Preparation and Stability of Silyl Adlayers on 2×1-Reconstructed and Modified Si(100) Surfaces

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Saturation-coverage silyl, -SiH3(a), overlayers were prepared from Si2H6 adsorption on three comparative surfaces: clean unmodified; D-precovered; and atomically roughened Si(100). Together with its precursor-mediated adsorption behavior, the surface reactivity of Si2H6 was found to be the highest on the unmodified Si(100)-2×1 surface. This was correlated with its dissociative adsorption mechanism, in which both the H3Si-SiH3 bond scission and the dual surface Si-SiH3(a) bond formation require a surface dangling bond ‘pair’. The unusually high thermal stability of -SiH3(a) on the unmodified surface was ascribed to a nearly close-packed -SiH3(a) coverage of ~0.9 monolayer and the consequent lack of dangling bonds on the silyl-packed surface.

Key words : Si(100), Disilane(Si2H6), Silyl(SiH3) Adsorption

I. Introduction

Driven by their importance in semiconductor device processes, both SiH4 and Si2H6 have been extensively studied for their reactions with Si and Ge surfaces for the past decades [1-2]. Both are known to dissociatively adsorb on those surfaces with negative barriers via precursor-mediated mechanisms at moderate substrate temperatures [3-4]. It has been suggested that dangling bonds are required for their spontaneous dissociative adsorption (chemisorption) at temperatures < 600 K [5-6]. The so-called atomic layer epitaxy (ALE) scheme is based on this self-limited reaction phenomenon, which enables the ultimate control of the layer-by-layer growth in silicon deposition techniques [5].

In general and particularly in heterogeneous catalysis, it is well known that the reactivity of a solid surface increases as the atomic-scale surface roughness increases. This is due to the increased number of unstable, less-coordinated atoms on such surfaces. As one of numerous examples, the dissociative adsorption of SiH4 occurs preferentially on defect sites on Si(100) and dissociative SiH4 chemisorption on Si(111)-7×7 is significantly enhanced by surface roughening with inert gas ion bombardments [3]. Hydrogen uptake, as a measure of the total number of dangling bonds per unit surface area, also increases on Si(100), Si(111) and Ge(100) once their stable atomic surface structures are disrupted or roughened [7].

Both SiH4 and Si2H6 dissociatively chemisorb on Si(100)-2×1 via a precursor-mediated channel at a surface temperature (T0) below 800 K [3-4]. Two competing mechanisms have been proposed for the dissociative Si2H6 adsorption on Si(100)-2×1: each physisorbed Si2H6 molecule reacts with (1) two
unrelated surface dangling bonds to give two silyl, 
-\text{SiH}_2(a), adspecies and (2) with paired dangling bonds 
within a surface dimer to give \text{SiH}_4(g) and silylene, 
-\text{SiH}_2(a), adspecies \cite{8}, Suda et al. \cite{5} proposed 
another mechanism in which \text{H}_2\text{Si}−\text{SiH}_3 bond dissociation 
and the dual surface \text{Si}−\text{SiH}_3(a) bond formation occur in 
a concerted fashion.

