these results independently, using x-ray photoelectron diffraction and high-resolution electron-energy-loss spectroscopy. We demonstrate that the Ge/Si place exchange already takes place, but to a limited extent, at room temperature. Moreover, we observe that increasing the H-exposure temperature intensifies Si surface segregation, which we correlate to Ge-H decomposition. From that, we deduce that the creation of free Ge surface dangling bonds strongly modifies the energetic balance at the surface and in turn favors Si segregation. We propose that the driving force for H-induced Si/Ge site exchange is mostly the thermodynamics involved in the modification of hydrogen populations with temperature.

Ge/Si(001) and $Si_{1-x}Ge_x$/Si(001) heterostructures have been extensively studied[1,2] because of their technological interest. As a consequence, the Ge/Si(001) system has become a model case for studying heteroepitaxial growth processes.[3–7] Up to now, most of the effort has been directed towards the determination of growth mechanisms with Ge films prepared with conventional molecular-beam epitaxy methods. Nevertheless, there are many advantages[8] in using vapor deposition and this explains the fact that these techniques are at the basis of most industrial processes in semiconductor technology. However, the use of gas sources may strongly differ from that of solid sources if hydrogen is present on the growth front,[9] specifically at growth temperatures below 500 °C for SiGe systems. In that case, H may act on the kinetics and mobility of atoms. Here we show that it also strongly modifies the energetic balance by reacting selectively with the distinct chemical adsorption sites present at the surface.

In a different context, hydrogen on covalent semiconductor surfaces is receiving considerable attention because it readily reacts with the surface dangling bonds to form stable hydrides. In some cases, unreconstructed ideal surface termination occurs that provides an ideal system for experimental investigation and theoretical modeling of the semiconductor surface. Moreover, as H_2 is one of the simplest adsorbates for studying adsorption, reaction, and desorption of molecules on semiconductors, it may serve as a prototype for understanding more complex molecules.

It has been shown recently that H induces Si surface segregation on 1.4 monolayer Ge-covered Si(001) surfaces.[10] In this paper, we confirm these results with x-ray photoemission diffraction (XPD) and high-resolution electron-energy-loss spectroscopy (HREELS). In addition, we demonstrate that the Ge/Si exchange already occurs at room temperature (RT) in support of the thermodynamic model favoring the formation of Si-H over Ge-H bonds at missing dimer lines. We also show that Si-H segregation is enhanced when increasing the temperature of H exposure. We correlate the development of Ge/Si site exchange with the increase in Ge-H decomposition with temperature. Based on these results, and on the knowledge of the H population on Ge-covered Si(001) surfaces,[11–15] we propose an energetic scheme that provides a simple thermodynamic explanation for both the enhancement of Si-H formation and the saturation of Si/Ge exchange mechanism.

Our experiments were carried out in a series of four interconnected ultrahigh-vacuum chambers (base pressure below 2×10^{-10} Torr). The first two compartments are dedicated to quick sample introduction, gas dosing (germane, disilane and hydrogen), and decomposition by means of an 1800-K heated tungsten filament, and ion bombardment facilities. A third chamber provides x-ray photoemission spectroscopy (XPS) and low-energy-electron diffraction (LEED) capabilities. A two level vacuum system houses the IB2000 (VSW Instruments Ltd.) HREEL spectrometer, consisting of double pass cylindrical deflectors in both the monochromator and analyzer.[16]

Substrates—$13\times15\,\mathrm{mm}^2$ in size—were cut from a 400-μm-thick Si(001) n-type (P-doped) wafer with $\rho = 5-10\ \Omega\,\mathrm{cm}$. Samples were resistively heated using a homemade power regulated and computer controlled power supply designed in our laboratory. The heating power was calibrated against temperature with a Cr-Al thermocouple clamped on the sample surface. Temperatures above 300 °C were further controlled with an infrared pyrometer (IRCON 300). To obtain the clean Si(001) 2×1, we followed the standard procedure of argon ion sputtering and annealing to 950 °C. Then, Ge was deposited, by thermal decomposition of GeH_4 onto the Si(001) surface held at 550 °C. The Ge coverage was controlled by adjusting both the feed gas pressure and the germane exposure time, calibrated against XPS measurements. With this preparation, we consistently obtained a sharp and well-contrasted LEED pattern, displaying the extra $2\times N$ ($N\geqslant8$) spots of reconstruction resulting from lines of missing dimer rows.[4] Atomic H was produced by W decomposition of 10^{-5} Torr of H_2 gas (uncorrected ion gauge reading). A 5-min dosing time was used for exposures

