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Formation and decomposition of $Ge_xSi_{1-x}(100)(2\times 1)$:H and $Ge_xSi_{1-x}(100)(1\times 1)$:2H

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Using high-resolution electron-energy-loss spectroscopy, we have investigated the formation and thermal decomposition of both the monohydride and the dihydride phases formed by exposing the (100) surface of Ge-Si alloys to atomic hydrogen. Ge monohydride and dihydride thermally decompose in the same temperature range as does Si dihydride (500 to 600 K) while Si monohydride persists to above 700 K. Using hydrogen as a marker, we were able to monitor the concentration of surface substrate atoms and found substantial Ge enrichment of the top surface layer relative to the bulk concentration. Variations in the surface composition as a function of temperature, bulk concentration, and H exposure were observed in some detail.

I. INTRODUCTION

High-resolution electron-energy-loss spectroscopy (HREELS) and low-energy electron diffraction (LEED) have been used to study both the (2×1)-monohydride and (1×1)-dihydride phases on the (100) surfaces of Ge-Si alloys. The thermal decomposition of both hydride phases has also been investigated and is observed to be accompanied by significant rearrangement of the substrate atoms. The Ge-Si alloys were prepared using molecular-beam epitaxy on Si(100) substrates.[1,2] Both hydride phases were prepared using atomic hydrogen.[3,4]

Recently, both the monohydride and the dihydride phases have been observed on the Si(100)(2×1) surface, characterized, respectively, by (2×1) and (1×1) LEED patterns.[3–5] For the Ge(100)(2×1) surface, only indirect evidence has been reported for monohydride formation based on ultraviolet-photoemission-spectroscopy and LEED measurements.[6,7] Dihydride formation on this surface has been considered a possibility,[6] but to our knowledge, confirmation of experimental and/or theoretical results has not been reported in the literature.

It is our purpose in this communication to present four main results. As the first result, we give direct evidence from our combined HREELS-LEED measurements for the formation of both the monohydride and the dihydride phases on the (100) surface of a $Ge_{0.2}Si_{0.8}$ alloy. Similar results for other substrate compositions will also be discussed. Secondly, by using atomic hydrogen as a marker it was possible to determine the concentration of Ge and Si atoms in the uppermost surface layer and to observe a marked segregation of Ge to the surface upon annealing. The third result is that, due to the lower activation energy for hydrogen desorption from Ge atoms relative to that from Si atoms, the thermal decomposition of the $Ge_xSi_{1-x}(100)(1\times 1)$:2H dihydride phase is more complex than seen for the Si(100)(1×1):2H surface structure and leads to an apparent increase in the Si surface concentration. The decomposition of the $Ge_xSi_{1-x}(100)2\times 1)$:H monohydride phase will also be discussed in this context. As our fourth result, we report that subsequent hydrogen exposure on partly annealed H-Ge_xSi_{1-x} surface reveals that Ge is still present on the surface.

II. EXPERIMENTAL

The HREELS experiments were performed in a Leybold Hereaus LHS 22 system equipped with a double-pass

HREELS spectrometer, LEED equipment, and an x-ray photoelectron-spectroscopy (XPS) apparatus. The resolution full width at half maximum (FWHM) of the EELS spectrometer was varied between 8 and 12 meV. The spectra shown in this paper were obtained with a primary energy $E_0 = 5.0$ eV for the condition of specular reflection ($\theta_i = \theta_f$) at an incident angle of 50°.

The $Ge_xSi_{1-x}(100)$ alloys were prepared at AT&T Bell Laboratories using molecular-beam-epitaxy on Si(100) substrates.[1,2] These alloy films were several thousand angstroms in thickness and were homogeneous throughout. It has been shown that such films have widely varying misfit dislocation densities as grown.[1,2] However, we do not believe that this will have any significant influence on our results since in even fully misfit-relieved films the overwhelming majority of atoms lie far away from dislocations on normally coordinated sites.

