

Coverage-dependent thermal reactions of digermane on Si(100)-(2×1)

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In this study, we examine the adsorption and thermal reactions of digermane (Ge_2H_6) on the Si(100)-(2×1) surface with high-resolution core-level photoemission spectroscopy using synchrotron radiation. At 325 K, the digermane dissociatively chemisorbed to produce GeH_3 , GeH_2 , GeH , and SiH species. The sticking coefficient at zero coverage deduced from the photoemission intensity is ~ 0.5 . Successive annealing of the digermane-saturated surface to higher temperatures causes further decomposition of GeH_3 and GeH_2 and the desorption H from GeH and SiH , leaving atomic Ge on the surface. In light of the sufficiently large chemical and surface shifts in their core-level binding energies for different surface species, those processes were identified by examining the evolution of Ge 3*d* and Si 2*p* line shapes. Experimental results indicate that the reaction for H release from GeH not only occurred in a large temperature range but also depended heavily on the Ge_2H_6 adsorption coverages. Two reaction routes for H release from Ge sites were used to describe the large reaction temperature spreads accurately. GeH decomposition by transferring the H atom to a surface Si dangling bond took place for low coverages at ≤ 590 K, and H_2 thermal desorption occurred for higher coverages in the range of 590–770 K. The former process of atom transfer of H from Ge to Si sites was directly observed in the Ge 3*d* and Si 2*p* photoemission spectra. [S0163-1829(96)04044-1]

I. INTRODUCTION

Surface processes during the growth of epitaxial silicon, germanium, silicon-germanium alloy, and ((Si)*m*(Ge)*n*)*p* superlattices by vapor-phase epitaxy (VPE) have received considerable attention^{1–5} owing to their rich fundamental interest and their vast applications in Si-based technology.⁶ Recently, two gas sources, disilane (Si_2H_6) and digermane (Ge_2H_6), were applied as molecular precursors for Si and Ge growth, respectively.^{7–9} Compared with GeH_4 , the gas source conventionally used in the industry, digermane has a lower decomposition activation energy (2.9 eV) for the Ge-Ge bond than that (3.8 eV) for the Ge-H bond in GeH_4 ;¹⁰ consequently, it offers many advantages, including a markedly higher sticking coefficient and lower substrate temperatures.

Klug, Du, and Greenlief and Ning and Crowell examined the low-temperature adsorption and thermal decomposition of digermane on Si(100)-(2×1) using a number of techniques including multiple internal reflection infrared spectroscopy,¹¹ temperature-programmed desorption (TPD),^{9,12,13} ultraviolet photoemission,¹⁴ and x-ray photoelectron spectroscopy.¹³ It is known that digermane adsorbs molecularly at 110 K or below. When the substrate is heated to ~ 150 K, a physisorbed digermane molecule decomposes into two GeH_3 radicals. As the annealing temperature is raised to 200 K, a partial decomposition of the GeH_3 groups was found. Over the temperature range of 500–900 K, a series of H_2 desorption peaks were observed in the TPD spectra. In the TPD study of Ge_2H_6 on Si(100) and D_2 on Ge/Si(100), both groups found, for high surface Ge coverages, three $\text{H}_2(\text{D}_2)$ desorption maxima α (590 K), β_2 (670 K), and β_1 (780 K). The three peaks were assigned for H_2

recombinative desorption from two of GeH , SiH_2 , and SiH surface species, respectively. Interestingly, the α desorption state is missing for low surface Ge coverages. These investigators accounted for their result by introducing an additional H release channel for GeH species: a H atom can transfer from the weaker Ge-H bond to a stronger Si-H bond while the surface Si dangling bonds are available at low coverages.

In this work, we investigate the adsorption and thermally induced (325–900 K) dissociation of Ge_2H_6 on Si(100)-(2×1) for various exposures. Our study utilizes high-resolution core-level photoemission spectroscopy using synchrotron radiation. The technique is based on the observation that both surface Si and Ge atoms of clean Si(100)-(2×1) and Ge-covered Si(100)-(2×1) exhibit a core-level shift to lower binding energies, but to higher bonding energies after bonding with H atoms.^{15,5} By monitoring the intensities and changes in binding energies of all the shifted Si 2*p* and Ge 3*d* core levels, the atomic processes on the surface are revealed. Although the above-mentioned TPD study contended that the H transfers from Ge to Si sites at low Ge_2H_6 coverages, their conclusion is indirectly based on the lack of H_2 desorption peak derived from Ge sites. Results in this study demonstrate that the H-induced shifted component develops in the Si 2*p* spectra, but simultaneously vanishes in the Ge 3*d* spectra for low coverages at ≤ 590 K. Such an occurrence undoubtedly demonstrates the atom transfer process.