In this report, data are presented that the 
dissociative adsorption of \text{Si}_2\text{H}_6 on \text{Si}(100)−2×1 is 
greatly suppressed when its surface atomic structure 
is disrupted either by energetic Ar\textsuperscript{+} ion bombardments 
or when its surface dangling bonds are passivated 
with D(a). This unusual reactivity behavior is 
ascribed to a dominant reaction mechanism in which 
both the \text{SiH}_3−\text{SiH}_3 bond dissociation and the 
formation of two surface \text{Si}−\text{SiH}_3 bonds concur at the 
dangling bond pair site of each \text{Si} dimer \cite{5}. In 
addition, it is found that the saturation \text{Si}_2\text{H}_6 
exposure at temperatures below 120 K leads to \sim 0.9 
ML of −\text{SiH}_3(a), which corresponds to a \Theta_H as high as 
\sim 2.7 ML (1 monolayer (ML) = 6.78 × 10^{14} \text{H atoms} \cdot \text{cm}^{-2}, the surface \text{Si} atom density). In 
contrast to the literature reports \cite{1-6,8}, the very 
high thermal stability of −\text{SiH}_3(a) on \text{Si}(100)−2×1 observed in this work is reconciled with the fact that 
almost all surface dangling bonds are nearly 
close-packed by −\text{SiH}_3(a). Such a high degree of 
−\text{SiH}_3(a) packing on \text{Si}(100)−2×1 was achieved only 
by the saturation adsorption of \text{Si}_2\text{H}_6 at a 
temperature low enough to saturate all surface 
dangling bond pairs each with a physisorbed \text{Si}_2\text{H}_6 molecule.

\section*{II. Experimental}

Experiments were all performed in a turbomolecular-
pumped ultra–high vacuum chamber with a base 
pressure $\sim 1 \times 10^{-10}$ Torr. Our lightly B–doped, 14–20 
Ω · cm resistivity \text{Si}(100) samples of a 0.5 × 15 × 20 
mm$^3$ size were coated with 2000 Å of tungsten 
sandwiched between 200–Å tantalum films to 
facilitate linear direct–current heating up to 1400 K. 
The samples were then clamped with a pair of 
tantalum clips mounted on an electrically insulated 
and LN\textsubscript{2}–cooled OFHC Cu block pair. The substrate 
temperature was monitored by a chromel–alumel (type 
K) thermocouple glued into a small hole near the 
sample edge with Aremco (Ultra\textsuperscript{TM} 516) high– 
temperature ceramic adhesive.

After a 5–K/s flash heating to 1300 K and 1 K/s 
cooling, our \text{Si}(100) sample was 2×1–reconstructed 
and clean without native oxide, as checked by Auger 
electron spectroscopy (AES), low–energy electron 
diffraction (LEED) and \text{H}_2 temperature–programmed 
desorption (TPD) features, Silane and disilane (both 
4\% in He; Voltaix) were dosed using a crimped 
capillary–controlled 3/8–inch diameter tubular doser 
positioned \sim 1 mm in front of the sample surface, 
\text{SiH}_4 and \text{Si}_2\text{H}_6 exposures were controlled by varying 
dosing time at a fixed reservoir pressure of 1.0 Torr 
behind a pinhole, Atomic D was generated by a hot (\sim 
1900 K) spiral W filament positioned in front of a 
0.25–inch diameter tubular D\textsubscript{2} gas doser facing the 
sample surface from a distance of \sim 3 cm.

TPD measurements were made with a shielded, 
differentially pumped quadrupole mass spectrometer 
(QMS) through a 3–mm diameter conical aperture 
positioned \sim 1 mm away from the sample surface. The 
small distance suppresses signal contributions from 
background sources. Multiplexed TPD spectra for various 
mass–to–charge ratio (m/e) values were taken with a 
fixed temperature ramp of 3 K/s following each gas 
exposure at a given surface temperature (T\textsubscript{s}).

\section*{III. Results and Discussion}

Multiplexed \text{SiH}_3\textsuperscript{+} (m/z = 31) and \text{H}_2\textsuperscript{+} (m/z = 2) 
TPD spectra taken off the \text{Si}(100)−2×1 surface pre–
exposed to Si$_2$H$_6$ at a $T_s$ of 105 K are displayed in Fig. 1. The QMS signals for all other SiH$_4$ ionization fragments (not shown) tracked the displayed SiH$_3^+$ desorption intensity at ~600 K with a correct intensity ratio, Si:SiH$_2^+$:SiH$_3^+$:SiH$_4^+$ = 60:37:100:80:7, determined in situ with the QMS for the back-filled SiH$_4$ gas, very close to the literature values [9]. Thus, the 600–K SiH$_3^+$ TPD peak represents the molecular SiH$_4(g)$ desorption. On the other hand, since the SiH$_3^+$ signal tracked those of all other fragments of Si$_2$H$_6$ with the correct relative ratio determined in situ [10], the extremely narrow SiH$_3^+$ peak at ~120 K was ascribed to the molecular Si$_2$H$_6$ desorption from its physisorbed multilayer(s). The H$_2^+$ TPD spectra show two distinct features ($\beta_1$ and $\beta_2$), the well-established associative H$_2(g)$ desorption from the surface-adsorbed mono- and di-hydride H atoms, respectively.