Before loading the sample in the EELS system, it was chemically etched for 20 sec in a 1:1 mixture of HF and H_2O. The sample was cleaned under UHV conditions with Ar^+-ion bombardment while being annealed at 600 K. Additional annealing at or just blow 700 K for 5 min produced a good (2×1) LEED pattern with two domains. The sample was heated resistively. After several such cleaning cycles, the carbon and oxygen concentration was below the detection limit ($<1/100$ monolayer) of the XPS spectrometer. One consequence of the above cleaning and annealing procedure was the segregation of the Ge to the surface to produce a Ge-enriched surface layer and a Si-enriched subsurface region.[8-10] In general, annealing sufficient to produce a good (2×1) LEED pattern resulted in an almost pure Ge surface on substrates with a $Ge_{0.4}Si_{0.6}$ composition and about a 75% surface Ge concentration on $Ge_{0.2}Si_{0.8}$ substrates. However, as a small thermal gradient ($\lesssim 50°$ C) existed across the sample during annealing, it was frequently possible to obtain workable areas on the surface with a higher Si surface concentration (e.g., 67%) and an acceptable (2×1) LEED pattern. Much of the data presented in this paper was done with these higher Si surface concentrations in contrast to our studies on the clean[10] and H_2O adsorbed[8,9] surfaces to be reported elsewhere.

The deposition of atomic hydrogen was done via the dissociation of molecular hydrogen at a hot tungsten filament (2200 K). The ionizer was located in line of sight at a distance of 5 cm to the sample. The H_2 pressure used for exposure was 5×10^{-6} torr. The base pressure in the system was in the 10^{-11} torr region. The monohydride was obtained after 2 min of hydrogen exposure while the sample was held at 520 K. (It was not possible to obtain a monohydride at 300 K without the simultaneous absorption of water presumably produced by the atomic hydrogen at the walls of the chamber. The presence of trace amounts of hydroxide contamination on the surface could be carefully monitored using the very intense 100 meV Si-OH bending mode in the HREELS spectrum.) The dihydride was prepared by exposing the sample for an additional 2 min at room temperature. The formation of the monohydride was characterized by a clear (2×1) LEED pattern and the dihydride by a (1×1) LEED pattern. Atomic hydrogen exposures substantially greater than that needed to form the dihydride resulted in marked disordering of the surface that resulted in the deterioration of both the LEED pattern and the EELS spectrum. These higher exposures corrode the surface to produce an amorphous, hydrogenated overlayer possibly containing trihydride species.

The sample was heated resistively and annealing times of 1 min were used during the hydride decomposition sequences. At the end of the experiment, the sample, together with its tantalum holder, was transferred to a separate UHV chamber for temperature calibration. A Chromel-Alumel thermocouple (0.1 mm) was mounted on the surface via spring tension, and the temperature was then monitored as a function of the input power which was used during the combined EELS-LEED measurements.

III. RESULTS

A. Monohydride and dihydride formation

The characteristic vibrational spectra of (a) the monohydride and (b) the dihydride phase are shown in Fig. 1. The dashed line indicates the spectrum for the clean $Ge_{0.2}Si_{0.8}(100)(2\times1)$ surface. For the (2×1) monohydride, two loss regions were observed, around 75 and 250 meV. Analogously with the monohydride on a pure $Si(100)(2\times1)$ surface, the hydrogen atoms only saturate the Si(Ge) dangling bonds of the surface dimer while leaving the dimer bond itself intact. Given the presence of both Ge and Si atoms on the surface, this geometry produces four hydride vibrational modes: the Ge-H (247 meV) and the Si-H (258 meV) stretching modes, and the Ge-H (70 meV) and the Si-H (78 meV) wagging modes. The stretching modes are clearly resolved in Fig. 1, but the wagging-mode region near 75 meV is not very well resolved due to the limited resolution used in this experiment. However, this feature is significantly broadened relative to the elastic peak, indicating the presence of two peaks due to the different surface species. The identification of two different features in the (70—80)-meV loss energy range is confirmed by the spectra obtained after partial thermal decomposition (Sec. III B 1).

When the dihydride phase is formed, the dimer bond is broken and two hydrogen atoms are bonded to each Si or Ge surface atom.[3,4,11] This introduces four new vibrational modes, the Ge-H and Si-H asymmetric stretching modes (not resolvable from the symmetric stretching modes with HREELS), and the Ge-H and Si-H scissor modes near 112 meV. As with the wagging modes, the scissor modes from the two different species are not clearly resolved. However, this feature is very characteristic of the dihydride phase and allows for an unambiguous differentiation between the two different kinds of hydride formation.