II. EXPERIMENTAL PROCEDURE

Our photoemission measurements were carried out at the Synchrotron Radiation Research Center located in the Hsinchu Science-based Industrial Park, Taiwan. Light from the

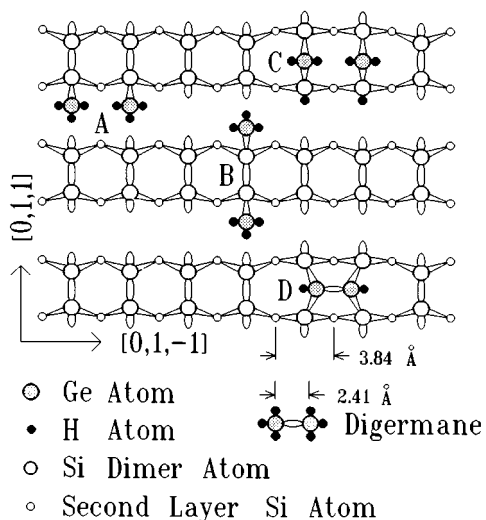


FIG. 1. Atomic model for the Si(100)-(2 \times 1) surface and schematic diagrams illustrating various bonding configurations of digermene fragments.

1.3-GeV storage ring was dispersed by a Dragon-type 6-m Low-energy Spherical Grating Monochromator. All the Ge₂H₆ adsorption, annealing, and Ge film growth samples were prepared *in situ* in a μ -metal 1×10^{-10} -torr ultrahigh vacuum system. Photoelectrons were collected and analyzed by a large hemispherical analyzer. The overall energy resolution was better than 120 meV.

The Si(100) samples (Wacker), of size $0.3 \times 1.2 \times 0.05$ cm³, were sliced from *n*-type wafers with a resistivity of about 20 Ω cm. The wafer's misalignment is about 0.5°. After degassing at 800 K for many hours, each sample was subjected to annealing at ~ 1400 K, following the standard procedure.¹⁵ Digermene (Voltaix, ultrahigh purity grade, 20% in He) was introduced into the chamber through a precision leak valve. The dosing pressure, in the 10^{-8} -torr range, was monitored by an ionization gauge which did not directly face the sample. The pressure readings of the ion gauge were corrected by the gauge sensibility of He and Ge₂H₆, which are about 0.18 and 2.4, respectively, relative to air.¹⁶ Annealing of the disilane-saturated sample was performed by resistive heating of the sample itself. The sample's temperature as a function of heating power was calibrated by attaching a small thermocouple to the center of the back face of an identical test sample. Each annealing lasted for 60 s.

III. RESULTS AND DISCUSSION

A. Atomic model for surface reactions

Figure 1 illustrates that the top atomic layer of Si(100)-(2 \times 1) surface is formed by rows of dimerized atoms. Each surface atom possesses a dangling bond which is highly reactive for chemisorption. The spacing between adjacent dimers in the same row is one lattice constant, 3.84 Å. The two atoms in a dimer pair are generally believed to be buckled, i.e., one of the dimer atoms is topologically higher than the other, as a consequence of further reducing the total surface energy.¹⁷

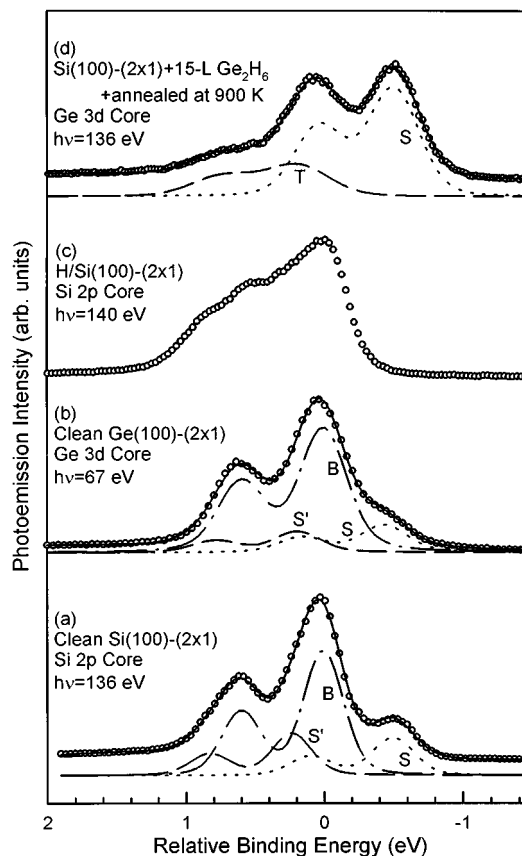
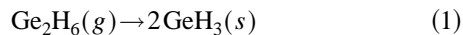


