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Mediation of chain reactions by propagating radicals during halogenation of H-masked Si(100): Implications for atomic-scale lithography and processing

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Scanning tunneling microscopy reveals a free radical-induced surface chain reaction in the chlorination of nanoscale patterns on an otherwise H-passivated (masked) Si(100). While scanning probe methods can be used to pattern active surface regions with single-bond precision, follow-up selective chemical vapor deposition with polyatomic molecules can produce various filling characteristics. On active surface regions, molecular Cl₂ undergoes an atom abstraction reaction in which a Si dangling bond abstracts one atom of the incident Cl₂ molecule while the complementary Cl atom is scattered away from the initial abstraction site either back into the vacuum or to be captured by a second dangling bond and adsorbed there, or to react with a nearby adsorbed H atom to form volatile HCl. In contrast, I₂ undergoes only dissociative adsorption on two immediately neighboring dangling bonds, whereby two I–Si bonds are formed simultaneously upon cleavage of the I₂ bond. The different chemisorption processes of the two model diatomic molecular gases place intrinsic limitations on atomic-scale lithography and processing: Adsorption of Cl₂ results in spillage over the prepatterned regions of active bonds. In contrast, adsorption of I₂ is a pair process and results in under-filling. © 2009 American Institute of Physics. [DOI: 10.1063/1.3122987]

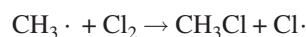
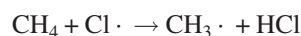
I. INTRODUCTION

Nanoscale device fabrication using scanning probe methods has attracted much interest in recent years.^{1–4} A fundamental requirement for precision fabrication is patterning and chemical processing at the atomic level. While lithographic patterning using a scanning tip can be performed one surface bond at a time in a predetermined manner,^{5,6} selective chemical processing based on exposure to molecular gases is by nature a stochastic process. Faithful retention of the lithographic pattern definition at the single-bond level can be difficult because of molecular geometrical constraints, multiple reaction pathways, and chain reactions.^{2,7–11} By using scanning tunneling microscopy (STM), this study explores these issues as they relate to two commonly employed procedures for Si(100) surface processing: (1) surface passivation with H as a resist and (2) selective gas-source molecular beam epitaxy on patterned nanoscale regions of bare Si(100). I₂ and Cl₂ are used as the model source gases in this present study; both of these molecules readily undergo scission to react with a bare Si(100) surface.^{12–14} While, ideally, areas of halogenation in each case would be fully defined by the bare regions with single-bond precision, it in fact is not. As will be describe below, some geometric arrangements of

patterned reactive bonds may limit the adsorption of diatomic molecules and some may trigger a chain of events that lead to additional adsorption beyond the bare regions. Since most gases that are used for surface treatment are polyatomic, geometrically constrained reactions are a common concern associated with selective-region processing.

Moreover, our experiments using I₂ and Cl₂ reveal unexpected and interesting differences between the two cases, which can be attributed to the significant differences between the bond dissociation energies and chemical reactivities of the two gases. While I₂ adsorption results in under-filling of the patterned regions, Cl₂ adsorption results in spillage, an ill-defined boundary, and a slight resist admixture. A detailed analysis of the results over various pattern configurations reveals the underlying reasons for the differences: I₂ adsorption is a simple pair process, while Cl₂ adsorption is an abstractive process that is followed by chain reactions that involve propagating hot Cl atoms (radicals).¹⁵

Organic gas-phase chain reactions that are mediated by propagating radicals are well known. A prototypical example is the halogenation of methane to form methyl chloride,



A Cl radical (Cl·) participates in the reaction and is consumed, but another is generated at the end of the cycle, allowing the process to be repeated. In contrast, I₂ does not

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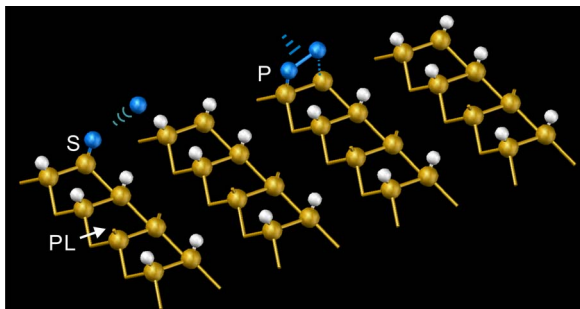


FIG. 1. (Color online) Si(100) surface that is mostly terminated by H (white). A diatomic molecule is shown in the process of being adsorbed onto a dimer dangling bond pair (P). Also shown is an isolated single dangling bond (S) that is involved in an abstractive adsorption process that generates a free radical. A linear array of dimer dangling bonds (PL) is indicated.

normally participate in such free-radical processes because the overall reaction is endothermic. These gas-phase results provide an interesting comparison to the results of the present study of surface chain reactions. An important difference is that surface chain reactions are topologically confined within a two-dimensional lattice, and STM can be employed for direct viewing of the reaction sites. The present study is the first to present experimental evidence of such surface chain reactions that involve hot adatoms, or free radicals. This study contrasts with an earlier work on a radical clock chain reaction that involve the adsorption of organic molecules with a C–C π -bond, in which the polyatomic adsorbate itself is the radical; such reactions can lead to self-directed growth that is analogous to polymeric synthesis.