From the well-separated stretching-mode intensities of Ge-H and Si-H between 240 and 260 meV, we can estimate a surface concentration of 33% for Ge and 67% for Si. This ratio holds for both the monohydride and the dihydride phases. This determination is based on the assumption of equal oscillator strength for both species.

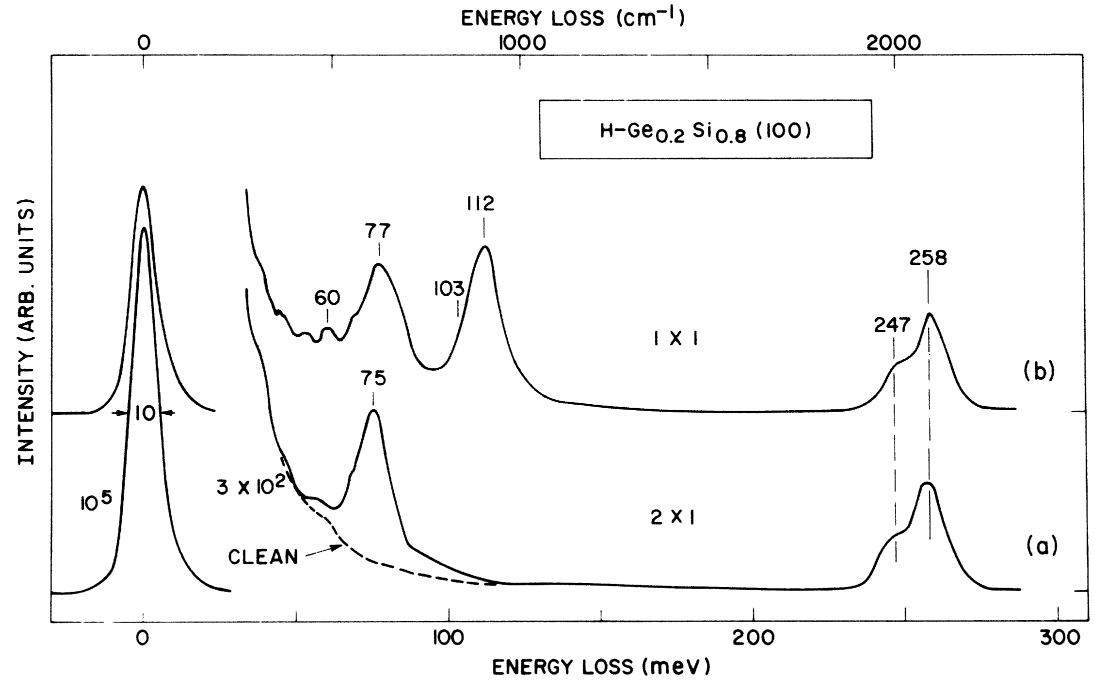

FIG. 1. HREELS spectra from the $Ge_{0.20}Si_{0.80}(100)(2\times1)$:H monohydride phase (a) and the (1×1):2H dihydride phase (b). The dashed line indicates the spectrum for the clean surfaces, $E_0=5$ eV, $\theta_i=\theta_f=50$.

Note that the Ge concentration at the surface is greater than in the bulk. Slightly higher annealing temperatures for the clean surface (e.g., 700° C) result in even higher Ge concentrations at the surface. This segregation is a result of the annealing procedure and has been confirmed by the previously mentioned HREELS-XPS studies on the clean surface[8,10] and by studies of the chemisorption of H_2O.[8,9]

B. Monohydride and dihydride decomposition

As mentioned above, isochronal annealing allows us to obtain additional information about the vibrational spectra in regions where similar modes from different surface species overlap. This is particularly important for complex structures like the $Ge_{0.2}Si_{0.8}(100)(2\times1)$:H and the $Ge_{0.2}Si_{0.8}(100)(1\times1)$:2H surfaces. Simultaneously, we