FIG. 2. Photoemission spectra (circles) for the Si 2*p* and Ge 3*d* core levels of (a) Si(100)-(2 \times 1), (b) Ge(100)-(2 \times 1), and (c) H/Si(100)-(2 \times 1) monohydride surfaces obtained by annealing the disilane-saturated Si(100) surface at 670 K. (d) The Ge/Si(100)-(2 \times 1) surface obtained by annealing the digermene-saturated Si(100)-(2 \times 1) surface at 900 K. The photon energies used are indicated. The solid curves are fits to the data. The curves labeled *B*, *S*, *S'*, and *T* are the results of a decomposition into individual components which consist of a pair of spin-orbit split peaks. The *B* component is derived from the bulk; *S*, *S'*, and *T* are surface related.

Figure 2(a) shows a surface-sensitive Si 2*p* core-level spectrum (circles) for clean Si(100)-(2 \times 1), and its least-squares fit (curves through the circles) with three decomposed components (curves labeled *B*, *S*, and *S'*). The fitting was obtained by the standard procedure.^{18,19} All individual components, consisting of a pair of spin-orbit peaks, are assumed to have the same Voigt line shape. As shown in previous studies, the *B* component corresponds to emission from the bulk. The *S'* component has a binding-energy shift of +0.23 eV from the *B* component, and is not visually resolved from the spectrum. However, several studies have verified its presence.^{15,20–22} The *S* component is located at around -0.51 eV relative to the *B* component, and is responsible for the small characteristic peak on the low bonding energy side. The *S* and *S'* components have been attributed to the emission from the surface dimer atoms (each have a dangling bond) and the second-layer atoms, respectively.¹⁵ Nevertheless, other assignments are available for the *S* and *S'* components, thereby accounting for the charge asymmetry between two buckled dimer atoms.^{20–22,23} However, such

an uncertainty does not affect our following discussion, since the focus here is, in part, only on the relative intensity of the S component, which is undoubtedly derived from the dimer layer. For brevity's sake, the interpretation mentioned above is referred to in the wording of the qualitative discussion; the changes required for other interpretation are evident. The line shape of the Ge $3d$ core spectrum and its decomposition of clean Ge(100)-(2 \times 1), taken from Ref. 5 and shown in Fig. 2(b), are quite similar to those of the Si $2p$ core of clean Si(100)-(2 \times 1). Figure 2(c), taken from Ref. 4, shows a photoemission spectrum for the H/Si(100)-(2 \times 1) monohydride surface obtained by annealing the disilane-saturated Si(100)-(2 \times 1) surface at 670 K. Notably, the spectrum shows a broad line shape with subtle features: the broad shoulder at 0.5–1.0 eV actually consists of two shoulders with a long tail to higher binding energies.

Since digermene has exactly the same molecular structure with disilane, the surface reactions of digermene on Si(100) can be expected to be quite similar to that of disilane on Si(100) and Ge(100), which had been previously studied.^{4,5} Similar to the Si-Si bond in disilane, the Ge-Ge bond in digermene is the easiest to cleave. Accordingly, two GeH₃ radicals are produced owing to the scission of the Ge-Ge bond upon adsorption. The GeH₃ radicals are highly reactive; once generated, they will react with nearby Si dangling bonds immediately. This picture of dissociative chemisorption had been confirmed by the presence of GeH₃ after warming the surface to 150 K from 110 K, at which temperature Ge₂H₆ is molecularly adsorbed on Si(100)-(2 \times 1). This reaction can be expressed as follows:



where (g) denotes a gas phase species and (s) an adsorbed surface species.

