Surface dihydrides on Ge(100): A scanning tunneling microscopy study

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We studied the atomic scale surface evolution of Ge(100) exposed at 300 K to gas-phase hydrogen atoms, H(g). Surface H(g) uptake created a 2 × 1:H phase, quickly reaching ~1 monolayer H coverage. However, in contrast to the Si(100) surface, dangling bonds of the Ge(100) surface could never be completely removed by H(g) due to their regeneration by highly efficient surface H abstraction. This, together with the instability of surface dihydrides, GeH₂(a), inhibited the large-scale formation of 3 × 1:H and 1 × 1:H phases. Short GeH₂(a) rows, present in small metastable 3 × 1:H domains formed near defect sites, were etched selectively by H(g), producing line defects. © 2002 American Institute of Physics. [DOI: 10.1063/1.1520329]

The interactions of hydrogen with semiconductor surfaces have been studied intensively.¹ It is well known that surface H(g) uptake on Si(100) produces three distinct phases depending on the substrate temperature (Tₛ) and H coverage (Θ_H): (1) a 2 × 1:H monohydride phase (Θ_H=1 monolayer (ML)) at ~600 K; (2) a 3 × 1:H phase with alternating mono- and dihydride rows (Θ_H=1.33 ML) at ~400 K; and (3) a 1 × 1:H dihydride phase (Θ_H=2 ML) at ~300 K.²⁻⁴ The latter two phases give di- and monohydride H₂ desorption peaks at 670 K (β₂) and 780 K (β₁), respectively.²⁻³ H(g) breaks the Si–Si backbond of SiH₂(a) at Tₛ<600 K, producing gas-phase SiH₄(g) via successive H additions.³⁻⁴

The 2 × 1:H monohydride phase formation on Ge(100) has been well established; however, there is ongoing debate with regard to the surface dihydride, GeH₂(a), formation. Temperature-programmed desorption (TPD) and infrared spectroscopic data have been used to claim that monohydrides, GeH(a), are the only surface species, even at a Tₛ as low as 300 K.⁵ On the other hand, high-resolution electron energy loss spectroscopy⁶ and TPD measurements⁷ indicated the presence of GeH₂(a) on Ge(100). Shimokawa et al.⁸ reported a strong dihydride H₂ TPD peak (β₂), concluding that the GeH₂(a) formation on Ge(100) at 300 K was as efficient as that of SiH₂(a) on Si(100).

In order to resolve this inconsistency, we present in this letter the results of our scanning tunneling microscopy (STM) and TPD investigations into H(g) reactions with Ge(100).

Experiments were performed in an ultrahigh vacuum chamber (~2 × 10⁻¹⁰ Torr) equipped with an OMCICRON VT-STM. The Ge(100) sample used here was p-type (B-doped; ρ=0.01~0.39 Ω cm) and cut into a 2 × 10 mm² piece. The sample was introduced into the UHV chamber without a pretreatment, and was then cleaned in situ with several cycles of a 30 min 1 KeV Ar⁺ ion sputtering at 700 K and a subsequent 10 min annealing at 900 K. STM confirmed the clean and ordered Ge(100) surface. H₂ gas was introduced into the chamber through a tubular doser controlled by a variable leak valve. Thermal H(g) was produced by cracking H₂ with a hot (~1800 K) spiral W filament positioned ~10 cm away from the sample surface. Exposures are reported here in Langmuirs (1 L=1 × 10⁻⁶ Torr s) of H₂, not H, because more than 98% of the measured chamber pressure increment is due to H₂. Tₛ was maintained at 300 K during the H(g) doses and STM imaging. All STM images were taken at V_sample =−1.8 V and I_t =0.1 nA, using electrochemically etched W tips.

Unlike the uniformly symmetrical 2 × 1 reconstruction of Si(100),² the adsorbate-free Ge(100) surface exhibits a stripe pattern of alternating asymmetrical c(4 × 2) and symmetrical 2 × 1 dimer domains, as shown in Fig. 1(a). This structure was well characterized by Zandvliet et al.⁹ Figure 1(b) shows the surface exposed to H(g) of 1500 L H₂ at a Tₛ of 300 K. The well-ordered 2 × 1:H structure of ~1 ML Θ_H is very similar to the Si(100)-2 × 1:H.³⁻⁴ The bright ball-like features, randomly distributed and each located on one end of a dimer, are attributed to unpaired or isolated dangling bonds. We made this assignment on the basis of our filled- and empty-state scans and an intense pair of scanning tunneling spectroscopy peaks symmetrically positioned near E_f. Note that the majority of the dangling bonds on this nearly monohydride-saturated surface are unpaired. Moreover, in sharp contrast to the Si(100) surface,¹⁰ a significant number of such unpaired dangling bonds survive even after prolonged H(g) exposures (see Figs. 2 and 3). We ascribe this to the highly effective surface H abstraction by H(g) [H(a) + H(g)→H₂(g)], which is expected by the much weaker surface Ge–H bond compared with that of Si–H.¹¹ An unpaired dangling bond would be created on a surface dimer originally with one H on each end as a consequence of a single H abstraction event.