II. EXPERIMENTAL DETAILS

In the experiment, clean Si(100)-(2 \times 1) surfaces were prepared by direct Joule heating of the substrate to \sim 1400 K. Subsequently, the chamber was backfilled with H₂ gas to 2×10^{-7} torr. A tungsten filament positioned in front of the sample, heated to 1800 K, was used to generate atomic H. The Si surfaces after saturation exposure to atomic H were mostly terminated by monohydrides, and each Si dimer dangling bond (DB) of the clean starting Si surface was terminated by a H atom. Also present on the surfaces was a small admixture of dihydrides, where the original Si–Si dimer bonds were broken to allow two H atoms to terminate each Si surface atom.^{16,17} Various nanoscale patterns of bare Si(100) were then formed by either mild thermal desorption at 650–720 K for 40–250 s or programmed STM tip-induced desorption of the H.⁵ Paired dangling bonds are most commonly observed after brief annealing of the monohydride surface at around 620–700 K^{17,18} and paired and unpaired DBs coexist in a mixture after annealing is prolonged.^{19,20} In tunneling-current induced hydrogen desorption, the tips were typically biased to a voltage of around -4 V and a tunneling current of 3 to 4 nA was used.

Vapors of I₂ and Cl₂ were introduced into the vacuum chamber through a precision leak valve and a tube facing the sample while tips were retracted for hundreds of nanometers. Figure 1 schematically depicts the dimerized surface atomic

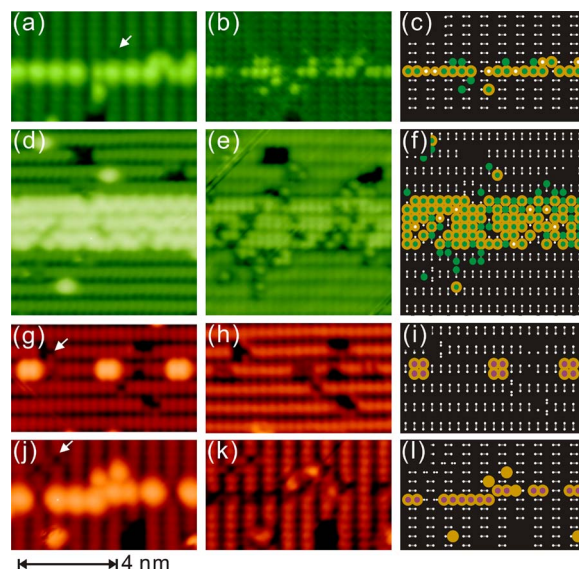


FIG. 2. (Color online) (a) STM image of H-terminated Si(100) surface with selected bonds reactivated by STM lithography. The arrow points to a dihydride dimer, which appears to have a dark center with bright sides (Ref. 16). (b) The same area after saturation exposure to Cl₂. (c) Schematic diagram of the area: Light gray (large yellow) circles indicate initial dangle bonds; dark gray (green) circles indicate adsorbed Cl, and small white circles indicate re-adsorbed H. (d)–(f) are similar to (a)–(c). (g)–(i) and (j)–(l) present similar results for I₂ adsorption. The apparent height for I-terminated sites often varies with tip conditions. Dark gray (purple) circles in (i) and (l) indicate I termination. Sample bias voltages V_s were approximately -2.0 V (a, d, e, f, g) and $+1.8$ V (b); tunneling current $I_t=0.2$ nA; $T=300$ K. The distance between two dimer rows is 7.68 Å. In STM lithography hydrogen was desorbed by electron injection at a sample bias $V_s=4.0$ V (a, d, j) and $V_s=3.8$ V (g) and a current $I_t=4.0$ nA. (a, j) The tip speed during STM desorption was 100 nm/s.

structure. A single dangling bond (S), a dangling bond pair (P), and a linear array of dangling bond pairs (PL) are shown. For clarity in the ensuing discussion, the STM images that relate to Cl₂ and I₂ adsorption are shaded in green and red, respectively.

III. RESULTS AND DISCUSSION

Figure 2 presents few selected results. The motion of the tip was programmed in a line mode or an area mode to cause hydrogen to be desorbed by tunneling electrons. Figure 2(a) shows an initial pattern that includes a linear array of dangling bond pairs, each of which appears as an oval-shaped bright site that is centered along a row of dimers, and a few S sites, each of which appears as a smaller bright site that is biased on one side of a dimer. After exposure to Cl₂, most of the dangling bond sites and some of the hydrogen sites become well-resolved less-bright spots, as seen in Fig. 2(b). These bright features are chlorine-terminated sites.²¹ None of the initial dangling bonds in Fig. 2(a), isolated or not, survives. Figure 2(c) schematically depicts the events; the large yellow circles indicate initial dangling bonds, and the small green circles indicate the adsorbed Cl after exposure. Most of the initial dangling bonds are now terminated by Cl, but a few become terminated by H (indicated by small white circles). In addition, several Cl adatoms are found at nearby sites, which were initially terminated by H. These extra Cl adatoms must be involved in reactions over the initially bare