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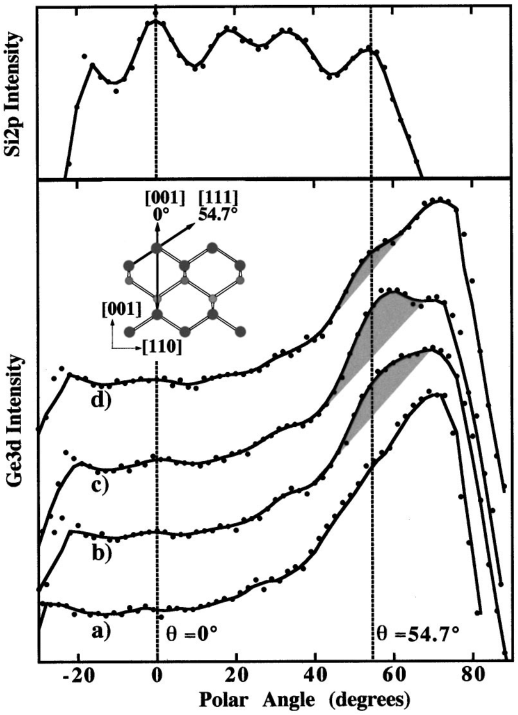

FIG. 1. Si2*p* (upper panel) and Ge3*d* (lower panel) XPD profiles recorded after (a) deposition of one Ge monolayer on Si(001) surface at 550 °C, (b) further exposed to atomic H at RT; (c) exposed at atomic H at 350 °C, and (d) annealed to 550 °C.

above 100 °C. When needed by the experiments (see below) and in order to saturate all the surfaces dangling bonds, the film was subsequently dosed at RT for 1 min.

Si2*p* and Ge3*d* core level emissions resulting from excitation with x-ray Al $K\alpha$ source were recorded as a function of polar angle along the [110] azimuth. For these kinetic energies (~1 keV), the electron intensity distribution modulates in such a way that it essentially reflects forward focusing along atomic rows, and is commonly designated as XPD.[17]

The XPD profiles obtained on clean and hydrogenated Ge-covered Si(001) surfaces are presented in Fig. 1. The upper panel displays the electron angular distribution emitted from the Si2*p* core level. The two main intensity maxima at 0° and ~55°, respectively correspond to forward focusing in the [001] and [111] direction, in the $(1\bar{1}0)$ plane of the diamond structure. In the lower panel, Fig. 1(a) shows the polar intensity distribution of photoelectrons emitted by Ge3*d* after deposition of one Ge monolayer on Si(001). As expected from the Stranski-Krastanov growth mode for Ge/Si(001),[18] there are no Ge emitters under the top Ge layer and the XPD profile only shows the intensity increase at grazing emission due to a better matching between the analyzer and x-ray illuminated foot print area, i.e., we measure here the instrumental response function. Following a RT atomic hydrogen exposure, a slight intensity reinforcement around 55° is observed in Fig. 1(b) on the XPD profile which otherwise remains essentially the same. This effect is further enhanced with H exposure at 350 °C as shown in Fig. 1(c). As schematically represented in the inset of the lower panel, the intensity maximum at 54.7° requires the presence of Ge emitters underneath the surface top layer, at least in the second layer.[18] From that, we can readily deduce that both RT and 350 °C hydrogenation of Ge/Si(001) partly led to site exchange of Ge atoms in the first layer with some Si underneath. At this point, we note that the experimental observation of surface atoms in dimer position, although slightly tilted out of the $(1\bar{1}0)$ diffraction plane, is probably made easier by the relatively poor angular acceptance of our spherical analyzer (estimated to be about 10°) combined to the ~10° diffusion angle of the Ge3*d* core level line. The Ge/Si place exchange induced by H exposure in the 260–330 °C temperature range, previously observed by means of Fourier transform infrared-attenuated total reflectance spectroscopy,[10] is now confirmed independently through these XPD data, with one supplementary fact that the mechanism already initiates at RT. In addition, Rudkevich *et al.*[10] reported the reversibility of the Ge/Si place exchange. Actually, starting from the preparation presented in Fig. 1(c) and by annealing at 550 °C for two minutes, we obtained the XPD profile displayed in Fig. 1(d). The structure at ~55° is strongly attenuated, and Fig. 1(d) is globally comparable to Fig. 1(a). This result indicates that most of the Ge atoms recover their initial bonding configuration in the first layer after heating at elevated temperature. However, the residual intensity modulation at ~55° seems to suggest that some Ge atoms are still occupying a second layer position.