No further intensity increases of the 120–K SiH$_3^+$, 600–K SiH$_4^+$, 660–K $\beta_2$ H$_2^+$, and 780–K $\beta_1$ H$_2^+$ peaks were observed above the 90–s dose, establishing the saturation Si$_2$H$_6$ exposure. The maximum $\beta_1$–H$_2^+$ peak intensity (90–s dose) was ~1.2–ML $\Theta_{H}$, calibrated against that of the monohydride–saturated surface ($\Theta_{H} = 1$) prepared by an H dose at ~600 K, while that of the 5–s spectrum was ~1.05 ML. The total $\beta_1$– and $\beta_2$–H$_2^+$ desorption of the 90–s spectrum was ~1.9 ML. This, together with the 600–K SiH$_4$ desorption amount of ~0.2 ML SiH$_3(a)$ estimated with the reported SiH$_4$/H$_2$ relative mass spectrometric sensitivity [11], gave a total surface H content of ~2.7 ML in the $T_s$ range between 120 K and 600 K. This value corresponds to an initial ~SiH$_3(a)$ surface coverage of ~0.9 ML, meaning the formation of a nearly close-packed silyl adlayer, i.e., ~90% of all surface dangling bonds are each covered with a ~SiH$_3(a)$. From the total estimated H coverage of ~2.7 ML and the absence of desorption of any H–containing species between 120 K and 600 K, it is deduced that the surface be mostly devoid of the further dissociated =SiH$_2(a)$ and ≡SiH(a) fragments. This unusually high packing degree of ~SiH$_3(a)$ and the lack of dangling bonds would prohibit further dissociation of ~SiH$_3(a)$ into =SiH$_2(a)$ and H(a) up to as high as 600 K. It can be reasonably speculated that two ~SiH$_3(a)$ on adjacent dimers collide each other to give SiH$_4(g)$ and =SiH$_2(a)$ at 600 K. It should be noted that this reaction pathway of ~SiH$_3(a)$ would be the unique one, unlike many others reported in the literature [1–6,8], as a result of the highly
Figure 2. H$_2^+$ (thin solid curves), and SiH$_3^+$ (thick solid curves) TPD spectra from Si(100) exposed to Si$_2$H$_6$(g) for 90 sec at the indicated surface temperatures (T$_{ads}$). The scale factors are for the three SiH$_3^+$ spectra.

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−SiH$_3$(a)−packed adlayer and the lack or deficiency of dangling bonds and lower hydrides. It is believed that the 120−K SiH$_3^+$ peak represents desorption of Si$_2$H$_6$ multilayer molecules weakly physisorbed on top of those strongly physisorbed on each dangling bond pair [12].

