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 (Ge₂H₆) on the Si(100)-(2×1) surface with high-resolution core-level photoemission spectroscopy using synchrotron radiation. At 325 K, the digermane dissociatively chemisorbs to produce GeH₄, GeH₂, 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 GeH₃ and GeH₂ 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 3d and Si 2p 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 Ge₂H₆ 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 H₂ 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 3d and Si 2p 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 owing to their rich fundamental interest and their vast applications in Si-based technology. Recently, two gas sources, disilane (Si₂H₆) and digermane (Ge₂H₆), were applied as molecular precursors for Si and Ge growth, respectively. Compared with GeH₄, 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 GeH₄; 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, temperature-programmed desorption (TPD), ultraviolet photoemission, and x-ray photoelectron spectroscopy. 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 GeH₃ radicals. As the annealing temperature is raised to 200 K, a partial decomposition of the GeH₃ groups was found. Over the temperature range of 500–900 K, a series of H₂ desorption peaks were observed in the TPD spectra. In the TPD study of Ge₂H₆ on Si(100) and D₂ on Ge/Si(100), both groups found, for high surface Ge coverages, three H₂(D₂) desorption maxima α (590 K), β₁ (670 K), and β₂ (780 K). The three peaks were assigned for H₂ recombinative desorption from two of GeH, SiH₂, 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 study, we investigate the adsorption and thermally induced (325–900 K) dissociation of Ge₂H₆ 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. By monitoring the intensities and changes in binding energies of all the shifted Si 2p and Ge 3d 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 Ge₂H₆ coverages, their conclusion is indirectly based on the lack of H₂ desorption peak derived from Ge sites. Results in this study demonstrate that the H-induced shifted component develops in the Si 2p spectra, but simultaneously vanishes in the Ge 3d 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
COVERAGE-DEPENDENT THERMAL REACTIONS OF... 16 959

1.3-GeV storage ring was dispersed by a Dragon-type 6-m Low-energy Spherical Grating Monochromator. All the Ge$_2$H$_6$ 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 0.3×1.2×0.05 cm$^3$, 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. Digermane (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 ultrahigh vacuum system. The wafer’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)-(2×1) 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.

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FIG. 1. Atomic model for the Si(100)-(2×1) surface and schematic diagrams illustrating various bonding configurations of diger-

mane fragments.

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Figure 2(a) shows a surface-sensitive Si 2p core-level spectrum (circles) for clean Si(100)-(2×1), 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. 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; 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.

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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 Si dangling atoms on the surface. 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)-(2×1), taken from Ref. 5 and shown in Fig. 2(b), are quite similar to those of the Si 2p core of clean Si(100) and Ge(100), which had been previously studied.5,6 Similar to the Si-Si bond in disilane, the Ge-Ge bond in digermane 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 absorbed on Si(100)-(2×1). This reaction can be expressed as follows:

$$\text{Ge}_2\text{H}_6(g) \rightarrow 2\text{GeH}_3(s)$$

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

Figure 1 also shows possible GeH3 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)-(2×1) 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:

$$\text{GeH}_3(s) + \text{Si}(s) \rightarrow \text{GeH}_2(s) + \text{SiH}(s),$$

$$\text{GeH}_2(s) + \text{Si}(s) \rightarrow \text{GeH}(s) + \text{SiH}(s),$$

$$2\text{GeH}_2(s) \rightarrow 2\text{GeH}(s) + \text{H}_2(g),$$

$$2\text{GeH}(s) \rightarrow \text{Ge}_2(\text{dimer})(s) + \text{H}_2(g).$$

FIG. 3. Photoemission spectra of the Ge 3d core level for various digermane exposures on Si(100)-(2×1) at $\sim$325 K. The binding energy is referred to as the corresponding Si 2p3/2 line of the bulk component. The intensity of each spectrum has been normalized to the incident photon beam intensity.

$$2\text{SiH}(s) \rightarrow 2\text{Si}(s) + \text{H}_2(g),$$

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 digermane on Si(100)-(2×1) at $\sim$325 K. The binding energy scale is referred to the B component of the Si 2p3/2 core level of clean Si(100). The main feature of the spectra is the monotonical increase of their integrated photoemission intensity as the digermane dose accumulates. The line shapes of the Ge 3d spectra remain essentially the same for all exposures above 1 L, thereby suggesting that...
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.

FIG. 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 digermane 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 digermane, 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 Ge$_2$H$_6$-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
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 GeH x-saturated 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 3d spectrum after annealing the GeH x-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).\textsuperscript{15,23} This finding is expected since all of the hydrogen has desorbed, and the Ge films performed by PEP 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.\textsuperscript{25} This is also evident by the fact that the integrated intensity of Ge 3d 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 3d 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 2p 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 3d spectra after a 900-K anneal. Moreover, the line shapes of the Ge 3d core above 770 K in Fig. 5(a) are quite similar, indicating the completeness of H 2 desorption from Ge sites. In the range 590–770 K, the intensity of the S component of Ge 3d slowly surges, marking H 2 desorption from GeH surface species [Eq. (5)]. Again, this temperature range correlates well with the α desorption state in the TPD spectra.\textsuperscript{12,13} The lower H 2 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 3d 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 H 2 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).\textsuperscript{5} At this annealing temperature, the corresponding Si 2p 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 3d 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 GeH x-saturated surface region. Both line shapes of the Ge 3d 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 3d 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,\textsuperscript{5} the most straightforward interpretation of Fig. 3 is that the major component of Ge 3d spectrum corresponds to the Ge dihydride (GeH 2) with possibly a few trihydrides (GeH 3); this interpretation correlates with that in a previous infrared study.\textsuperscript{9}

Interestingly, the relative emission of GeH to GeH 2 is larger at low GeH x 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 3d core-level spectra for Si(100)-(2×1) exposed to 0.2- and 1-L GeH x, 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 GeH x adsorption at 325 K, the line shapes of the Ge 3d core reflect the combination of GeH 1, GeH 2, 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) H 2 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
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:

$$\text{GeH} \rightarrow \text{Si} + \text{SiH}.$$  \(7\)

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 digermane 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 GeH\(_x\) coverage is sufficiently high, no nearby open Si sites are available for GeH decomposition through H diffusion; thus recombinative desorption of H\(_2\) from Ge sites [Eq. \((5)\)] takes place. The emergence of the \(\alpha\) 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 digermane-saturated surface through the temperature range of the \(\alpha\) desorption peak also corroborates this desorption mechanism.

**IV. SUMMARY**

High-resolution core-level photoemission with synchrotron radiation was employed to study the adsorption of digermane on Si(100)-(2\(\times\)1) at near room temperature, and subsequent pyrolytic decomposition and hydrogen desorption at elevated temperatures. Initial digermane 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 digermane-saturated surface leads toward H-reduction surface reactions. In contrast to Si\(_2\)H\(_6\)/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 Ge$_2$H$_6$ coverages; reaction (2) is favorable for higher coverages.

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