Figure 1 also shows possible Ge₂H₆ chemisorption geometries. In adsorption configuration A , two GeH₃ fragments bond onto adjacent dangling bonds of two dimers in the same dimer row separated by 3.84 Å. Configuration B involves two dangling bonds of the same dimer, separated by about 2.4 Å. The Ge-Ge bond distance of Ge₂H₆ measures 2.41 Å.²⁴ Despite their differences in the Si-Si separation, both configurations were observed by scanning tunneling microscopy in the similar disilane-on-Ge(100)-(2 \times 1) system.⁵

The adsorbed GeH₃ radical may decompose to form a GeH₂ by releasing a hydrogen atom to a nearby Si dangling bond, as shown in configuration C in Fig. 1. To reduce the surface free energy further, GeH₂ may decompose to form GeH by either H₂ thermal desorption or by transferring the H atom to available open Si sites. Finally, all hydrogen atoms will evolve into the gas phase at even higher temperatures and the Ge deposition is completed. The above reactions can be constructed as follows:

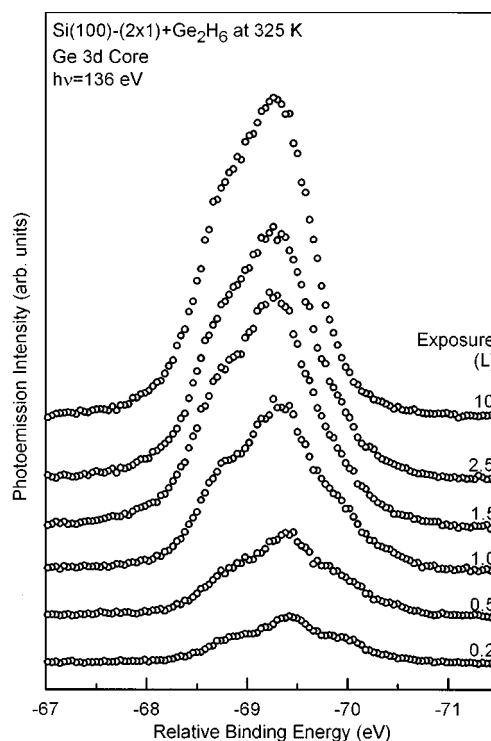
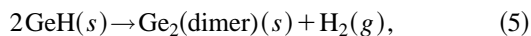
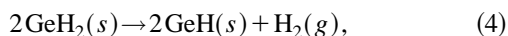
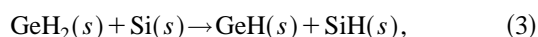
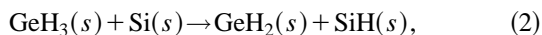
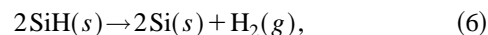


FIG. 3. Photoemission spectra of the Ge $3d$ core level for various digermene exposures on Si(100)-(2 \times 1) at \sim 325 K. The binding energy is referred to as the corresponding Si $2p_{3/2}$ line of the bulk component. The intensity of each spectrum has been normalized to the incident photon beam intensity.

and



where (s) and (g) indicate a surface species and desorbed gas molecules, respectively.

B. Room-temperature adsorption

Figure 3 shows Ge $3d$ core-level spectra for various exposures of digermene on Si(100)-(2 \times 1) at \sim 325 K. The binding energy scale is referred to the B component of the Si $2p_{3/2}$ line of clean Si(100). The main feature of the spectra is the monotonical increase of their integrated photoemission intensity as the digermene dose accumulates. Figure 4 plots the integrated intensity versus the digermene dose. The photoemission signal linearly increases at extremely low coverages and saturates after a total exposure of \sim 10 L (1 L = 10^{-6} torr s). The intensity is scaled in a manner in which the saturation coverage is set at 0.4 (ML) (1 ML = 6.8×10^{14} cm⁻²), as obtained in a previous study.¹³ Based on the slope of the linear region at low Ge₂H₆ coverages, an initial sticking coefficient of about 0.5 is derived. Restated, every digermene molecule striking the surface has a 50% likelihood of sticking to the surface. This value is almost the same as that found for Si₂H₆ adsorption on Ge(100)-(2 \times 1), indicating the similarity in their adsorption dynamics.⁵

The line shapes of the Ge $3d$ spectra remain essentially the same for all exposures above 1 L, thereby suggesting that

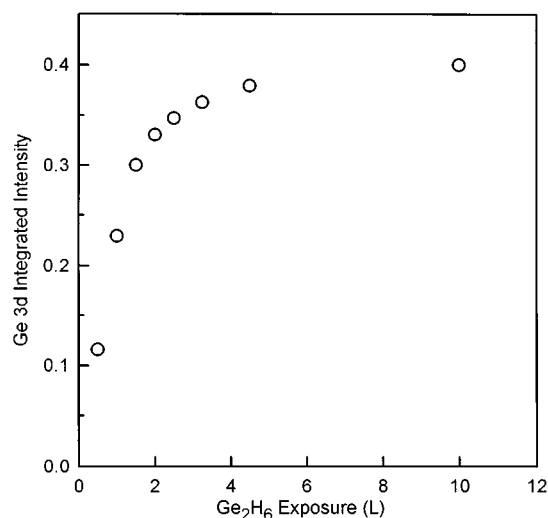


FIG. 4. Integrated intensity of the Ge 3d spectra shown in Fig. 3 as a function of digermene exposures. The intensity for saturation coverage is scaled to be a 0.4 ML (see text).