Similar information is obtained using the HREELS technique. Data were collected in specular geometry (incident equal to reflected angle $\theta = 65°$) at 6 eV primary beam. The energy resolution—as deduced from the full width at half maximum (FWHM) of the reflected elastic electron beam—ranges from 32 to 40 cm^{-1}, and the count rate varies from 2 to 10×10^5 cps. The latter was usually slightly lower after deposition of Ge monolayer than on the clean Si(001) surface. In Fig. 2(a), we present the HREELS spectra recorded at RT immediately after H dosing the Ge-covered Si(001) surface at various temperatures (150–350 °C). Next, in order to tag the surface atoms with hydrogen, the surface was further exposed to atomic H at RT [Fig. 2(b)] to ensure the saturation of all surface dangling bonds. The loss features are well documented.[19–22] Here, our interest will bear on the stretching vibrations of Ge-H approximately at 250 meV and Si-H at 261 meV. As shown elsewhere,[23,11] these modes mostly reflect the monohydride population and provide—at monohydride saturation—indirect information about Ge and Si surface composition. From the lowest curve of Fig. 2(b), we can determine from the stretching mode relative intensities that approximately 80% of the surface was initially covered with Ge. The situation is unchanged with a surface preliminary H exposed at 150 °C. For H exposure above this temperature, Ge and Si atoms exchange their place more efficiently and the Si-H stretching mode grows in intensity. On the contrary, annealing at 550 °C and subsequently H dosing at RT (upper spectrum in Fig. 2(b)) restores the Ge-H to Si-H ratio to the value we have measured after the initial H exposure at RT. Again the reversibility of site exchange[10] is demonstrated.

Using an *ab initio* pseudopotential plane-wave method, Rudkevich *et al.*[10] compared the surface energy difference of Si(001) surfaces containing one monolayer of Ge either as top or as second layer, considering both clean and monohydride terminated surfaces. They calculated that a clean Ge-

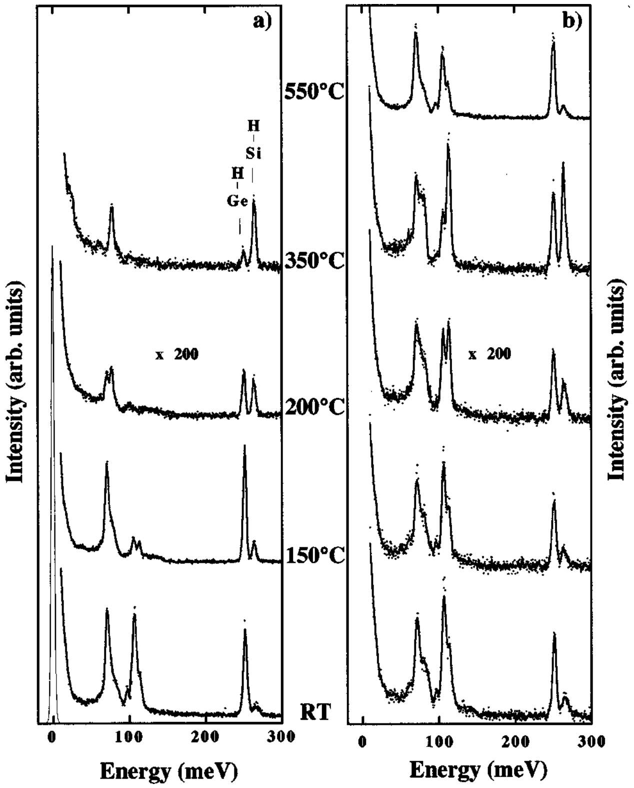

FIG. 2. HREELS spectra recorded at RT in specular mode ($\theta = 65°$) at 6 eV primary beam energy on monolayer Ge-covered Si(001) (a) after dosing at RT and elevated temperatures and (b) with supplementary H exposure at RT.

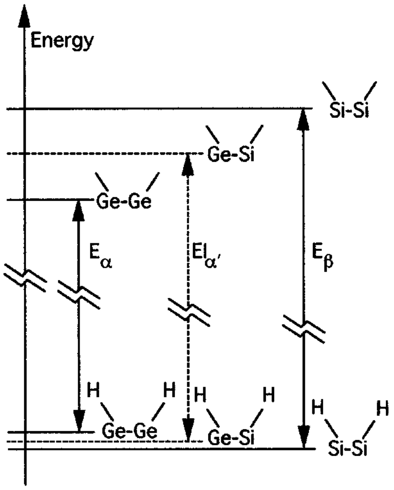

FIG. 3. Schematic representation of the plausible energetic arrangement of the various possible surface dimer configurations. To help the discussion, we have superimposed the energetic diagram proposed for desorption energies E_α, E_β, and $E_{\alpha'}$, for monohydride decomposition from pure Ge-Ge, Si-Si, and mixed Ge-Si dimers, respectively.

