How dissociated fragments of multiatomic molecules saturate all active surface sites—H$_2$O adsorption on the Si(100) surface

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Abstract
A fundamental question for the adsorption of any gas molecule on surfaces is its saturation coverage, whose value can provide a comprehensive examination for the adsorption mechanisms, dynamic and kinetic processes involved in the adsorption processes. This investigation utilizes scanning tunneling microscopy to visualize the H$_2$O adsorption processes on the Si(100) surface with a sub-monolayers (<0.05 ML) of chemically-reactive dangling bonds remaining after exposure to (1) a hydrogen atomic beam, (2) H$_2$O, and (3) Cl$_2$ gases at room temperature. In all three cases, each of the remaining isolated single dangling bonds (sDB) adsorb and is passivated by either of the two dissociation fragments, the H or OH radical, to form a surface Si–H and Si–OH species. A new adsorption mechanism, termed ‘dissociative and asynchronous chemisorption’, is proposed for the observation presented herein. Upon approaching a sDB site, the H$_2$O molecule breaks apart into two fragments. One is chemisorbed to the sDB. The other attaches to the same or the neighboring passivated dimer to form a transition state of surface diffusion, which then diffuses on the mostly passivated surface and is eventually chemisorbed to another reactive site. In other words, the chemisorption reactions of the two fragments after dissociation occur at different and uncorrelated time and places. This adsorption mechanism suggests that a diffusion transition state can be an adsorption product in the first step of the dissociative adsorption processes.

Keywords: adsorption mechanism, chemisorption, water molecule, Si(100), scanning tunneling microscopy, H$_2$O, dissociative adsorption

(Some figures may appear in colour only in the online journal)

Introduction
Dissociative chemisorption of diatomic or multiatomic molecules onto metal and semiconductor surfaces is one of the most fundamental surface chemical reactions in the practical applications, such as atomic layer epitaxy, catalyzed reactions, and dry etches, etc [1–8] The typical mechanism of the dissociative chemisorption of a gas molecule F$_1$–F$_2$ describes that two new bonds are created simultaneously, or within tens of femtoseconds [1], between the two fragments, F$_1$ and F$_2$, and the substrate surface while the molecular bond is cleaving [9, 10]. In this scenario, two or more immediately neighboring active surface sites are present to break the
molecular bond in favor of new bonds to the surface—S–F_1 and S–F_2, where S denotes a surface atom. Accordingly, the final chemisorbed positions for the two fragments should be less than two surface lattice constants (SLC) from each other. If the chemisorption reaction is spontaneous, the overall reaction is exothermic, i.e. \( E_{\text{ad}} = E_{S-F_1} + E_{S-F_2} - E_{F_1-F_2} > 0 \), where \( E_{\text{ad}} \), \( E_{S-F_1} \), \( E_{S-F_2} \) and \( E_{F_1-F_2} \) are, respectively, adsorption energy and the bond energies of S–F_1, S–F_2 and F_1–F_2. The adsorption energy \( E_{\text{ad}} \) reflects the energy surplus upon adsorption of a F_1–F_2 molecule.

Other types of the dissociative adsorption such as the ‘hot-adatom’ [2, 11], and ‘cannon-ball’ trajectories over the surface [8, 12, 13], and the abstractive adsorption mechanism have also been reported [14–17]. In hot-adatom and cannon-ball reactions, both fragments are chemisorbed also within a hundred femtoseconds [8]. However, the two adsorbed species are well separated by a distance of several to tens of SLCs. Even though there are plenty of neighboring chemically active sites, the energies released are dissipated before the free radicals each form a chemical bond with an active site. In the abstractive adsorption, a gas molecule dissociates as it hits a surface; one fragment is ejected into the gas phase while the other fragment is selectively chemisorbed [18]. In either of the above-mentioned less-common chemisorption mechanisms, the formation of the first adsorbate-surface bond alone releases enough energy to break the molecular bond (\( \Delta E_{S-F_1/F_2} \)) and, therefore, only one active site is needed for the reactions to occur spontaneously.