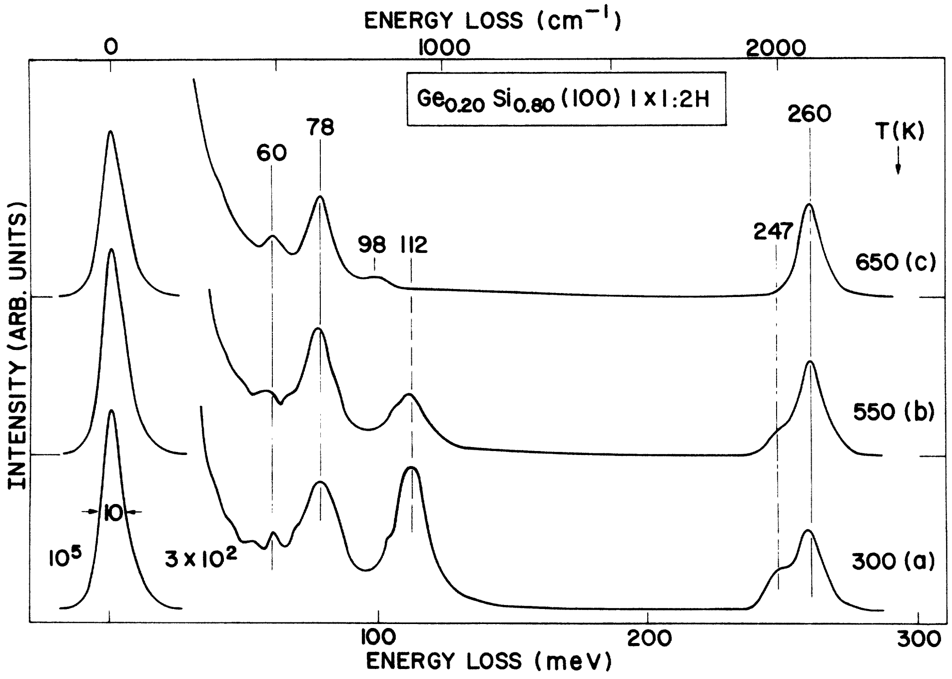

FIG. 2. Typical HREELS spectra taken after isochronal annealing of the (1×1):2H dihydride phase at the different annealing temperatures: (a) 300, (b) 550, and (c) 650 K.

gain information about the thermal stability of the different species present at the surface.

1. Dihydride decomposition

In Fig. 2 is shown a typical sequence of spectra taken during the decomposition of the dihydride phase. During this run, the sample was heated at successively higher temperatures for 1 min, and then the HREELS spectra were measured with the heating power off. No significant changes in the spectrum occur below about 500 K. After annealing to 550 K, however, the intensity of the Ge-H stretching mode at 247 meV is markedly reduced as is the scissor-mode intensity at 112 meV. Additional heating up to 650 K completely removes the scissor-mode intensity for both Ge-H and Si-H as well as the Ge-H stretching-mode intensity. Apparently, both Ge-H monohydride and dihydride decompose in the same temperature range as does the Si-H dihydride on this surface. The Si-H stretching and wagging modes both remain intense after heating to 650 K, however, indicating that the Si-H monohydride is stable at these temperatures on the alloy surface. (Additional heating to above 700 K is necessary to completely decompose this species.) As can be seen in Fig. 2, the FWHM of the wagging mode is sharply reduced after this heating sequence corresponding to the removal of the Ge-H species. The small peak at 98 meV is due to a small quantity of OH on the surface and is indicative of the fact that the surface is no longer completely passivated by hydrogen at all sites. Additional information about the presence of available chemisorption sites (presumably in the form of Ge dangling bonds) after this annealing sequence will be presented later in this paper.

In Fig. 3 a more detailed description of this hydride decomposition sequence is given. Here, the absolute intensities of the stretching, scissor, and wagging modes are shown as a function of the temperature to which the sample has been heated together with the intensity of the elastically scattered electrons. Also shown are the FWHM of the scissor and wagging modes as well as that of the elastic peak. After heating to near 500 K, there is a slight reduction in the Ge-H stretching-mode intensity accompanied by a slight increase in the Si-H stretching-mode intensity. A corresponding decrease in both wagging- and scissor-mode intensities is observed. The scissor-mode intensity reduction is most pronounced and indicates the onset of the dihydride decomposition which is completed by 650 K. The decrease in the FWHM of the wagging mode was described above and attributed to the preferential loss of Ge-H. The constant FWHM of the scissor mode is in sharp contrast to the behavior of the wagging mode and seems to indicate that both the Ge-H and Si-H dihydride species decompose at the same rate. This result is somewhat surprising given the stability of the Si-H monohydride relative to the Ge-H monohydride.