the relative abundances of various surface Ge hydride species are quite independent of exposures. The broadness of the line shape can be attributed to disorder, the presence of different hydride species on the surface, and possibly vibrational excitations of Ge-H bonds, which are observed in the spectra of gas-phase molecules. The line shapes of the spectra for dosages below 0.5 L are, however, different from those for the higher exposures. Section III C further examines the implication of this difference.

C. Annealing of Ge₂H₆-adsorbed Si(100)-(2×1) surfaces

Figures 5(a) and 5(b) show the Ge 3d and Si 2p core-level spectra, respectively, for the starting clean Si(100)-(2×1) surface and the same surface exposed to 15-L digermene at 325 K followed by successive 60-s anneals to a higher temperatures as indicated. All the spectra were taken with a photon energy of 136 eV. At this dose, the surface was saturated by digermene, as shown in Fig. 4. Again, the binding-energy scale of Fig. 5(a) is referred to as the *B* component of the corresponding Si 2p line in Fig. 5(b). By using this internal energy reference, the effect of banding due to the surface changes is eliminated. The bottom spectrum in Fig. 5(a) was obtained from the Ge₂H₆-saturated surface near room temperature. Its line shape is rather broad, indicating multihydride species and disorder on the surface. As the annealing temperature increases to 590 K, the line shape sharpens, as shown by the deepening of the valley between the two spin-orbit-split peaks. The line shape shifts toward a lower binding energy by about 0.3 eV. At 650 K and above, another feature begins to appear on the lower-binding-energy side, about -70.51 eV relative to the bulk component of the Si 2p_{3/2} line.

From visual inspection of the bottom two spectra in Fig. 5(b), the *S* component of the Si 2p spectrum for clean Si(100)-(2×1) obviously disappears after saturation exposure at 325 K. The Si 2p line shape exhibits shoulderlike features on the higher-binding-energy side, and matches Fig. 1(c) in many ways. The position of Si 2p spectra remains roughly the same below 590 K. Around 590 K, the line shape changes slightly, and shows an overall shift toward lower