A fundamental question for the adsorption of any gas molecule on surfaces is its value of saturation coverage, which is typically measured in percentage with respect to the density of active surface sites. A long-standing puzzle exists for the dissociative chemisorption with multiple adsorption configurations: some systems can fully saturate all active surface sites but some cannot. Many molecules, such as I_2 [19], H_2O [20], PH_3 [21], AsH_3 [22], and Si_2H_6 [23], cannot fully saturate all chemically-active surface sites on the Si(100) surface, even though they dissociate and chemisorb spontaneously at low coverages. The saturation coverages range from sub-monolayers to 0.98 ML. Lack of two neighboring sites due to random fillings of the lattice sites, adsorbate–adsorbate repulsive interactions, and/or steric hindrance could slow down or even stop further adsorption at high coverages. Examples of fully saturated cases, such as Cl_2, HCl, and HBr on the same Si(100) surface, are fewer [17, 24, 25]. Why the above-mentioned reasons that slow down or prevent some dissociative processes do not occur on these systems thus require further investigation and modeling.

STM is an excellent tool to study the gas adsorption mechanisms as it can examine both the adsorbates and the adsorbent surface in atomic resolution. To identify the adsorption configuration for each chemisorption reaction, a very small amount of gas molecules is typically introduced onto clean and well-ordered surfaces, on which ordered arrays of reactive sites are available for chemisorption [24, 26–28]. The reactants on the surface for a specific chemisorption reaction are thus unspecified and naturally assumed to be surface atoms that eventually form bonds with the adsorbates. The lack of information on the initial state or the specific reactants participating in an adsorption reaction can result in the oversimplification of the interpretations of the reaction pathways.

Here we have used several univalent radicals—hydrogen atoms, hydroxyl and chlorine radicals, to mask most reactive sites on a Si(100) surface and leave only a low density of single and paired dangling bonds (pDB) for the H_2O adsorption. These reactive sites are isolated and well separated. STM images are taken and examined over the same surface areas before and after the chemisorbed molecules are introduced into the vacuum chamber, so reactants and products for each chemisorption reaction are atomically resolved.

1. Methods

The scanning tunneling microscopy measurements were performed in an ultra-high-vacuum chamber with a base pressure of 1.0 \( \times 10^{-10} \) Torr. The boron-doped Si(100) samples of a resistance \( \sim 10 \Omega \) cm were mounted on holders made of Ta and Mo. Both the sample holders and the samples were out-gassed for 12 h at 900 K. The initial clean Si(100)-(2 × 1) surfaces were prepared by brief direct Joule heating at \( \sim 1400 \) K with subsequent radiation quenching. STM images are all taken at RT with a sample voltage \( V_s \), around \(-2.3 \) V and tunneling current \( I_t = 0.2 \) nA.

H-terminated Si(100)-(2 × 1) surfaces (H:Si(100)-(2 × 1)) were prepared by standard procedures [6, 29]. Bare DBs were formed by brief, mild thermal desorption at 700 K. The Cl termination was made by Cl_2 gas exposure using a solid-state electrochemical cell derived from an AgCl pellet doped with 5% CdCl_2. A voltage applied across the cell produced Cl ions that diffused to a Pt mesh electrode and desorbed as Cl_2. Typical emission current of AgCl gun is \( \sim 15 \) μA. Exposure time is used to control the amount of exposure. 4800 μA s is enough to saturate all the surface dangling bonds on Si(100).

The molecular H_2O was introduced into the UHV chamber through a precision leak valve and a quartz tube pointing toward the sample surface. Therefore, the actual dosage was higher than the apparent H_2O exposures calculated from the chamber backfilled pressure and time in terms of Langmuir (L) (1 L \( \nabla \) 10^{-6} Torr s). The typical backfilled pressure for H_2O is \( \sim 2 \times 10^{-8} \) Torr and the dosage is controlled by exposure time. On the clean Si(100) surface, \( \geq 95 \% \) of the surface dangling bonds are terminated by either H or OH species upon 1.5 L H_2O exposure.