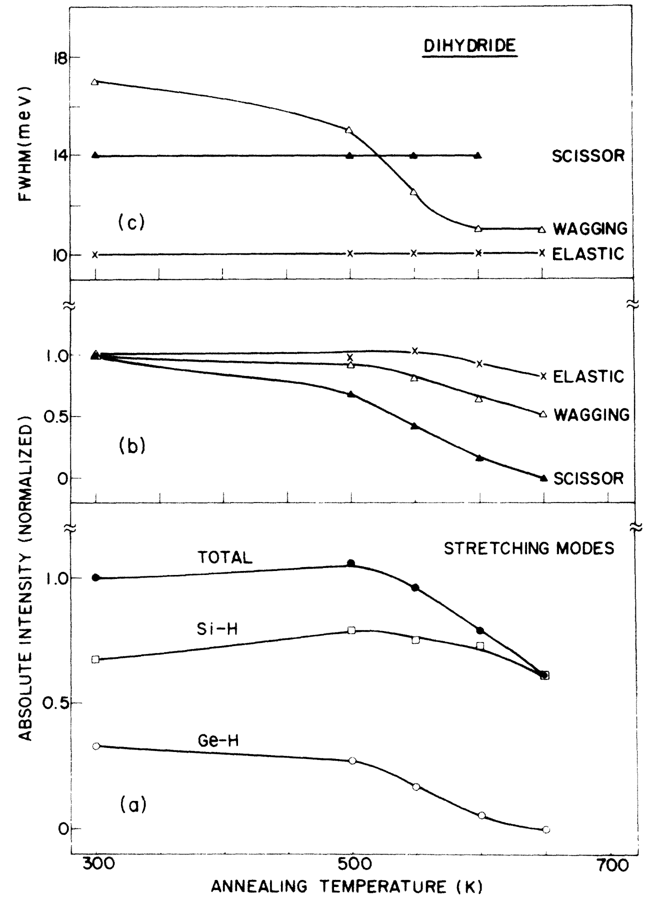

FIG. 3. Dihydride decomposition: absolute intensities (normalized to 1 at 300 K) are shown as a function of annealing temperature for (a) total stretch (●), Ge-H stretch (○), and Si-H stretch (□); (b) wagging (△), scissor (▲), and elastic reflection (×) modes; (c) half-width (FWHM) for wagging- (△) and scissor- (▲) mode intensities and for the elastic reflection (×) are also shown as a function of annealing temperature.

The fact that the FWHM of the elastic peak remains constant while its intensity decreases by only about 20% following this heating sequence would seem to indicate that there is a small, but not negligible, roughening of the surface. This may correspond to the slight increase in the Si-H intensity near 500 K. As the surface was effectively saturated with H prior to this heating sequence, an increase in Si-H intensity (presumably due to the transfer of H from Ge-H species) implies that more Si bonding sites have been made available at the surface. This could result either from the exchange of some surface Ge's with subsurface Si's or possibly from the formation of Si trihydride species accompanying the breaking of Si backbonds. However, the absence of vibrational features corresponding to the trihydride species and the decomposition of the dihydride would seem to make this latter possibility extremely unlikely. The fact that a major reconstruction of the surface follows this heating sequence is apparent from the observed (2×1) LEED pattern. The (1×1) dihydride phase has been converted into a structure that has (2×1) periodicity and Si-H monohydride species, but is markedly different from the monohydride phase prepared by exposing the clean surface to atomic hydrogen. The (2×1) structure prepared by decomposing the dihydride contains no Ge-H groups even though Ge is present on the surface as is shown by the next experiment.

