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Hydrogen population on Ge-covered Si(001) surfaces

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A series of isochronal annealing experiments have been performed using high resolution electron energy loss spectroscopy in order to probe the thermal decomposition of monohydride and dihydride species from Ge-covered Si(001) surfaces. The Ge coverage was varied from submonolayer until completely covering the silicon surface. The films were exposed to atomic hydrogen at room temperature and the intensities of the hydrogen vibrational features were monitored as a function of annealing temperature. Marked steps in the stretching mode intensities are observed, directly connected to monohydride decomposition. The existence of a desorption state specific to surface alloying is thus clearly identified in the Ge-H stretching intensity temperature dependence curve, interpreted as involving the recombinative desorption of two hydrogen atoms from mixed Ge-Si dimers. From the scissors mode intensity variation, it is deduced that both Ge and Si dihydride species decompose simultaneously at all coverages, and that it always occurs before monohydride desorption takes place. Furthermore, we observe the Ge-H_2 formation enhancement due to the presence of the neighboring silicon atoms. Finally, the desorption of all hydride species is shown to be boosted when increasing the Ge contents at the Si(001) surface. To summarize this study, the complete experimental desorption diagram of the hydrogen population, as functions of both stoichiometry and temperature, is presented.
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I. INTRODUCTION

Chemisorption of hydrogen on covalent semiconductor surfaces is receiving considerable attention both for its technological and scientific interests. Hydrogen can readily react 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. On the other hand, H_2 is one of the simplest adsorbates to study adsorption, reaction, and desorption of molecules on semiconductors and may serve as a prototype to understand more complex molecules.

Indubitably, hydrides also play a central role in growth processes such as chemical vapor deposition (CVD).[1] Upon decomposition of reactants on the substrate surface, stable hydrides are formed. Eventually, hydrogen atoms act as site blockers,[1] preventing further adsorption and gas reaction. However, by modifying the hydride composition at the surface, the opposite effect can be obtained and hydrogen may play the role of a surfactant.[2,3] More generally, growth processes are driven by thermodynamics and kinetics at the atomic level,[4] which can be considerably influenced when hydrogen is present. Therefore, modeling growth in CVD as a first step requires the exact knowledge of the population of adsorbed sites and of the modifications brought by changes in temperature and/or surface composition.

Amongst the various techniques used to probe desorption, thermal desorption spectroscopy (TDS) has been widely used.[5–9] It is easy to install experimentally and allows the access to fundamental quantities such as activation energies or adsorption energies, order of desorption, which are valuable information to be directly compared with theory. However, because hydrogen is only accessible as a molecule in its gas phase it is usually necessary to use a complementary technique[10] in order to connect the TDS hydrogen desorption features with the related bonding configurations at the surface.

In turn high resolution electron energy loss spectroscopy (HREELS) detects atoms and molecules while they are still adsorbed at the surface. Chemical adsorption sites and hydride composition may thus often be determined unambiguously.[11] By using this vibrational spectroscopy, Schaefer *et al.*[12] were the first to successfully study the thermal decomposition of hydrogen on SiGe alloys. Moreover, they established that the combination of HREELS with atomic hydrogen could be used as a probe of the surface composition in semiconductor alloy.[13]

Recently, we performed HREELS studies of post-grown surfaces of $Si_{1-x}Ge_x$ prepared by hot-wire CVD at $\sim 350\,°C$.[14] We found that because of the presence of neighboring silicon atoms some Ge-H bonds were stabilized at this (relatively elevated) temperature. Moreover, when this temperature is used to grow alloys, the surface undergoes a metal-semiconductor transition occurring with changes of stoichiometry,[15] and apparently connected with the apparition of free surface dangling bonds deriving from the modifications in hydrogen population.

All these phenomena have motivated a series of isochronal annealing experiments in order to accurately determine the desorption temperatures of hydrides from Ge-covered Si(001) surfaces. The Ge/Si(001) system is often used to simulate SiGe alloys and a picture of the initial growth stage seems now to be well established.[16]

II. EXPERIMENTAL

The experimental setup consists of a series of four interconnected ultrahigh-vacuum chambers (UHV) with 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 a 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, with a double pass cylindrical deflector in both the monochromator and analyzer according to the design of Ibach.[17]

Substrates, $13\times15\,\mathrm{mm}^2$ in size were cut from a 400 μm thick Si(001) n-type (P-doped) wafer with $\rho=5-10\,\Omega$ cm. The clean Si(001) 2×1 was obtained in the usual way: cycles of argon ion sputtering and annealing to 950 °C. Within our experimental setup, the best Ge films were obtained with a technique derived from catalytic-CVD (Ref. 18) and UHV-CVD (Ref. 19), i.e., by W-filament decomposition of GeH_4 onto the Si(001) surface held at 350 °C, followed by a brief flash annealing at 600 °C. This procedure always resulted in a sharp and well contrasted LEED pattern, 2×1 at low Ge coverage and displaying the extra $2\times n$ ($n\geqslant8$) spots of missing dimers rows[20] expected for a Ge monolayer on Si(001). Atomic H was produced by W-decomposition of 10^{-5} Torr of H_2 gas (uncorrected ion gauge reading) and surfaces exposed during 5 min. As shown in the next section, this 3000 L dose ($1\,\mathrm{L}=10^{-6}$ Torr s) leads to monohydride saturation of the surface as well as dihydride formation. The LEED pattern converts from 2×1 to 1×1, for pure Si surface as well as with submonolayer Ge coverages. However, the 2×1 superstructure subsists faintly but still observable for nearly complete Ge monolayer.