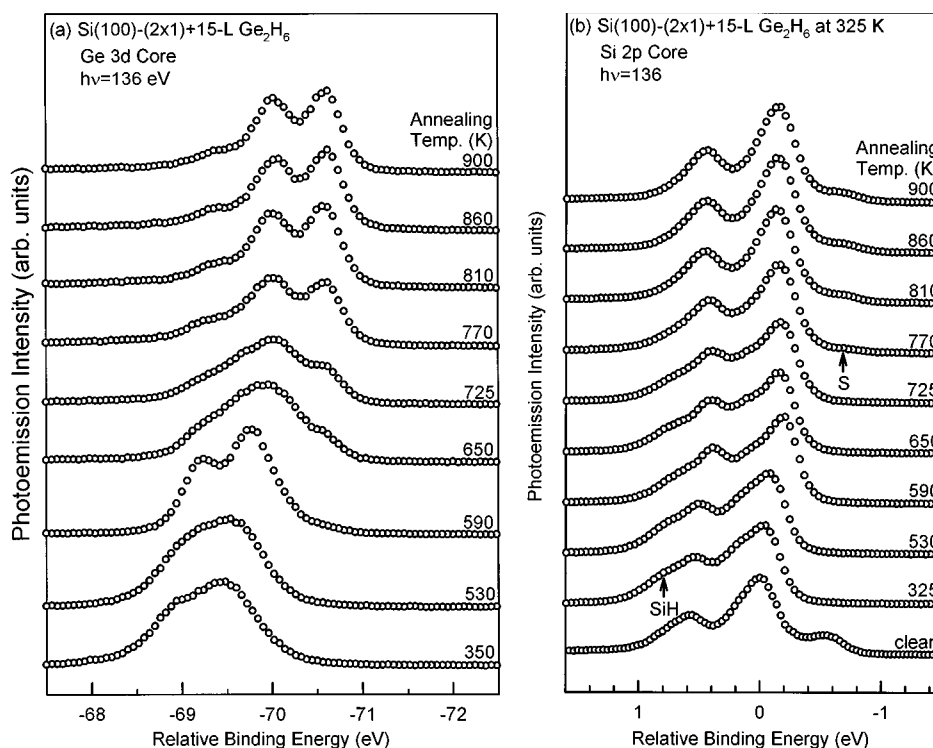


FIG. 5. Photoemission spectra for (a) Ge 3d and (b) Si 2p core levels for Si(100)-(2×1) saturated by a 15-L digermene exposure at room temperature followed by progressive annealing to various temperatures as indicated. The relative binding energy scale refers to the Si 2p_{3/2} line of the bulk component. The arrows labeled *S* and SiH indicate the positions for emission from the open dimer atoms and H-induced Si sites. The bottom Si 2p spectrum in (b) and the top Ge 3d spectrum in (a) are reproduced in Fig. 2 for displaying their decomposition into individual components.

binding energies. In the range 590–725 K, the line shape remains mostly unchanged. Beyond 725 K, the *S* component gradually reappears. At 860 K and above, the relative intensity of the *S* component to the bulk is about 30% of the original clean surface, indicating a partial removal of the Si dimer atoms.

As mentioned earlier, previous TPD studies demonstrated that the hydrogen thermal desorption from the Ge₂H₆-covered Si(100) surface was completed at 900 K. At this temperature, atomic Ge is the final reaction product on the surface. Figure 2(d) provides a detailed picture of the Ge 3*d* spectrum after annealing the Ge₂H₆-saturated surface at 900 K and its fitting with two components, labeled *S* and *T*. This spectrum is quite similar to that obtained from the Ge/Si(100) surface by means of molecular-beam epitaxy (MBE).^{15,23} This finding is expected since all of the hydrogen has desorbed, and the Ge films performed by VPE and MBE are the same. Contrary to Si indiffusion on the Ge(100) surface, the interface between a Ge overlayer and the Si(100) surface is sharp, as confirmed in many studies.²⁵ This is also evident by the fact that the integrated intensity of Ge 3*d* spectra in Fig. 5(a) remains nearly constant during annealings up to 900 K. Also, the Ge-covered Si(100) surface exhibits the same dimer structure. Overall, we can conclude that the *S* component in Fig. 2(d) has the same atomic origin as that in clean Si(100) and Ge(100). Since no indiffusion of Ge into the bulk occurs, the *T* component is undoubtedly surface or subsurface related. However, further information regarding its structural implication cannot be derived at this point. The presence of *S* intensity in Ge 3*d* core level is also justified by the partial removal of the photoemission yield of the *S* component in the clean Si(100).

Since the *S* component characterizes the open dimer atoms, its gradual reappearance in Si 2*p* spectra [Fig. 5(b)] between 725 and 860 K suggests the hydrogen desorption from SiH monohydride radicals [Eq. (6)]. The observation of this reaction temperature region is fairly consistent with the β1 desorption state centered at 780 K for a monohydride Si surface in the TPD spectra. As discussed above, open Ge dimer atoms contribute to the majority photoemission intensity of the Ge 3*d* spectra after a 900-K anneal. Moreover, the line shapes of the Ge 3*d* core above 770 K in Fig. 5(a) are quite similar, indicating the completeness of H₂ desorption from Ge sites. In the range 590–770 K, the intensity of the *S* component of Ge 3*d* slowly surges, marking H₂ desorption from GeH surface species [Eq. (5)]. Again, this temperature range correlates well with the α desorption state in the TPD spectra.^{12,13} The lower H₂ desorption temperature and the associated desorption activation energy of GeH, as compared to SiH, can be rationalized by the fact that a Ge-H bond is weaker than a Si-H one.

At 590 K, the Ge 3*d* core in Fig. 5(a) exhibits a relatively sharp line shape, consisting essentially of only one component with some broadening possibly due to vibrational excitations. As discussed above, the H₂ desorption from GeH and the simultaneous Ge dimer formation start to take place immediately above 590 K. Naturally, this spectrum can be attributed for Ge monohydride species. The difference in binding energies between this spectrum and the *S* component is about 0.9 eV. Taking into account the surface-to-bulk shift of about 0.5 eV, we can infer that a chemical shift (and possibly

some contribution from final state shifts) of ~0.4 eV occurs for GeH formation. This binding-energy shift is roughly the same as that of SiH formation on Si(100)-(2×1).⁴ At this annealing temperature, the corresponding Si 2*p* core-level spectrum in Fig. 5(b) shows a line shape quite similar to that of the H/Si(100)-(2×1) monohydride surface, although the subshoulder at the high-binding-energy side, reflecting the H-induced chemical-shifted component, shows relatively smaller emission intensity. This is conceivable since part of the surface Si sites is not covered by H, but by Ge, which should cause only a slight chemical shift due to the similar electronegativity between Si and Ge.