Direct proof that the Ge atoms are not completely removed from the surface during dihydride decomposition was obtained by reexposing the annealed surface to atomic hydrogen at room temperature. In this experiment, the clean alloy surface had initially been heated slightly higher than in the previous experiment. This resulted in an approximately 75% Ge enrichment of the surface. However, as is shown in Fig. 4, the Ge-H species are also almost completely decomposed after isochronal heating to 650 K on this surface as well. In addition, there is a simultaneous increase in the Si-H stretching-mode intensity (though, as before, it does not completely compensate for the loss in Ge-H intensity). The dashed line in Fig. 4 shows what occurs when this annealed surface is reexposed to atomic hydrogen (5×10^{-6} torr, 100 sec) at 300 K. The reappearance of a strong Ge-H stretching mode at 247 meV indicates that a substantial portion of the surface was composed of Ge atoms with available dangling bonds. From the observation of a broad scissor-mode intensity at 112 meV, not shown here, it is evident that an unsaturated dihydride phase was formed. This is consistent with the observation of a (1×1) LEED pattern with weak half-order spots. These half-order spots completely disappear after additional hydrogen deposition, for which a (1×1) LEED pattern is obtained.

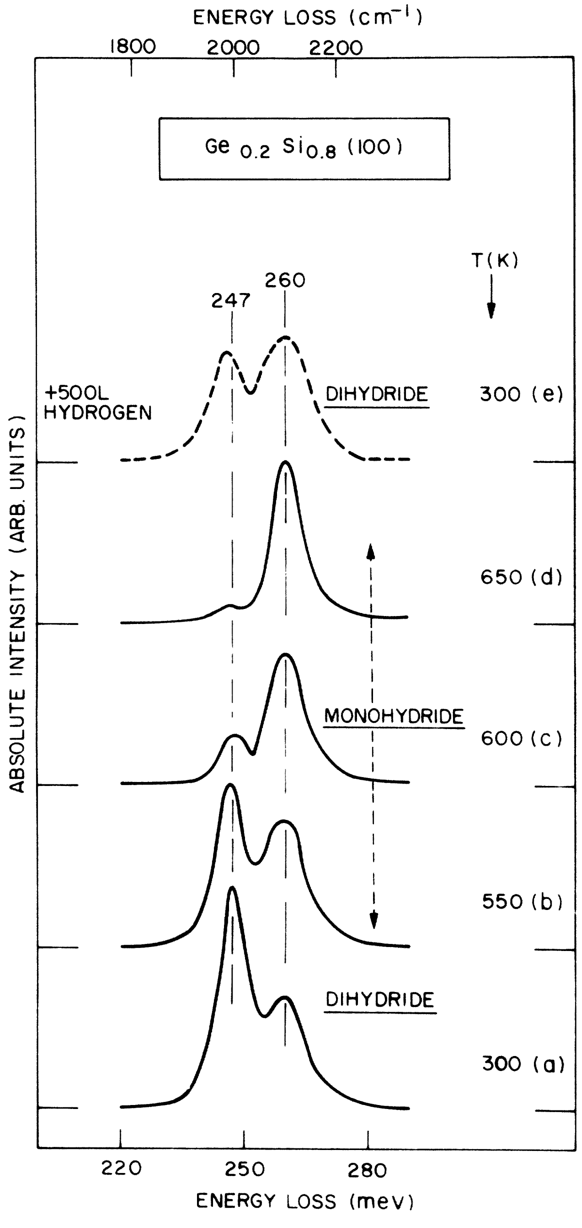

FIG. 4. Ge-H and Si-H stretching-mode intensities as a function of the annealing temperature. The dashed line (e) was obtained after subsequent 500-L hydrogen exposure of the annealed surface (d); nominal *surface* concentration is $Ge_{0.7}Si_{0.3}$.

2. *Monohydride decomposition*

In Fig. 5 are shown typical results for the partial decomposition of the monohydride phase discussed in Sec. III A. The spectra show a drastic attenuation of the elastic peak intensity as well as of the wagging- and stretching-mode intensities as a function of the annealing temperature. A direct comparison [Figs. 5(a) and 5(b)] between the Ge-H and Si-H stretching-mode intensities at 247 and 258 meV, respectively, makes it obvious that, for the monohydride phase, the activation energy for hydrogen desorption from Ge surface sites is lower than from Si surface sites. In Fig. 6 the absolute intensities of the relevant modes are plotted as a function of annealing temperature. After heating to temperatures above 550 K, the Si-H stretching-mode intensity starts to decrease, typical hydrogen desorption behavior from Si sites involved in dimer bonds on pure Si(100) surfaces.[3] Hydrogen desorption from Ge sites is, however, much more abrupt, and no Ge-H stretching mode is observed above 600 K. Simultaneously, the elastic intensity [Fig. 6(b)] is strongly reduced, indicating a decrease in surface order relative to that found for the (2×1) monohydride phase at room temperature.