2. Results and discussion

The Si(100)-(2 × 1) surface is composed of parallel rows of Si dimers [29, 30]. A bare silicon dimer (denoted by –Si–Si–) has one dangling bond (represented by a short dash) on each of the two dimer atoms and is also referred to as a pDB. A dangling bond orbit is half-filled and chemically active, offering a natural site for chemisorption of a univalent atom/free radical. To further reduce the total energy, the two dangling bonds in a pDB form a weak π-bond, the dimer buckles, and a charge transfer occurs from the down Si atom to the up Si atom [31].
As a result, the $p(2 \times 2)$ and $c(4 \times 2)$ structures consisting of alternative buckling dimers are seen in the STM images and the intrinsic properties of the clean Si(100) becomes quite complex [32, 33]. Upon dosing atomic hydrogen on a clean Si(100) surface at $\sim 590$ K, the $\pi$-bond in a bare Si dimer is replaced by two strong Si–H bonds while the dimer structure remains intact, yielding an H:Si(100)-(2 $\times$ 1) surface composed of symmetric monohydride dimers (H–Si–Si–H) [29].

Like an atomic hydrogen, an OH radical attaches to a surface silicon dangling bond. Previous studies have shown that a H$_2$O molecule dissociates into two fragments, H and OH, on the Si(100) surface at a sample temperature above $\sim 130$ K [34–36]. If each of the two fragments terminate one dangling bond on two sides of one dimer, the product is referred to as the on-dimer configuration, i.e.

$$H_2O(g) + –Si–Si– \rightarrow H–Si–Si–OH + \sim 2.4 \text{ eV.}$$ (1)

where the energies in equation (1) and other equations hereafter are estimated from relevant bond energies in reference ([37]). If two fragments are chemisorbed onto two neighboring dangling bonds on two dimers in the same row, the outcome is called interdimer configuration: [20, 36, 38–40]

$$H_2O(g) + –Si–Si–(nd1) + –Si–Si–(nd2) \rightarrow –Si–Si–H(nd1) + –Si–Si–OH(nd2) \sim 2.1 \text{ eV,}$$ (2)

where g, nd1, and nd2 denote a gas species and the two neighboring dimers, respectively. The combination of the above two adsorption configurations for the H$_2$O saturated Si(100) surface (represented by (H, OH):Si(100)-(2 $\times$ 1)) is covered by monohydride dimers H–Si–Si–H, mixed H–Si–Si–OH dimers, and small percentage of mono-hydroxyl HO–Si–Si–OH dimers. The apparent height over an OH adsorption site (represented by Si–OH) in the filled-state STM images is slightly higher than that of an Si–H site by $\leq 0.3$ Å, depending on the tip condition and bias. Thus, an STM image for (H, OH):Si(100)-(2 $\times$ 1) resembles that of H:Si(100)-(2 $\times$ 1) [36].

2.1. H$_2$O adsorption on DBs surrounded by Si–H sites

Both sDB (H–Si–Si–) and pDB’s are generated upon brief annealing of the H:Si(100)-(2 $\times$ 1) surface at $\sim 700$ K due to H$_2$ desorption followed by adsorbate diffusion [41, 42]. In figure 1(a) two types of bright protrusions according to size are discernible. Symmetric oval-shaped bright protrusions each centered along a dimer row are larger and each is attributed to a pDB, where the $\pi$-bonded state has higher efficiency of electron transfer between the tip and the surface. Each of the relatively smaller bright protrusions occupies one side of a dimer and is attributed to a sDB. After a 4.5 L exposure of H$_2$O molecules, all protrusions in figure 1(a) are gone and the surface resembles closely that of H:Si(100)-(2 $\times$ 1), as shown in figure 1(b). This observation suggests that the dangling bonds on either sDB’s or pDB’s are each terminated by an H or OH radical dissociated from H$_2$O molecules at RT and form monohydride dimers H–Si–Si–H, mono-hydroxyl HO–Si–Si–OH dimers, or mixed H–Si–Si–OH dimers [36, 43]. Due to the small height difference between a Si–H and a Si–OH site, it is estimated that most pDB sites are transformed into H–Si–Si–OH dimers and that more sDBs are transformed to the Si–OH species than that to the Si–H ones. However, the exact ratio of the two products cannot be deduced from the images due to their small z-height differences.