For annealings below 590 K, the line shapes of Ge 3*d* core levels are rather broad, which is expected for the presence of different hydride species and disorders. The combination of two major components in these spectra is further evident from those in Fig. 3 in the low Ge₂H₆ dose region. Both line shapes of the Ge 3*d* core for 0.2- and 0.5-L dosages clearly show that a shoulder is located on the lower-binding-energy side. The binding energy of the shoulder is aligned with the Ge 3*d* spectrum in Fig. 5(a) after a 590-K anneal. In that respect, the shoulder is also characteristic of GeH fragments. Since dihydride and trihydrides should exhibit higher chemical shifts than monohydrides by about 0.17–0.35 eV,⁵ the most straightforward interpretation of Fig. 3 is that the major component of Ge 3*d* spectrum corresponds to the Ge dihydride (GeH₂) with possibly a few trihydrides (GeH₃); this interpretation correlates with that in a previous infrared study.⁹

Interestingly, the relative emission of GeH to GeH₂ is larger at low Ge₂H₆ dosages. This is most probably owing to the lack of nearby Si dangling bond for H release at a higher Ge hydride adsorption fragment population, in that the surface diffusion rate is quite small at room temperature.

D. Annealing behavior with low digermane dose

Figures 6(a) and 6(b) show Ge 3*d* core-level spectra for Si(100)-(2×1) exposed to 0.2- and 1-L Ge₂H₆, respectively, at the various annealing temperatures indicated. From the intensity calibration shown in Fig. 3, the Ge coverages for 0.2-L dose is about 0.05 ML, and for 1 L, 0.23 ML. Upon Ge₂H₆ adsorption at 325 K, the line shapes of the Ge 3*d* core reflect the combination of GeH₃, GeH₂, and GeH, as discussed in Sec. III C. After annealing at 590 K for 60 s, the spectrum with the 0.2-L dose is quite similar to the one annealed at 900 K. Figure 6(b) shows that the spectrum after a 650-K anneal consists primarily of the *S* component. In Fig. 5(a), visual inspection indicates clearly that the similar line shape for the 900-K anneal appears at 770 K. Since the final reaction product is Ge dimers on the surface, the H liberation from the Ge hydride adsorption fragments is obviously completed at 590, 650, and 770 K for 0.2-, 0.5-, and 15-L exposures, respectively.

The large spread in the reaction temperature for H release from Ge sites for different Ge coverages is impossible for usual desorption mechanism with a single activation energy barrier. As suggested in the TPD studies mentioned above, two possible pathways are (i) H₂ desorbs into space by recombination from two GeH species, as stated in Eq. 5; and (ii) H liberates from a Ge-H bond, diffuses to a nearby open

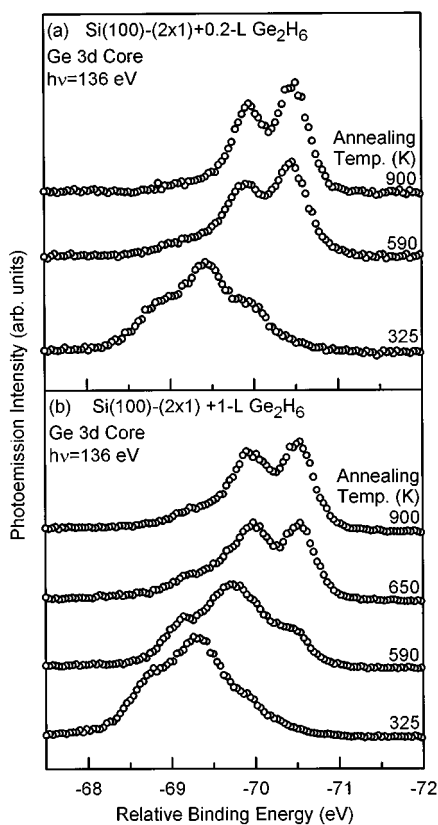
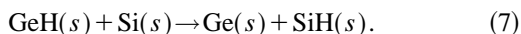


FIG. 6. Photoemission spectra of Ge $3d$ core levels for various annealing temperatures as indicated. The sample is clean Si(100)-(2 \times 1) and exposed to (a) 0.2 L and (b) 1 L of digermene at \sim 325 K.