From the diminution of the total wagging-mode intensity with increasing temperature [Fig. 6(b)] desorption (or possibly diffusion) of the hydrogen from the surface is assumed. From the simultaneous reduction of the intensity of the elastic peak, surface roughening is inferred. The slight increase in the intensity of th Si-H stretching mode up to around 550 K for both the monohydride and the dihydride should be considered in this context. It would seem to indicate that the surface concentration of Si atoms was increasing either by replacing Ge atoms and/or as a result of the roughening process. Similar results are seen when H_2O chemisorbed on the $Ge_xSi_{1-x}(100)(2\times1)$ surface is thermally decomposed.[8] The data presented in Figs. 4—6 are in the form of absolute intensities. If they had been presented in a reduced form by normalizing to the elastic peak intensity (a somewhat dubious procedure in this case) the increase in the Si-H stretching-mode intensity at intermediate temperatures would be even more pronounced.

It is of interest to compare the behavior of the elastic peak intensities for the monohydride and the dihydride surfaces as a function of annealing temperature. While that for the monohydride displays marked temperature dependence in this annealing region, the elastic peak intensity for the dihydride surface remains essentially con-

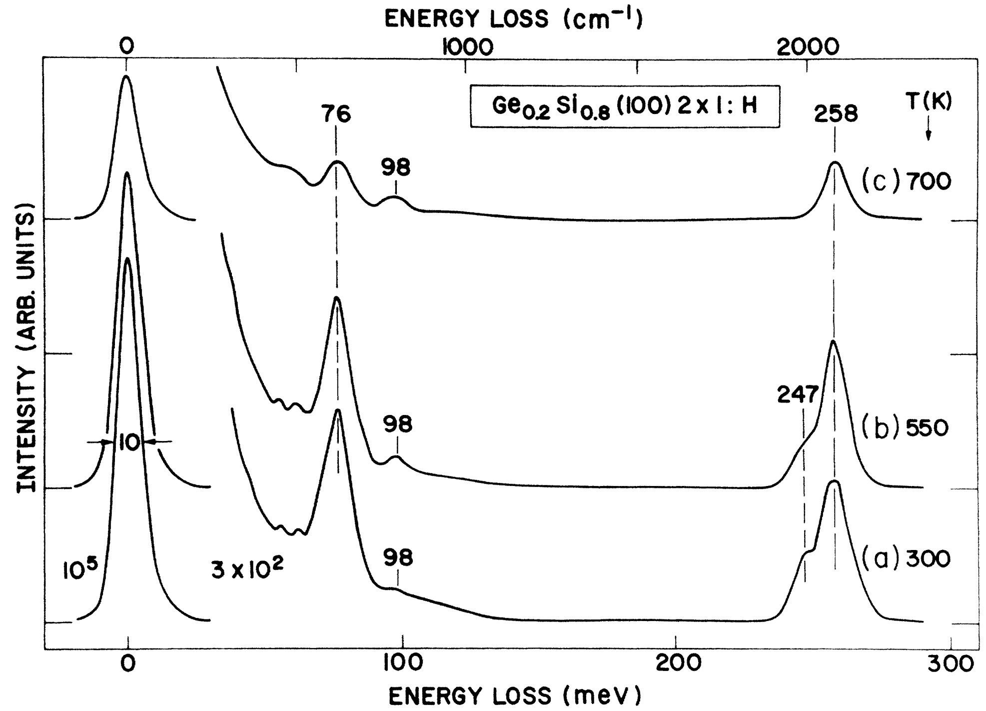

FIG. 5. Typical HREELS spectra demonstrating the decomposition of the (2×1):H monohydride phase at the different annealing temperatures (a) 300, (b) 550, and (c) 700 K.