The adsorption process for an H$_2$O molecule on a pDB surrounded by monohydride dimers in figures 1(a) and (b) can be interpreted as that of a clean Si(100) surface through the reaction equation (1). It is also exothermic and spontaneous. However, the transformation of an sDB to an H or OH adsorption site observed herein is unexpected and needs a new reaction mechanism. It demonstrates that upon encountering a sDB site surrounded by monohydride species, a H$_2$O molecule still dissociates spontaneously at RT with a small or no barrier. An abstractive adsorption provides a seemingly simple explanation and involves only the adsorption site as the second dissociative fragment B (OH or H) which bounces back into the...
vacuum simultaneously:

\[
\text{H}_2\text{O}(g) + \text{H–Si–Si–} + \rightarrow 0.6 \text{ eV}
\rightarrow \text{H–Si–Si–OH} + \text{H}(g);
\]

(3)

\[
\text{H}_2\text{O}(g) + \text{H–Si–Si–} + \rightarrow 1.9 \text{ eV}
\rightarrow \text{H–Si–Si–H} + \text{OH}(g).
\]

(4)

However, the negative adsorption energies in equations (3) and (4) prohibit the OH and H retraction to occur at RT.

Previous studies have observed the migration of H and OH on both clean and hydrogen passivated surfaces at moderate temperatures [35, 42, 44, 45]. Calculations have shown that the symmetric bridging position (SBP) is the transition state for the intradimer diffusion with an energy barrier in the range of 1.5 ± 0.5 eV [46, 47]:

\[
\text{H–Si–Si–F2} + (1.5 ± 0.5) \text{ eV} \rightarrow \text{H–Si–F2–Si–},
\]

(5)

where Si–F2–Si indicates a transition state for F2 (H or OH) at SBP.

By combining equations (1)–(5), one can find that the adsorption of the second fragment at SBP, either on the same dimer (equation (6)) or the neighboring dimer (equation (7)) is exothermic and can occur spontaneously at RT:

\[
\text{H}_2\text{O}(g) + \text{H–Si–} \rightarrow \text{H–Si–F2–Si–F1} \\
+ (0.9 ± 0.5) \text{ eV},
\]

(6)

\[
\text{H}_2\text{O}(g) + \text{H–Si–} + \text{H–Si–H} \\
\rightarrow \text{H–Si–F1} + \text{H–Si–F2–Si–H} \\
+ (0.9 ± 0.5) \text{ eV}.
\]

(7)

Equations (6) and (7) state that, upon attachment of F1 onto a sDB, the second fragment F2 is simultaneously adsorbed into the transition state configuration due to the lack of a neighboring dimer. F2 then diffuses across the mostly passivate surface to another chemisorption site. That is, the chemisorption proceeds stepwise and the two fragments form chemisorption bonds at different times and uncorrelated places on the surface. The two possible processes (equations (6) and (7)) can thus be referred as dissociative and asynchronous chemisorption.

To a certain extent, the dissociative and asynchronous chemisorption is similar to the ‘hot-atom’ type dissociative adsorption: the molecule approaching the surface dissociates upon forming new electronic bonds with the surfaces, but the two fragments are chemisorbed at a distance up to tens of SLCs. However, in dissociative and asynchronous chemisorption, one fragment is chemisorbed immediately on the sDB and the second radical can only form a weaker bond with the surface, forming a mobile transient similar to the physisorbed precursor state. The time and place for the final chemisorption of the second fragment depends on the surface density of the remaining active sites, not due to energy dissipation.