In the present study, HREELS data were collected in specular geometry (incident equal to reflected angle $\theta=65°$) with primary beam energy set to 6 eV. This energy approximately corresponds to a maximum in the reflected elastic peak intensity for both the clean and hydrogenated silicon surfaces and therefore, though weak, the dipole activity is expected to be maximal. The energy resolution, as deduced from the full width at half maximum (FWHM) of the reflected elastic electron beam is $\sim$40 cm^{-1}, with a count rate ranging from 2 to 10×10^5 counts per second. After germanium deposition, the elastic intensity was usually slightly lower than the one measured on the clean Si(001) surface. This may reflect structural defects in film morphology, but may be due as well to a displacement in the $I(V)$ curve local energy maximum. On the contrary, the elastic intensity which is mostly constant during an annealing experiment, strongly reduce by a factor 2 to 4 with monohydride decomposition because of the disorder introduced by the desorption process at the surface.

A home made power-regulated and computer-controlled power supply was specially designed in our laboratory in order to perform isochronal annealing experiments. 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 IR pyrometer (IRCON 300). For the present desorption experiments, the sample was gradually annealed at increasing temperatures for a constant 120-second period. An HREELS spectrum was taken between each heating step, after cooling the sample down to 60 °C or below.

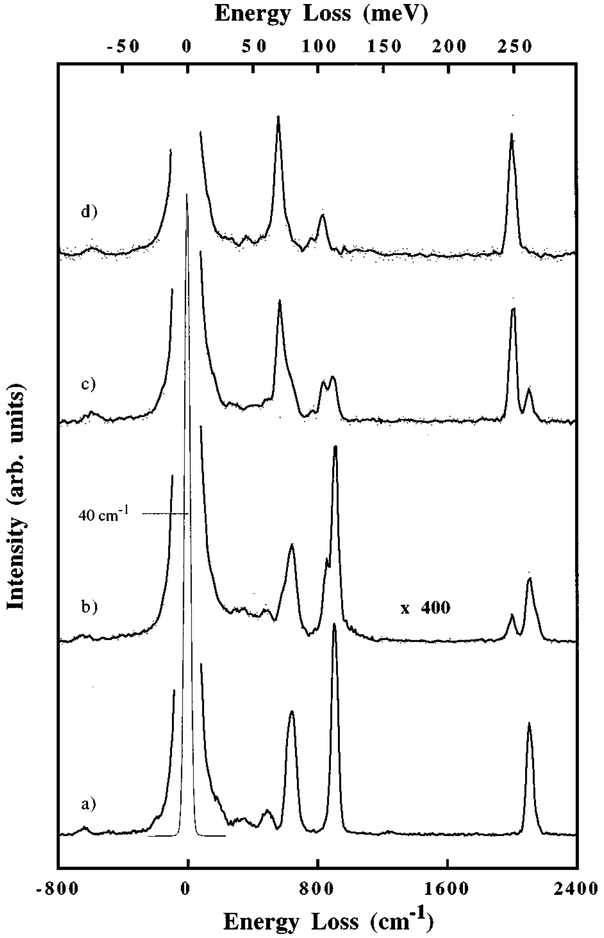

FIG. 1. HREELS dipole spectra recorded on various surface preparations, after a RT atomic hydrogen exposure (equivalent to a 3000 L H_2 dose). (a) Hydrogenated Si(001) 1×1 surface. Hydrogenated Ge-covered Si(001) surface, with germanium films resulting from (b) 100 L, (c) 270 L, and (d) 1170 L, GeH_4 exposure. Specular scattering geometry with 6 eV primary beam energy and $\theta=65°$.