Fig. 2 shows the T$_d$−dependent Si$_2$H$_6$ uptake for a fixed 90−s dose. It can be seen that the dissociative Si$_2$H$_6$ adsorption increases with decreasing T$_d$ in the entire T$_d$ range studied. This behavior is typical of precursor−mediated chemisorption processes, in accord with previous suggestions [3−4]. Note that the β$_1$−H$_2$ peak intensity of the TPD curve for the 600−K dosing temperature corresponds to Φ$_d$ of 0.55, far short of passivating the surface dangling bonds. This is attributed to the short lifetime and the consequently reduced concentration of Si$_2$H$_6$ trapped in its physisorption well on the surface at the temperature. Note that the 600−K SiH$_4$ desorption is detected only when there are H atoms exceeding 1 ML on the surface, which is the case for all the spectra of T$_{ads}$ < 300 K, suggesting the thermal instability of −SiH$_3$(a) below 600 K when there are adjacent dangling bonds. The 600−K SiH$_3^+$ peak intensities of the bottom 6 spectra (T$_{ads}$ = 125 to 600 K) are all lower than that (saturation value) of the top spectrum (T$_{ads}$ = 105 K). This suggests that the dissociation of physisorbed Si$_2$H$_6$ into −SiH$_3$(a) and the subsequent −SiH$_3$(a) dissociation into =SiH$_2$(a) and ≡SiH(a) occur before all surface dangling bond pairs are filled with physisorbed Si$_2$H$_6$ molecules when the surface temperature is ≥ 125 K. The Si$_2$H$_6$ dissociation into −SiH$_3$(a) and the successive −SiH$_3$(a) decomposition into =SiH$_2$(a) and ≡SiH(a) are known to take place readily when surface dangling bonds are available at temperatures as low as 148 K [8], but slowly over several minutes at room temperature [13]. This suggests that our short saturation dosing time of 90 s, together with the very low dosing temperature of 105 K, has ensured the nearly complete packing of all dangling bond pairs each with a physisorbed Si$_2$H$_6$ molecule. The rather mobile, weakly physisorbed Si$_2$H$_6$ molecules in the multilayer would also fill in the empty dangling bond pair sites. After the 90−s saturation Si$_2$H$_6$ dose at 105 K, almost all surface dangling bond pairs would thus be covered each with a strongly physisorbed Si$_2$H$_6$ molecule [12]. Upon annealing, the remaining weakly physisorbed Si$_2$H$_6$ in the multilayer would desorb at 120 K and the strongly physisorbed Si$_2$H$_6$ molecule in the precursor state on a dangling bond pair would then dissociate into two −SiH$_3$(a) groups [12,14]. These close−packed −SiH$_3$(a) groups are believed to sustain up to 600 K, at which two −SiH$_3$(a) groups would collisionally react to produce disproportionation products, =SiH$_2$(a) and
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SiH4(g). This reaction scheme is well in agreement with all the aspects of the experimental data of this work.

The H2+ and SiH3+ TPD spectra obtained with the Si2H6 saturation dose at 125 to 600 K in Fig. 2 clearly show total H uptakes smaller than that with the 105−K dose. This suggests that Si2H6 dissociates first into two −SiH3(a) upon adsorption and that −SiH3(a) quickly decomposes into =SiH2(a) and =SiH(a) at T_ads ≥ 125 K, consuming more surface dangling bonds. The further decomposition −SiH3(a) would occur successively faster at a higher T_ads, reducing the number of dangling bond pairs [15]. The strongest 600−K SiH4(g) desorption from the 105 K−dosed surface in turn supports the high −SiH3(a) coverage (~0.9 ML) or the total H content (~2.7 ML) on the surface prior to the SiH4(g) desorption at 600 K.

In order to examine the importance of the surface dangling bonds for the dissociative SiH4 adsorption, the Si(100)−2×1 surface was precovered with D prior to the saturation Si2H6 dose. Fig. 3 and Fig. 4 show H2+, HD+, D2+ and SiHxDy+ TPD spectra following a 90−s saturation Si2H6 dose at 105 K to the Si(100)−2×1 surface precovered with ~ 0.4 and ~ 1.0 ML D, respectively. The 120−K Si2H6 desorption (not shown) was observed from these D−precovered Si(100)−2×1 surfaces, implying that the weakly physisorbed Si2H6 molecules on the Si2H6− and D−precovered Si(100)−2×1 surface have the same similar adsorption energy [12]. The bottom 4 spectra for the various ionized fragments (m/z = 30−33) reflect the presence (Fig. 3) and absence (Fig. 4) of molecular SiHxDy (x + y = 4) desorption, the final reaction product of dissociation fragment, −SiH3(a). The SiHxDy desorption, together with HD and H2 desorption, is indicative of the SiH4 dissociative adsorption. The results of Fig. 4 clearly indicate that