2.2. Toward the fully saturated surface for H\textsubscript{2}O on the Si(100) surface

Upon the exposure of 1.5 L H\textsubscript{2}O molecules, figure 2(a) shows that the dimer row structure remains intact; the dangling bonds on the clean Si(100) surface are about 95% terminated by the dissociated H or OH fragments, forming Si–H and Si–OH species, consistent with the literature [36, 43]. As mentioned in section 3.1, the Si–OH sites have a slightly higher apparent height than that of the Si–H sites and appear brighter in the occupied-state images. After an additional 1.5 L H\textsubscript{2}O exposure, some unreacted sDBs (indicated by the white arrows in figure 2(a)) are transformed into either Si–H or Si–OH sites. Similar transformations of sDB to Si–H/Si–OH species occur after additional 4.5 L H\textsubscript{2}O exposure, as figure 2(c) exhibits. The total unreacted dangling bonds, which are mostly sDBs, drops from ∼5.0% (figure 2(a)) to ∼4.1% (figure 2(b)), then to 2.8% (figure 2(c)), whose value is close to that (2.6%) in an earlier report [36]. Again, it can be estimated that more sDBs are transformed to the Si–OH species than Si–H, but the exact ratio of the two products cannot be deduced from the images.

The above-mentioned observation indicates that the dissociative and asynchronous chemisorption takes place not only on the H:Si(100)-(2 × 1) surface but also on (H, OH):Si(100)-(2 × 1). Notably, subtle differences exist between the two surfaces: the remaining sDBs/pDBs can be completely terminated on the H:Si(100)-(2 × 1) surface (figure 1(b)), but about 0.02 ML sDBs remain upon H\textsubscript{2}O saturation exposure on the (H, OH):Si(100)-(2 × 1) surface at RT. Also, the reaction probability is significantly lower on (H, OH):Si(100)-(2 × 1). These differences are possibly due to the existence of the monohydroxyl HO–Si–Si–OH dimers and mixed H–Si–Si–OH dimers. The OH adsorbates can effectively hinder the insertion of a radical F2 onto the SBP due to its steric and electronic configuration.

2.3. H\textsubscript{2}O adsorption on DBs surrounded by Cl adsorbates

After the exposure of 4000 μA·s Cl\textsubscript{2} at room temperature, about 96% of dangling bonds are saturated by Cl, forming mostly the monochloride dimer (Cl–Si–Si–Cl). The remaining ∼4% bright protrusions are presumably thermodynamically stable pDB’s as each set of bright protrusion is imaged as bright ‘triplet’ feature; each set consists three neighboring dimers in the same row as shown in figure 3(a) [48, 49]. However, unlike the symmetric apparent height of a pDB created by thermal desorption, the two bright monochloride dimers on both sides of the centered pDB often appear asymmetric, i.e. one side of the monochloride monohydride dimer is brighter than the other. Thus, an asymmetric triplet feature might be an sDB as well, which is a characteristic resulting from the competing kinetic processes [24].

After the exposure of 12.0 L H\textsubscript{2}O vapor, all bright features disappear as shown in figure 3(b). By comparing figures 3(a) and (b), the atomic model is presented in figure 3(c). A previous report at similar imaging condition shows that the apparent height of a Si–H site is lower (darker) than that of a Si–Cl site [6]. Config. K corresponds to one dimer, in which one side is slightly darker than the other. It is assigned to an H–Si–Si–OH
Figure 2. 154 × 154 Å² filled state STM images of the clean Si(100)-(2 × 1) surface after H₂O exposure of (a) 1.5, (b) 3.0, and (c) 7.5 L at RT. A few bright protrusions occupying a dimer are pDB (labeled P). The rest of bright spots occupying one side of a dimer are single dangling bonds (S). The green arrows in (a) and (b) point to reacted sDB that disappear in (b) and (c), respectively.