III. RESULTS AND DISCUSSION

A. General aspect in HREEL spectra analysis

Let us first present typical HREEL spectra obtained on Si(001) surfaces with various Ge coverages, and subsequently exposed to atomic hydrogen at RT: the bare Si(001) surface [Fig. 1(a)], the Si(001) surface covered with a germanium film resulting from 100 L [Fig. 1(b)], 270 L [Fig. 1(c)], and 1170 L [Fig. 1(d)] GeH_4 exposure. In the latter case, the surface is completely covered by the Ge film. The loss features present on the HREEL spectra are well documented.[21–23] They are commonly referenced as the stretching and bending modes for Si-H (2105, 625 cm^{-1}) and Ge-H (2000, 580 cm^{-1}) related to monohydride configuration on dimers. The Si-H_2 (900 cm^{-1}) and Ge-H_2 (840 cm^{-1}) scissors modes correspond to dihydride formation consequent to dimer bond breaking. On silicon surfaces partially covered with Ge [Figs. 1(b) and 1(c)], the FWHM on the elastic peak (40 cm^{-1}) permits us to clearly distinguish be-

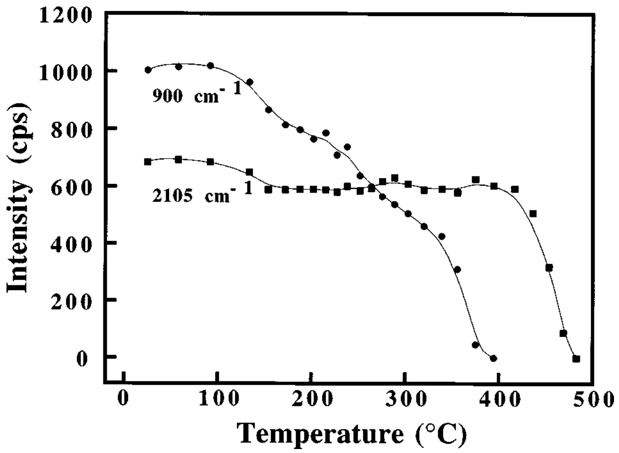

FIG. 2. The 2105 cm^{-1} stretching mode (squares) and 900 cm^{-1} scissors mode (circles) intensity variation as a function of annealing temperature, on the RT (1×1) hydrogenated Si(001) surface.

tween the Ge-H and Si-H stretching modes as well as to identify the scissors mode intensity maxima. This is obviously not the case for the bending vibrations. Indeed on the Si(001)-3×1 hydrogen induced reconstruction, another loss feature connected with the presence of dihydrides was resolved at low temperature (110 K) from the Si-H bending and interpreted as the 640 cm^{-1} wagging mode of Si-H_2.[24] Although it has not been observed so far, we also expect a Ge-H_2 wagging mode to exist in this energy range. In consequence, due to the difficulty of interpreting the 600–700 cm^{-1} range in the present work, we will restrict ourselves to the analysis of the stretching and scissors mode intensity behaviors.

Up to now, we have implicitly assumed that the stretching modes are a vibrational signature exclusively related to the monohydride populations. Indeed, this is not straightforward since, for instance on silicon surfaces, a Si-H_2 stretching mode was theoretically predicted[25] and is actually resolved by infrared reflection spectroscopy[26] split by ~8 cm^{-1} from the monohydride stretching mode. In fact, very recently, by using the last generation of HREEL spectrometer combined with highly resistive sample substrates, Tautz and Schaefer[27] have demonstrated the possibility of observing all the vibrations predicted for the Si(001) hydrogenated surfaces. For the particular scattering geometries they used, both dipole and impact selection rules seem to collapse, and they found that both antisymmetric and symetric modes, arising from terraces as well as steps, from mono-, di-, and even trihydrides species, contribute to the stretching intensity.

However, let us now consider Fig. 2 that displays the absolute intensity of the stretching and scissors modes as a function of the annealing temperature, measured after room temperature (RT) hydrogen exposure of bare Si(001) surface. Obviously, the two losses behave quite differently from each other as the temperature increases. The intensity of the 900 cm^{-1} scissors mode is nearly constant up to 100 °C, then continuously decreases up to 350 °C, and more abruptly (over less than 50 °C) drops to zero. The scissors vibration is not anymore detectable above 400 °C. Over the whole temperature range the stretching mode intensity remains basically unperturbed. To conclude on this point, with the data presented on Fig. 2, there is not clear correlation between the scissors and stretching modes intensities. This observation also applies for the complete set of measurements we are going to report and also agrees well with the earliest observations of Frotzheim.[21] Consequently we assume in the following that the intensity variations of the scissors and stretching modes distinctively and respectively depict the changes brought in monohydride and dihydride populations at the surface.

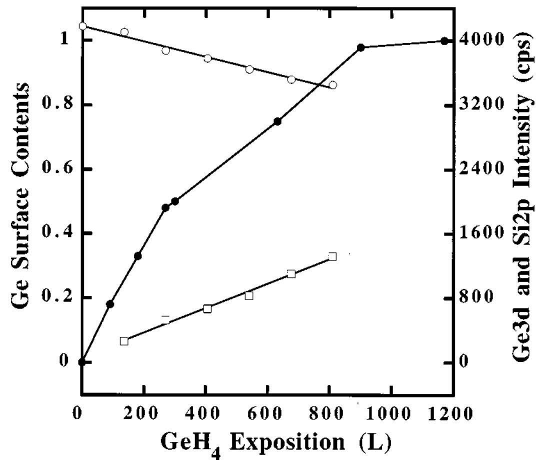

FIG. 3. Ge surface contents deduced from HREELS by measuring the relative intensities of the stretching modes (closed circles) compared with the intensity variation of the Si2*p* (open circles) and Ge3*d* (open squares) core levels measured by x-ray photoemission, as a function of germane exposure.