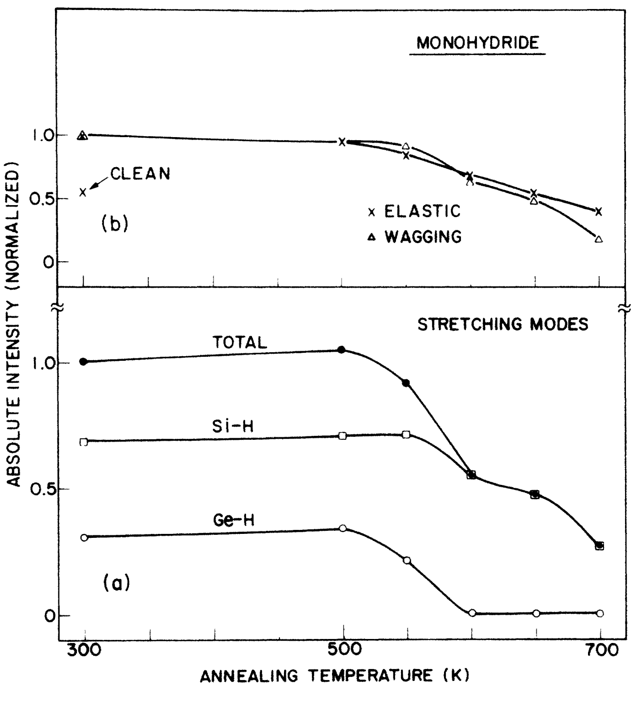

FIG. 6. Monohydride decomposition. Absolute intensities are shown as a function of annealing temperature for (a) total stretching mode (●), Ge-H stretch (○), and Si-H stretch (□); (b) wagging mode (△) and elastic reflection (×) intensities. The intensities were normalized to 1 at 300 K.

stant. At first this might appear to be inconsistent behavior given that the dihydride does decompose into a monohydride and parallel development might then be expected to follow. However, as noted earlier in this paper, the monohydride produced by decomposing the dihydride is not the same as produced by the "direct" process at lower temperatures. Furthermore, formation of the dihydride is a much more drastic process than monohydride formation to the extent that the dimer bonds between the surface atoms are actually broken. This may result in some mobility of the surface atoms, possibly allowing for an increase in the degree of perfection of order among the surface atoms. Unlike the situations above 500 K this mobility apparently does not extend to the Si-rich sublayer. We make this statement because surface stoichiometries are seen to be essentially identical for both the monohydride and the dihydride when formed on surfaces subjected to the same sample preparation procedures.

In order to prevent changes in the bulk composition or excessive segregation of Ge to the surface, temperatures in excess of 700 K were not used in these experiments. Therefore, residual hydrogen remaining on the surface after annealing to this temperature was removed by sputtering and the surface reordered for subsequent experiments by using the annealing procedure described in the experimental section.

IV. SUMMARY

We have observed both the formation and thermal decomposition of monohydride and dihydride phases on the (100) surface of Ge-Si alloys. The use of HREELS makes possible an unambiguous identification of these two phases and of the surface species. Exposures were made using atomic hydrogen. Both the Ge dihydride and the Ge monohydride species thermally decompose in essentially the same temperature range as do the Si dihydride species (500–600 K). The Si monohydride species, however, is less labile and persists at reduced concentrations to above 700 K.

Measurements of the Ge-H and the Si-H stretching-mode intensities allowed us to monitor the substrate-atom composition of the surface. In this study surface enrichments producing about a 33% Ge concentration were observed for a substrate with a nominal 20% bulk Ge concentration with annealing temperatures of about 650 K. Higher annealing temperatures and/or higher bulk concentrations resulted in greater surface segregation of the Ge atoms. In the presence of hydrogen, the concentration of surface Si atoms is seen to increase above about 500 K, though Ge is not completely removed from the surface by this procedure. A similar inversion of the surface concentration at higher temperatures is seen for Ge-Si alloy surfaces upon which H_2O has been dissociatively chemisorbed.[8] The ability to monitor changes in the substrate-atom surface composition of compound materials is one of the most significant aspects of this study.

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