Si site, and forms a Si-H bond. Because a Si-H bond is stronger than a Ge-H bond, the latter route is energetically practical and can be described as follows:



If Eq. (7) is to occur, the annihilation of surface Si dangling bonds (left-hand side) and the concurrent formation of SiH monohydride species (right-hand side) should provoke the replacement of the emission of the S component (derived from Si dangling bonds) in Si $2p$ spectra by the H-induced shifted component upon the rise of the emission from the S component in the Ge $3d$ spectra (shown in Fig. 6). Indeed, all these changes in line shapes of Si $2p$ spectra were experimentally observed. Figure 7 shows the Si $2p$ core-level spectra corresponding to the Ge $3d$ spectra in Fig. 6. The bottom spectrum in Fig. 7(a) shows the Si $2p$ spectrum for Si(100) with a 0.2-L digermene dose. Upon bonding with absorption fragments GeH_x and H, the relative intensity of the S component declines and the Si-H peak mounts. Here the Si-H peak can be best understood by examining the changes of the relative depth of the valley between the two spin-orbit peaks. After annealing to 590 K, the emission intensity of the S component drops and the Si-H peak builds up further. Similar changes between the lower two spectra in Fig. 7(b) are also evident.

Notably, the reaction in Eq. (7) requires surface Si dangling bonds. If the Ge_2H_6 coverage is sufficiently high, no nearby open Si sites are available for GeH decomposition

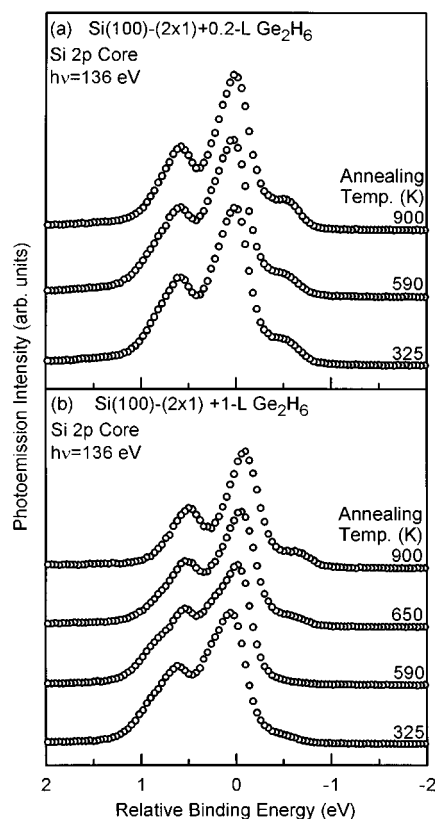


FIG. 7. Photoemission spectra of Si $2p$ core levels for various annealing temperatures as indicated. The sample is clean Si(100)-(2 \times 1) and exposed to (a) 0.2 L and (b) 1 L of digermene at \sim 325 K. Again, the relative binding energy refers to corresponding Si $2p_{3/2}$ bulk components of corresponding Si $2p$ core levels.

through H diffusion; thus recombinative desorption of H_2 from Ge sites [Eq. (5)] takes place. The emergence of the α desorption state at higher coverages in the TPD spectra lends support to this reaction. The saturation of the Si-H peak in Fig. 5(b) for digermene-saturated surface through the temperature range of the α desorption peak also corroborates this desorption mechanism.

IV. SUMMARY

High-resolution core-level photoemission with synchrotron radiation was employed to study the adsorption of digermene on Si(100)-(2 \times 1) at near room temperature, and subsequent pyrolytic decomposition and hydrogen desorption at elevated temperatures. Initial digermene adsorption at room temperature causes the formation of GeH_3 , GeH_2 , and GeH surface species; in addition, the sticking coefficient is around 0.5. At higher adsorbed GeH_x coverage, the main adsorption fragments are GeH_3 and GeH_2 , owing to the lack of nearby Si dangling-bond sites. Annealing the digermene-saturated surface leads toward H-reduction surface reactions. In contrast to $\text{Si}_2\text{H}_6/\text{Si}(100)$ system in which surface reactions can be described by stepwise decomposition of SiH_3 radicals, two reaction pathways for hydrogen release from

GeH were observed: (1) the H atom transfers to Si with dangling bonds through surface diffusion, and forms a higher strength SiH bond; or (2) the H atom undergoes recombinative desorption directly over the Ge sites. Reaction (1) was found to occur at lower temperatures and at lower Ge₂H₆ coverages; reaction (2) is favorable for higher coverages.

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