From Figs. 1(b) and 1(c) it can be seen that varying the germane exposure leads to a change of the relative Ge-H and Si-H stretching mode intensities. Indeed, in previous studies, Schaefer *et al.*[12,13] have demonstrated the possibility of using hydrogen and HREELS to probe the surface composition in SiGe alloys. By assuming equal oscillator strength for Ge-H and Si-H bonds, we estimate that 25 and 75 % of the surface are covered with Ge atoms, respectively for the preparations corresponding to the spectra of Figs. 1(b) and 1(c). However, the surface composition still may not directly reflect the exact Ge (submonolayer) coverage, since such a simple evaluation depends on the growth model. This point is better illustrated with Fig. 3. We have measured the XPS intensity, taken near grazing incidence to increase the surface sensitivity, as a function of the GeH_4 exposure and observed both a linear decrease of Si2*p* and linear increase of Ge3*d* core level signals, demonstrating that a constant growth rate is achieved. On the other hand, the surface composition x evaluated with HREELS, also plotted on Fig. 3, deviates from a simple linear law above 300 L germane exposures for which 50% of the surface were covered with Ge. From that, one would simply conclude that more than a Ge monolayer is necessary to completely bury the silicon surface, because of defects in the two-dimensional Ge island for instance. Still, we want to mention the possibility that the hydrogen exposure actually modifies the film morphology. Indeed, it was recently demonstrated that above 250 °C,[28] atomic hydrogen induces Si surface segregation. In fact, we will show elsewhere experimental indications that the Ge-Si site exchange mechanism[28] already takes place at room temperature, but this point is beyond the scope of the present paper.[29]

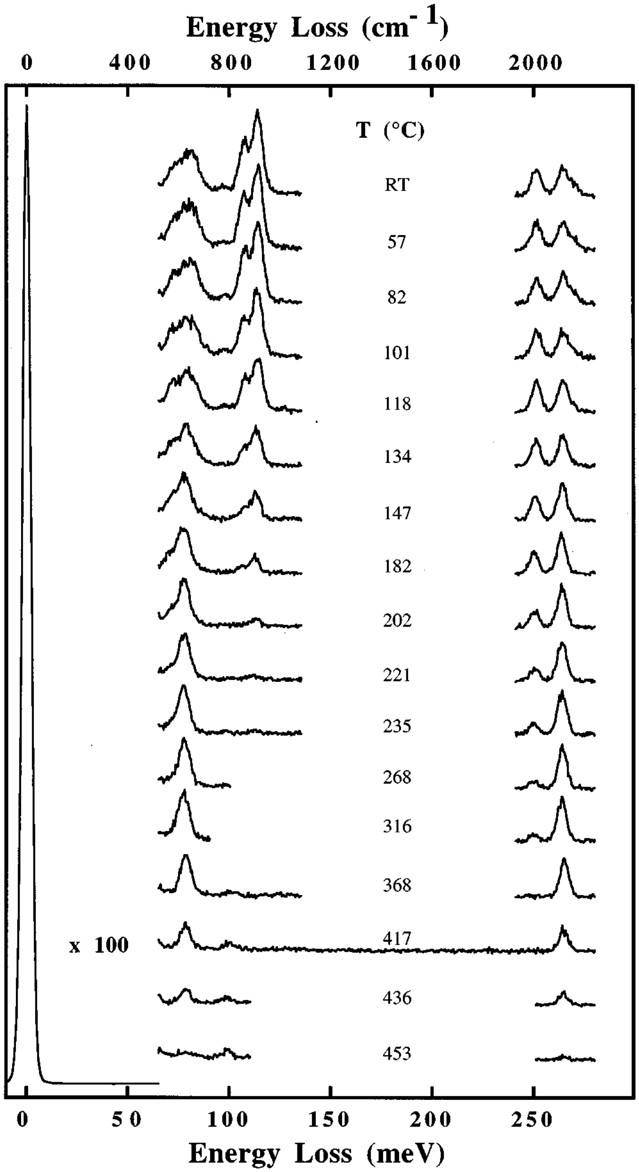

FIG. 4. HREELS spectra at 6 eV primary energy and $\theta = 65°$ specular angle, recorded during an isochronal annealing experiment.

Some of the HREELS spectra taken during a typical isochronal annealing experiment, which depict the intensity behavior of the stretching and scissors modes as a function of the annealing temperature, can be found in Fig. 4. The HREELS spectrum recorded immediately after RT H-exposure indicates that for this preparation, approximately half of the silicon surface is covered with Ge atoms. As the temperature increases, we observe that the intensity of the various vibrational features eventually decrease reflecting hydride desorption from the surface. Similar series of spectra were obtained, varying the Ge contents at the surface, and intensities of stretching and scissors modes were quantitatively extracted by fitting each spectrum with Gaussian curves. We thus obtained the isochronal annealing intensity curves that we present in the next two sections. To simplify the discussion we describe the stretching vibration evolution separately from the scissors one in the next two sections, although both modes have been measured simultaneously on the HREELS spectra.