![Figure 3](image1.png)  
**Figure 3.** TPD spectra from Si(100) with 0.4−ML D only (top 3 curves) and from Si(100) with a 0.4−ML D precoverage followed by a 90−sec Si2H6(g) exposure at 105 K (bottom 7 curves), respectively. The mass−to−charge ratio (m/z) values and the corresponding mass fragments monitored by the multiplexed TPDs are indicated.

![Figure 4](image2.png)  
**Figure 4.** TPD spectra from Si(100) with 1−ML D only (top curve) and from Si(100) with a 1−ML D precoverage followed by a 90−sec Si2H6(g) exposure at 105 K (bottom 7 curves), respectively.
the dangling bond passivation by D(a) effectively suppresses the dissociative Si₂H₆ adsorption, confirming the literature reports [3,5–6,8].

In order to assess the importance of the dangling bond dimer structure with respect to the dissociative adsorption of Si₂H₆, the Si(100)–2×1 was bombarded with 1 keV Ar⁺ ions at 300 K prior to a 60–s Si₂H₆ dose at 105 K, ion bombardments largely destroy the dimer row structure (dangling bond pairs) and create highly unstable, less–coordinated Si atoms on the surface [16]. H and SiH₄ uptakes increase with atomic–scale roughening of the Si surfaces [3,7], indicative of an increase in the number of dangling bonds on the surface. However, the dissociative Si₂H₆ uptake, monitored by the SiH₃⁺ (600 K) and H₂⁺ (660 K and 780 K) desorption in TPD, turned out to be significantly smaller on the roughened surface, as shown in Fig. 5. In accord with this, the stronger SiH₃⁺ and H₂⁺ desorption intensities at ~120 K indicate that more weakly physisorbed Si₂H₆ molecules desorb molecularly from the ion–roughened surface. The nearly complete suppression of both the 600–K SiH₃⁺ and β₂–H₂⁺ desorption indicates that the surface dangling bond pair, not the dangling bond itself, plays a key or more important role in the dissociative adsorption of Si₂H₆. The total H₂ desorption amount from the ion–bombarded surface was estimated to be ~1 ML, which should be significantly smaller than the number of dangling bonds on the roughened surface. This confirms evidently that the dissociative Si₂H₆ sticking probability is much higher on the surface with paired dangling bonds than the roughened surface even with a higher dangling bond density. These results strongly support the following Si₂H₆ physisorption and the subsequent dissociation pathway on Si(100)–2×1: the preferred configuration of physisorbed Si₂H₆ is such that H₃Si–SiH₃ bond is parallel to the surface Si–Si dimer bond and the concerted H₃Si–SiH₃ bond scission and dual Si–SiH₃(a) bond formation, in good accord with the model proposed by Suda et al. [5].

An uptake comparison for SiH₄ and Si₂H₆ on the Si(100)–2×1 surface is presented in Fig. 6. The TPD spectra for the two saturation exposures, 90–sec, Si₂H₆ and 360–s SiH₄, clearly show that Si₂H₆ adsorption leads to the higher SiH₃(a) and H(a) coverages on Si(100)–2×1. However, this difference was mostly eliminated on the Ar⁺–bombarded surface. The fact that the maximum desorption intensity of the SiH₃⁺ from the saturation SiH₄ dose (360–s) is much smaller than that from the saturation Si₂H₆ dose (90–s) is in good agreement with the high –SiH₃(a) coverage and Si₂H₆ adsorption mechanism involving the dangling bond pair [5, 17].