We now turn to the controversy regarding GeH₂(a) formation on Ge(100).⁵⁻⁸ To address this issue, we exposed the Ge(100)-2 × 1:H surface at 300 K to H(g) of 3000 L H₂,
twice that for the STM image of Fig. 1(b). The resultant surface image is displayed in Fig. 2(a). There are a small number of local $3 \times 1$ H domains (circled areas). The monohydride dimer rows in the $3 \times 1$ domains are out of phase with the background surface monohydride rows (boxed area). For the Si(100) surface, it has been suggested that the $2 \times 1$:H-to-$3 \times 1$:H transition occurs via a local $1 \times 1$:H transition state Si(100) as illustrated in Fig. 2(b). Recombinative H$_2$ desorption, due to the steric repulsion between the H atoms of two adjacent GeH$_2$(a) species, would reduce GeH$_2$(a) in numbers. Due to the significantly weaker Ge–H bond energy ($\sim 3.1$ eV) compared with that of Si–H ($\sim 3.4$ eV), such repulsion-driven H$_2$ desorption [Fig. 2(b)] is more likely to occur on Ge(100) than on Si(100) and was indeed observed during H(g) exposure at 300 K by Shimokawa et al.$^8$ The high residual dangling bond density, maintained by the efficient H abstraction due again to the weak Ge–H bond, would further hinder the GeH$_2$(a) production on Ge(100). The large-scale $1 \times 1$:H or $3 \times 1$:H phase formation would thus be very difficult. Figure 3(a) and 3(b) show that the $2 \times 1$:H phase is largely maintained even after extensive H(g) exposures. Dangling bonds, mostly unpaired, are still present and GeH$_2$(a) rows are rarely seen. Instead, line defects develop along the otherwise GeH$_2$(a) rows within $3 \times 1$:H domains, which is indicative of selective GeH$_2$(a) etching. This result is closely analogous to the surface evolution of Si(100) upon H(g) exposure at $T_s$ between 450 and 550 K.$^3$ The large, irregular bright features are ascribed to the etching intermediate, GeH$_1$(a).$^4$

Figure 3(c) shows H$_2$ TPD measurement for two different Ge(100) surfaces. The TPD taken off the smooth surface shows a single monohydride peak ($\beta_1$) only, consistent with our STM images and early work,$^5$ but not with the recent result of Shimokawa et al.$^8$ However, the TPD for the roughened surface gives an additional, dihydride peak ($\beta_2$). This indicates that GeH$_2$(a) can be readily formed by H(g) once the surface dimer bonds are broken. The very unstable GeH$_2$(a), even if formed temporarily by H(g) on the atomically smooth Ge(100) surface, would quickly return to GeH(a) by collision-induced H$_2$ desorption [2GeH$_2$(a) → HGe–GeH + H$_2$(g)] or by dissociation [GeH$_2$(a) + dangling bond (DB) → 2GeH(a)] to fill a nearby dangling bond generated by H abstraction. Only those GeH$_2$(a) stabilized by nearby surface defects would form a local $3 \times 1$:H domain and would be amenable to additional H(g) and subsequent etching, as shown in Figs. 3(a) and 3(b). Thus, the surface GeH$_2$(a) concentration would vary widely depending on the surface defect density and roughness, leading to the inconsistent literature results respect to GeH$_2$(a) formation on Ge(100).$^5$–$^8$

From their observed dihydride collision-induced H$_2$ desorption and strong $\beta_2$—H$_2$ TPD peak, Shimokawa et al.$^8$
speculated that the GeH$_2$(a) formation would be as efficient on Ge(100) as on Si(100). Our STM and TPD results, however, consistently suggest that H(g) reaction with the HGe–GeH dimer bond to form GeH$_2$(a) on the atomically smooth Ge(100) surface at 300 K is very limited even after a H(g) exposure of ~67 times that required for the ~1 ML $\Theta_{\text{H}}$. The highest temperatures for the 3×1:H and 1×1:H formation on Si(100) are ~400 and ~300 K, respectively. Moreover, the $\beta_1$ and $\beta_2$ peak temperatures are ~200 and ~150 K lower respectively, on Ge(100) than on Si(100). From this trend, we speculate that the $T_s$ for large-scale formation of GeH$_2$(a)-containing phases on Ge(100) would be lower than 300 K.

In summary, our results show that the Ge(100)-2×1:H phase is stable to additional H(g) as a result of continuous surface dangling bond regeneration by highly efficient H abstraction and of the immediate dissociation of unstable GeH$_2$(a), if formed temporarily, at a $T_s$ as low as 300 K.

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