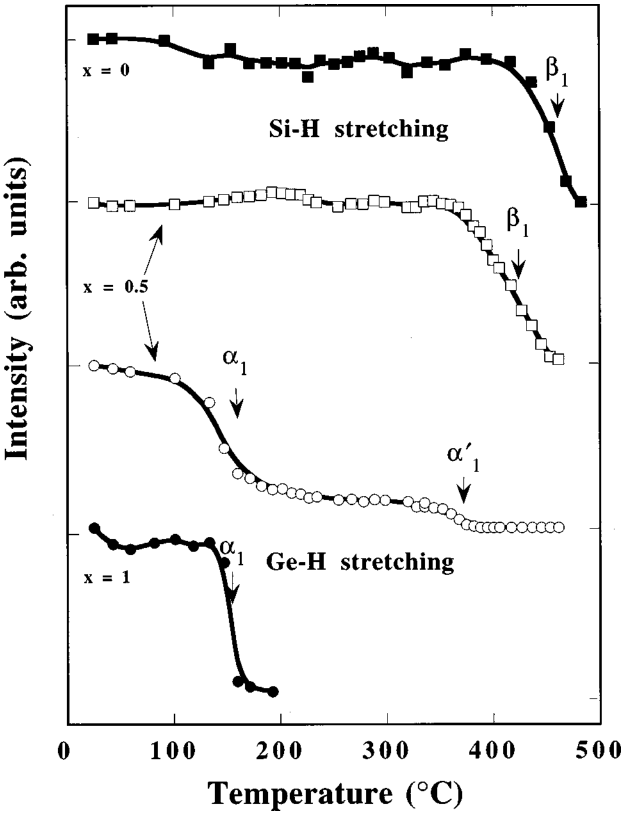

FIG. 5. Desorption curves for the 2105 cm^{-1} (squares) and 2000 cm^{-1} (circles) losses associated to the Si-H and Ge-H stretching modes. Full symbols correspond to a surface composed of pure Si ($x = 0$) or Ge ($x = 1$) element. Data on a mixed ($x = 0.5$) GeSi surface are shown with open symbols.

B. Monohydride decomposition

The intensity variation of the stretching modes with annealing temperature is presented on Fig. 5 for three different surface compositions relevant to the present discussion. For clarity, intensities have been normalized to the spectrum initially recorded after the RT H-exposure, i.e., before starting the annealing procedure. The upper and lower desorption curves were measured on surfaces consisting of pure Si ($x = 0$) and pure Ge ($x = 1$) composition. The marked step in the intensity curves allows the clear identification of the Si-H and Ge-H decomposition temperatures. The desorption temperature for H from Si dimers, which we note β_1, is measured at ~470 °C on Si(001) surface. Similarly, we found that Ge-H decomposes around ~190 °C. As expected, these values are slightly lower than those reported by TDS on Si(001) (~525 °C) (Refs. 30 and 31) and Ge(001) (~290 °C) (Ref. 32) surfaces, because the latter technique uses a linear ramp of finite rate that shifts the temperature desorption maxima towards higher values.[33]

The two curves at the center of Fig. 5 represent the intensity variation of the Si-H and Ge-H stretching modes at a surface with mixed ($x = 0.5$) composition. In this case, the behavior of the Si-H stretching mode intensity is qualita-

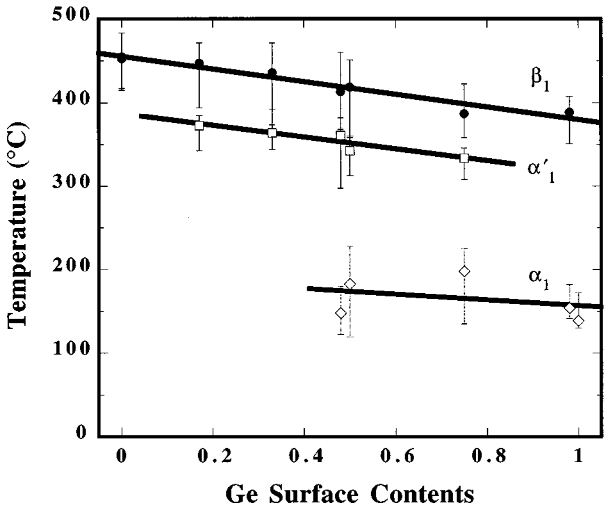

FIG. 6. Diagram of desorption temperatures for monohydrides. The full circles represent the Si-H decomposition temperature, and the open symbols, the two temperature steps α_1 (diamonds) and α_1' (squares) observed on the Ge-H stretching intensity. The error bars represent the temperature extention of the steps.