The estimated Θ_H of ~2.7 ML, accomplished by the
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Figure 6. H$_2$ (thin curves) and SiH$_3$ (thick curves) TPD spectra from Si(100) exposed to SiH$_4$ (bottom 3 curves) and Si$_2$H$_6$ (top curve) for the times and at the surface temperatures indicated in the figure.

Figure 7. A ball–stick diagram for the physisorbed Si$_2$H$_6$, each on top of a dangling bond pair in a dimer, and chemisorbed –SiH$_3(a)$ on Si(100)–2×1. Surface dangling bonds are represented as lobes. The Si–Si bond lengths are approximately 2.40, 2.35 and 2.33 Å for the surface dimer, the bulk lattice and Si$_2$H$_6$, respectively [17].

saturation Si$_2$H$_6$ chemisorption, requires that 90% of the surface dangling bonds of Si(100)–2×1 are SiH$_3(a)$–bonded over a wide $T_s$ range between 120 K and 580 K. The very high packing density and thermal stability of –SiH$_3(a)$, despite the expected steric hindrance between –SiH$_3(a)$ groups, are interesting. It has been suggested that –SiH$_3(a)$ on Si(100)–2×1 can be stable up to ~600 K in the absence of surface dangling bonds [3]. The inhibited –SiH$_3(a)$ dissociation is therefore a result of its high coverage of ~0.9 ML, implying a nearly close-packed full monolayer, as depicted schematically in Fig. 7. The H$_3$Si–SiH$_3$ bond scission of the speculated configuration of physisorbed Si$_2$H$_6$ and the dual surface Si–SiH$_3$ bond formation can be speculated to occur concertedly. The relevant bond lengths indicated in the caption of Fig. 7 are in good agreement with such a picture.

IV. Conclusion

Low-temperature (< 120 K) adsorption of Si$_2$H$_6$ on Si(100)–2×1 leads to a silyl, –SiH$_3(a)$, adlayer of ~0.9 ML. This nearly close-packed –SiH$_3(a)$ adlayer is unusually stable up to ~600 K, at which two –SiH$_3(a)$ on adjacent dimers within a dimer row collide to give a gaseous SiH$_4(g)$ molecule and a silylene, =SiH$_2(a)$, adspecies [15]. The dangling bond pair on Si(100)–2×1 was found to be a preferred Si$_2$H$_6$ physisorption site and a lowest-barrier site for the concerted chemisorption reaction, i.e., the scission of the H$_3$Si–SiH$_3$ bond and the formation of dual surface
Si–SiH₃(a) bonds.

References

Si(100)-2×1 표면과 개질된 Si(100) 표면 상에서 실릴 (Silyl) 흡착층의 형성과 안정성

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깨끗한 Si(100)-2×1, D를 먼저 흡착시킨 Si(100)-2×1, 그리고 이온 빔에 의해 원자 수준으로 거칠어진 Si(100) 등의 세 가지 표면에 각각 Si2H6의 흡착시켜 포화 실릴(-SiH3(a)) 흡착층을 형성시키고 실험적으로 비교 고찰하였다. 전구체 흡착 거동 (기작)과 함께 Si2H6의 표면 분해(화학)흡착 반응성은 개질을 시켜주지 않은 깨끗한 Si(100)-2×1 표면에서 가장 크게 나타났다. 이 결과는 화학흡착 반응 즉, H3Si-SiH3 결합 분해와 두 개의 Si-SiH3(a) 표면결합 형성이 표면의 Dangling Bond Pair 상에서 동시에(Concertedly) 일어난다는事が 발견되었다. 또한 Si(100)-2×1 표면에 흡착된 -SiH3(a)의 매우 높은 열적 안정성은 ~0.9 ML나 되는 표면 밀도도와 함께 실릴기로 조밀하게 흡착된 표면에 Dangling Bond가 존재하지 않는 것에 의한 것으로 밝혀졌다.

주제어: 실리콘(100), 다이사일렌(Si2H6), 실릴(SiH3) 흡착.

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