terminated surface is energetically more stable than an Si-terminated one, and found the reverse order for hydrogenated surfaces. The thermodynamic feasibility of the Ge/Si place exchange has thus been demonstrated. However, if one neglects monohydride decomposition in this temperature range, the Ge concentration is expected to grow with increasing temperature, but the opposite trend was actually observed[11] and this is also clear in Fig. 2(a). Increasing the H-exposure temperature led to a decrease of surface Ge atoms. Based on temperature programmed desorption (TPD) data, Rudkevich *et al.* neglected monohydride desorption below 320 °C. However, the desorption temperatures provided by TPD with 5 K/s heating rate are higher than those actually observed in a static annealing experiment. Yet, there are some drastic modifications of the hydrogen population between 150 and 450 °C,[11] which we presently believe provides the thermodynamic driving force for the exchange phenomenon. This change of H population with temperature is clearly seen by correlating the surface concentration determined after dosing at elevated temperature [Fig. 2(a)] with those measured after subsequent H dosing at RT [Fig. 2(b)]. At 150 °C, the relative intensities of the stretching bonds are comparable to those measured at RT. The Ge-H stretching mode is even slightly more intense. Above 200 °C, the Ge-H relative intensity begins to drop and the Si-H stretching vibration largely dominates at 350 °C. However, the observation of only small numbers of Ge-H bonds at high temperature on Figure 2(b) is not uniquely due to the disappearance of Ge atoms from surface position as described above: it mostly reflects H desorption from Ge above 150 °C.[11] By comparing Fig. 2(a) with Fig. 2(b) we see that supplementary H adsorption on Ge is possible by dosing at RT from what we can readily deduce that H incompletely saturates the Ge surface dangling bonds at high temperature. Indeed, the determination by HREELS of the hydrogen population on Ge-covered Si(001) surface[11] shows that most Ge-H bonds are decomposed below 200 °C, due to paired hydrogen desorption from Ge-Ge dimers and that only few Ge-H bonds subsist up to ~350 °C, corresponding to H adsorbed on the Ge atoms involved in mixed Ge-Si dimers.[24]

Summarized in Fig. 3, we propose the following picture to interpret our results. The thermal decomposition of germane on Si(001) at 550 °C implies the formation of Ge-Ge dimers (for a complete monolayer). There is no interdiffusion and the Ge atoms remain at the surface because the formation of Ge-Ge dimers lowers the surface free energy in comparison to a surface terminated with Si-Si dimers. Following the RT H exposure, the place exchange of a Ge with a Si atom is thermodynamically feasible[10] and the H-Si-Si-H energy is lower than the H-Ge-Ge-H one (Fig. 3). However, because this energy difference is relatively small, the mechanism most probably only takes place where the atomic H ''sees'' the Si atoms, that is to say at the location of missing dimer rows[10,25] where the exchange-barrier is the lowest.[25] At this temperature, the process quickly saturates, provided we neglect the possibility of place exchange at the defects generated by bond breaking (etching) due to dihydride (or higher hydrides) formation. There is basically no modification to be expected up to 150 °C because the H population is unchanged[11] and the energetics remains similar to those at RT. When temperature is increased above 200 °C, the thermal energy eventually exceeds the energy necessary to overcome the desorption energy E_α, and in turn prohibits the formation of Ge-H bonds on pure Ge dimers.[11] The energetic balance is thus very unfavorable to allow Ge-Ge with free surface dangling bonds to remain at the surface. Then, there will be a competition between the energy gained by stabilizing H-Si-Si-H units at the surface and the energy needed for the diffusion process. Moreover, the picture is probably further complicated by the possibility of creating mixed Ge-Si dimers[24] with a reactivity slightly lower towards atomic H, but quite comparable to the Si-Si dimers, as evidenced by the proximity of the desorption temperatures (and likely the desorption energies E_α, and E_β).[11] The presence of H-Ge-Si-H at the surface should represent a good compromise because only half of the Ge atoms from the initial monolayer composition need to diffuse from the upper layer to the second layer underneath. Besides, despite a higher energy barrier for monomer compared to dimer exchange,[25] the presence and formation of hydrogenated heterodimers provide a simple explanation for the saturation of the place exchange before its completion.

To sum up, we have studied the Ge/Si place exchange induced by hydrogen at one monolayer Ge-covered Si(001) surface, using XPD and HREELS. We have confirmed previous experimental works[10] and extended the observation of the exchange process down to RT. We have correlated the increase of Si at the surface with the decrease of Ge-H bonds with increasing temperature. Based on energetic considerations, we have proposed that H may favor the formation of mixed Ge-Si dimers, providing a clue for the saturation of the exchange mechanism before its completion. We hope this work will stimulate further theoretical work.

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