tively unchanged but Si-H desorption now occurs at lower temperature. This result is in-line with the often-reported observation that a much easier route for Si-H decomposition is opened by the presence of Ge.[5,7–9] Interesting and quite remarkable is the Ge-H stretching mode intensity that largely differs from its evolution on a surface with pure Ge composition. This time, the Ge-H decomposition occurs in a two step process. For the intermediate stoichiometry of Fig. 5, the Ge-H stretching intensity first drops by 85% at ~190 °C (we will refer to this desorption step as α_1). Note that this temperature approximately corresponds to the H-desorption temperature of the pure Ge surface. However, 15% of the initial intensity is preserved up to 350 °C temperature at which the Ge-H stretching mode vanishes (α_1' step) from the HREELS spectra.

The above measurements and set of data taken for various Ge-covered Si(001) surfaces, are summarized on Fig. 6. Each point stands for the temperature at half maximum measured on each step, whereas the error bars reflect the step temperature extent. Obviously, α_1' is always detected as a marked step. This result is to be brought together with the observation of stable Ge-H bonds at 350 °C on $\mathrm{Si}_{1-x}\mathrm{Ge}_x/\mathrm{Si}(001)$.[14] Now, in view of the present result, we can readily conclude on the existence of a specific hydrogen adsorption site that derives from surface alloying. Here again, all the features disappear at lower temperature with the increasing of Ge surface coverage. It indicates that Si-H decomposition is boosted by the presence of Ge, and reciprocally Ge-H desorption is delayed under silicon environment. We note that within our experimental energy resolution, it was not possible to detect any shift in frequency that would indicate a change of the Si-H or Ge-H bond strength.

Concerning Ge-H desorption, the relative height of the α_1' step is greater for small Ge contents ($x<0.4$). Then, as the Ge coverage is increased, α_1 rapidly develops and this is the only step in the Ge-H desorption curve measured for coverages above $x>0.8$. We have summarized these results on Fig. 7 where the intensities of α_1' and α_1, relative to β_1, are plotted as a function of the surface Ge contents. Because of our definition by HREELS of the surface Ge contents x, the sum of intensities lies on the $y=x$ dotted line. For $x\sim0.2$, the lowest Ge contents used in our experiments, α_1' already seems to culminate at its maximum relative intensity. Above $x=0.4$, the intensity of α'_1 is strongly reduced and almost all the Ge-H decompose as α_1, at low temperature.

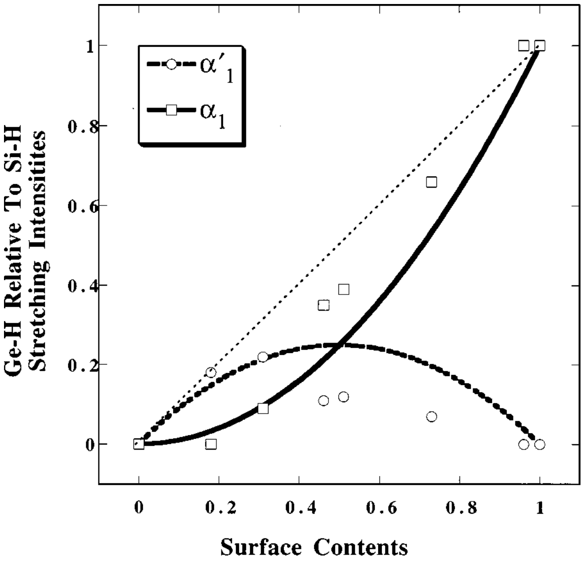

FIG. 7. Ge-H stretching modes partial intensity, that is to say, normalized to the total intensity of stretching modes. The full line represents the x^2 hydrogen population on Ge atoms belonging to pure Ge-Ge dimer. The dashed line is the $x(1-x)$ law for Ge-H on mixed Ge-Si dimers.