Figure 3. 154 × 106 Å² filled state STM images of a nominal Cl:Si(100)-(2 × 1) surface after nearly saturated Cl₂ exposure (a) before and (b) after saturation (12 L) exposure to H₂O. (c) Schematics of the adsorption configurations for the rectangular area enclosed in (a) and (b). The yellow, green, red, and white circles represent a dangling bond, chlorine (before adsorption), oxygen, and hydrogen atoms, respectively.

species following the on-dimer adsorption (equation (1)). Config. I in figure 3(c) corresponds to a chemisorption site that is dark on one side; it is assigned to a Cl–Si–Si–H dimer, indicating that the initial state of a site I is likely a sDB before water exposure. Equations (6) and (7) can be rewritten for the Cl:Si(100)-(2 × 1) surface as follows:
we took an alternative approach. After a small amount of H$_2$O exposure, the unreacted dangling bonds are terminated by Cl atoms to prevent further adsorption of any residue gases. The initial adsorption configurations are thus kept intact, although some H adsorbates might be abstracted by Cl radical during the Cl$_2$ exposure [6]. As figure 4 displays, about 30% of dark depressions are clustered adsorption sites, in consistence with a previous report [35]. The formation of 2D adsorbate islands generally indicates the notable diffusivity of adsorbates before chemisorption and the adsorption processes is precursor mediated. The rest of the dark sites can be identified as Si–H adsorption species, Si–OH adsorption species, inter-dimer configuration C, and on-dimer configuration U. Their relative population densities, $n_{\text{H}}, n_{\text{OH}}, n_{\text{C}}$ and $n_{\text{U}}$, are about 17%, 15%, 27%, and 41%, respectively. The processes leading to isolated Si–H and Si–OH species can be complex and are not discussed here. The ratios of $n_{\text{C}}$ to $n_{\text{U}}$ is about 0.7, much smaller than that (5.0) in reference [39]. Even though the abstraction reactions can alter the relative densities, the abstraction probabilities are likely similar for the U and C configurations, leaving $n_{\text{C}}$/ $n_{\text{U}}$ unaltered. The values and images obtained herein thus provide a useful reference for further study. I$_2$ and Br$_2$ molecules are less reactive than Cl$_2$. The future use of I$_2$ and Br$_2$ for passivation might be to reduce the abstraction reaction and, therefore, preserve the initial H$_2$O adsorption configurations.

3. Conclusions

Traditional studies of molecular chemisorption are performed on clean surfaces, which have repetitive arrays of reactive sites. At low coverage, the reactants for a specific chemisorption reaction are thus indeterminate and often assumed afterward to be the surface atoms that form bonds with adsorption fragments. Herein, the reactive surface sites are first passivated with univalent hydrogen, hydroxyl, and chlorine radical and only isolated and paired reactive sites remain for the exposure of the gas molecules. On these masked Si(100) surfaces, the reactants are thus well defined prior to chemisorption. Atomic resolved STM is then employed to examine the reactants and products before and after the chemisorption of H$_2$O molecules.

In all three cases, each of the remaining sDB’s chemisorb either of the two dissociation fragments, the H or OH radical, to form a surface Si–H and Si–OH species. According to thermodynamics calculations, the second fragment should also be adsorbed on the surface, but it is not found in the vicinity of the passivated sDB. These results cannot be understood by the exoergic dissociative chemisorption mechanism, in which two immediately neighboring dangling bonds are needed to form two new bonds with the two fragments. The ablative adsorption, in which the second fragment is bound back to the vacuum on site, is also not allowed due to the negative adsorption energy.

In the newly proposed ‘dissociative and asynchronous chemisorption’ the molecule breaks apart into two fragments upon approaching an active site (sDB in the case of Si(100)), on which only fragment is chemisorbed. However, the other fragment reacts with an immediately neighboring surface site to form a meta-stable complex, then diffuses across the
surface and eventually relaxes to a stable chemisorbed configuration. Unlike the conventional scenario for the dissociative chemisorption, the two fragments become chemisorbed at different times and uncorrelated places. This adsorption mechanism not only provides a logical explanation for our experimental findings at near saturation coverage, but might occur also at low coverages in principle. It also sheds light on the puzzle of how some molecules requiring two active bonds for dissociatively chemisorption on a surface can still saturate all active surface sites.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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