We may now go further into the discussion by recalling some recent advances on the growth of submonolayer of Ge/Si(001). Patthey *et al.*[16] have examined the surface core level shifts in high resolution photoemission measurements during the initial growth of Ge on Si(001) and have demonstrated the existence of mixed asymmetric Ge-Si dimers. Moreover, they found that this growth mechanism is predominant at very low coverage and that the formation of buckled Ge dimers over Si(001) only occur near monolayer completion. Presently, recent theoretical works favor the formation of mixed Ge-Si dimers against formation of pure Si-Si or Ge-Ge dimers,[34] at least for half monolayer Ge coverage.[35] For very low Ge coverages, Ge atoms are likely to be surrounded mostly by Si. By assuming that during the brief annealing period, all the atoms of the Ge film dimerize to lead the observed (2×1) LEED pattern, a majority of Ge atoms are expected to be involved in bonding with Si. The hydrogen dose used in the present experiments, as well as the observation of dihydride units (see Fig. 1 and next section) ensure that all the surface dangling bonds are saturated with hydrogen. Yet, it is generally admitted that the desorption mechanism of monohydrides on Si(001) (Refs. 30, 36, and 37) and Ge(001)-2×1 (Ref. 32) consist of a pairing model, in which a paired set of hydrogen atoms desorb from a single dimer unit. It allows to account for the energetics involved by π bonding, as well as the first order desorption kinetics observed by TDS. β_1 and α_1 thus derive from the recombinative desorption of hydrogen from pure Si-Si and Ge-Ge dimers. With a similar scheme and in the framework of the mixed Ge-Si dimers model, desorption feature α'_1 is interpreted as the result of *hydrogen recombinative desorption from mixed Ge-Si dimers*. Correlatively, considering a random distribution of Ge atoms embedded in a two-dimensional Si matrix, the quantity of H desorbing from the Ge atoms belonging to mixed Ge-Si dimers, is predicted to depend on the Ge contents x as $x(1-x)$ represented as a dashed curve on Fig. 7 (renormalized to 1), the second H is provided by the Si. The x^2 law for the H population on pure Ge-Ge dimer pairs is shown as a full curve. There is a qualitative agreement between the HREELS data (Fig. 7) and this simple statistical model. Still, the measurements deviate from the predictions, particularly at high coverage. On one hand, it may indicate that with more Ge added at the surface, preferential Ge-Ge pairs are formed to the detriment of mixed Ge-Si dimers. The formation of a top layer of buckled Ge layer is then favored, both in agreement with the observations of Patthey *et al.*[16] and theoretical calculations.[35] On the other hand, the relative intensity in HREELS may not be directly proportional to the Ge coverage. In particular, H modifies the morphology of the Ge films already at room temperature,[29] because the Si-H formation is thermodynamically favored against free Ge dangling bonds, inducing partial Si segregation at the surface.[28,29]

Considering the recombinative desorption mechanism from mixed dimers, one would expect a two-step decrease for the Si-H stretching intensity, never detected during these experiments. We see two reasons that actually would hinder this observation. First, the hydrogen desorption temperatures from Si-Si and Ge-Si are very close, and secondly, the Si-H bonds formed on the Ge-Si dimers always represent a small percentage (a maximum of ~20%) of the entire Si-H population.

As additional arguments to establish mixed Ge-Si dimers as a specific hydrogen adsorption site, we note that in recent infrared reflection spectroscopy experiments,[38] two distinct vibrational features were assigned to the stretching of Si-H and Ge-H isolated modes localized in the mixed dimers. Also, Kim *et al.*[9] have interpreted their D_2 temperature-programmed desorption spectra by fitting with four second-order peaks, one corresponding to D_2 desorption from mixed Ge-Si monodeuteride dimers (referenced as β'_1 in their paper).

C. Dihydrides decomposition

The variation of the scissors mode intensity with temperature has already been presented on Fig. 2 for the RT hydrogen-exposed Si(001) surface. It was shown that instead of observing a sharp temperature transition, dihydride decomposition occurs rather continuously, over a wide temperature range. The desorption process only accelerates around 350 °C. Also on Fig. 1, the 845 cm^{-1} Ge-H_2 scissors mode was observed, for all Ge contents. The existence of dihydrides on germanium surfaces was for some time a subject of controversy.[39–41] Anyway, the presence of Ge-H_2 was reported by all the authors studying H-adsorption on Ge(001) (Ref. 23) or SiGe(001) (Refs. 12–15) surfaces with HREELS demonstrating its highest sensitivity to dihydride species as compared to other hydrogen-sensitive techniques. Still, although the same hydrogen dose was used in all the preparations, a large difference is observed in the scissors to stretching modes intensity ratio, when comparing the fully Ge-covered surface [Fig. 1(d)] to the Si(001) one [Fig. 1(a)]. On one hand, it seems that dihydride formation is more difficult on Ge(001) than on Si(001) surface. But this result could also reflect a smaller dipole activity for the Ge-H_2 scissors vibrations. However, because a correlation exists between the development of the scissors mode and the disappearance of the 2×1 LEED pattern,[23] we assume that its intensity actually reflects the amount of dihydride units at the surface.

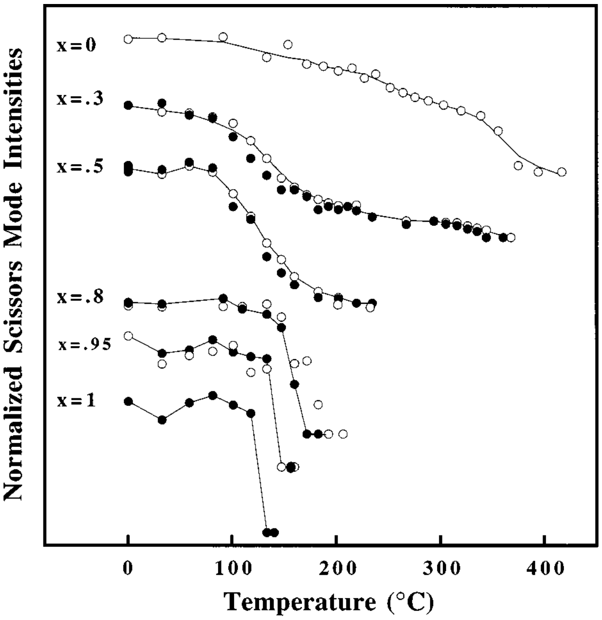

FIG. 8. Isochronal annealing desorption curves recorded on the 840 cm^{-1} of Ge-H_2 (closed circles) and 900 cm^{-1} of Si-H_2 (open circles) scissors modes. The Ge surface contents x are indicated on the left of each desorption curve, as they are deduced from the relative intensity of the stretchings.

Thus, on Fig. 1(b), despite the low Ge contents, the Ge-H_2 scissors mode intensity is about three times the intensity of the Ge-H stretching vibration and, as shown on Fig. 1(c), it does not develop further by increasing the Ge contents. Hence, we can readily conclude that Ge-H_2 formation is strongly enhanced due to the presence of neighboring silicon atoms. We propose the following interpretation. Dihydride formation results from surface energy gained over breaking dimer bonds. We assume that more energy is gained by forming dihydrides on a surface terminated with Si rather than Ge. At low Ge coverage, we have seen in the previous section that the statistical distribution ensures that the Ge are likely surrounded by silicon, far enough from other Ge atoms, and thus mainly involved in Ge-Si mixed dimers. Considering the fact that the monohydride desorption temperature from mixed dimer lies in between the monohydride desorption temperatures from Si-Si and Ge-Ge dimers, it is reasonable to assume that the energy gained in breaking Ge-Si bond also lies between the pure Si-Si and Ge-Ge dimers. Hence, a mixed dimer is more easily broken than a Ge-Ge dimer, which explains the increased contribution of the 845 cm^{-1} loss to the dipole spectra [Figs. 1(b) and 1(c)] on alloyed surfaces.

The scissors modes intensities and temperature dependence as a function of surface Ge contents are presented on

Fig. 8, normalized to their intensities measured after RT hydrogen exposure. From these data, it is remarkable that Ge-H_2 *and* Si-H_2 *simultaneously decompose, for all* Ge *coverages*. This observation strongly contrasts with the distinct desorption temperatures measured for monohydrides (Fig. 6) relevant to H_2 departure from each dimer species. In fact, the present result demonstrates that Si and Ge are involved in a common and undiscernible H_2 desorption process. Moreover, because the H_2 desorption temperatures are found to be drastically lowered with an increasing of the Ge contents, from what we deduced that desorption is initiated by the Ge atoms. Considering either the recombinative or the self-associated desorption processes[42] for Ge-H_2 decomposition, we propose that the appearance of reactive free dangling bonds concomitantly implies dimer reconstruction, i.e., bonding of Ge with a neighboring atom independently of its Si or Ge chemical nature. Finally, it is noted that dihydrides always desorb before monohydrides, whatever the Ge coverage. This desorption mechanism is consistent and mirror to the adsorption process. Indeed, starting from the hydrogenated Ge-covered Si(001) surface, with increasing temperature, dihydride desorption takes place, together with the 2×1 surface reconstruction, and then monohydride decomposition follows, first from Ge-Ge, than Ge-Si and finally Si-Si dimers. Reciprocally, during an adsorption experiment, by increasing coverage, H adsorbs first on Si-Si then Ge-Ge dimers dangling bonds, and dihydrides happens through breaking of dimer bonds and disappearance of the related 2×1 surface reconstruction. The present result suggests a reconsideration of the assignment of desorption features in TDS. First, Ge-H_2 was not always taken into account[5,9]—or with a distinct desorption temperature from Si-H_2 (Ref. 6)—and secondly Si-H_2 was always considered as decomposing at higher temperature than Ge-H, which is true only when hydrogen desorption temperatures from surfaces made with pure elements are compared. Finally, it is interesting to note that the presence of an even small quantity of Ge on the silicon surface will considerably decrease the desorption temperatures for dihydrides. The latter species strongly hinder gas reaction at low temperature in CVD and the strong decrease in the H_2 population brought by the presence of Ge provides a simple explanation for the growth rate enhancement often reported with SiGe growth.

IV. CONCLUSION

By monitoring the hydrogen vibrations with HREELS, we have determined the population of adsorption sites on Ge-covered Si(001) surfaces as a function of Ge coverage and temperature. A new desorption feature specific to the alloy is clearly identified and associated to mixed dimer adsorption sites. It is proposed that because the energy gained in breaking a Ge-Si bond is greater than the one gained in breaking a Ge-Ge bond, the presence of Si facilitates the formation of Ge-H_2 species. Reciprocally, simultaneous Si-H_2 decomposition is favored because dimerization indifferently occurs with a Si or Ge neighboring during Ge-H_2 decomposition.

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