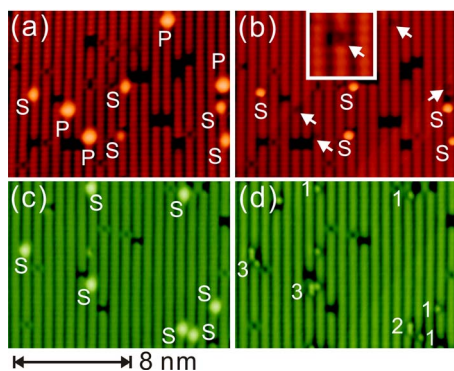


FIG. 3. (Color online) (a, c) STM images (size $154 \text{ \AA} \times 120 \text{ \AA}$, taken with a sample bias of -1.9 V , $I_t=0.2 \text{ nA}$, $T=300 \text{ K}$) of a $\text{Si}(100)\text{-(}2 \times 1\text{):H}$ after annealing at $\sim 700 \text{ K}$ for 120 s. Dangling bond pairs (P) and isolated single dangling bonds (S) are indicated. (b) and (d) are corresponding images after saturation exposure to I_2 and Cl_2 , respectively. Arrows in (b) point to monoiodide dimers. Inset in (b) shows enlargement of an area that contains a monoiodide dimer. Numbers in (d) are the numbers of chlorine atoms around each original S site.

$\text{Si}(100)$ region, as they are all within a distance of a few unit cells from one of the initial dangling bonds. The results shown in Figs. 2(d)–2(f) reinforce the above observation. A band of densely packed dangling bonds [centered bright areas in Fig. 2(d)], following exposure to Cl_2 , become mostly Cl-terminated, but a few sites become H-terminated. None of the dangling bonds survives and extra Cl adatoms are present in nearby areas. This spillage of Cl into areas that are terminated by H yields an ill-defined boundary between the H- and Cl-terminated areas.

In Fig. 2(g), three bare regions, each with two neighboring P sites (and therefore a total of four dangling bonds), were created by tip-induced desorption on the initial surface; these appear as bright features. Figure 2(h) shows the same area after saturation exposure to I_2 . The bright features become dark, corresponding to I termination [indicated in Fig. 2(i) by small red circles]. No reaction was detected over the hydrogen-terminated regions, indicating that the H resist is robust against I_2 exposure. Figure 2(j) shows an array of P sites and a few S sites. After saturation exposure to I_2 , all P sites become dark, while the S sites remain bright. The results, summarized in Fig. 2(l), show conclusively that I_2 adsorption is a pair process. A consequence of this pair mechanism is that bare nanoscale areas of $\text{Si}(100)$ are under-filled after I_2 exposure if not all of the initial dangling bonds are in pairs.

Figure 3 displays the results obtained over a larger area, in which a number of isolated S and P sites were created by mild thermal annealing at $\sim 700 \text{ K}$ for two minutes. The S and P sites can be easily distinguished (by viewing magnified images), as the P sites are much brighter and symmetric about a dimer row, while the S sites are dimmer and biased on one side of the dimer row. After I_2 adsorption, the P sites become terminated by I, but the S sites do not, as seen in Fig. 3(b). These results are consistent with the pair adsorption mechanism mentioned above. In Cl_2 adsorption, all dangling bonds become terminated by Cl, and additional Cl adatoms are found in nearby areas in many of the cases examined (the total number of Cl adatoms is indicated for each case in the

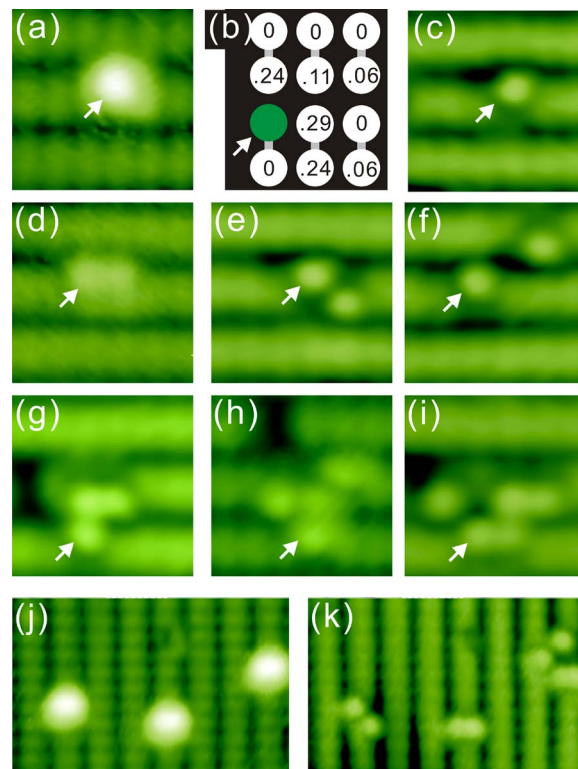


FIG. 4. (Color online) (a) S site on $\text{Si}(100)\text{-(}2 \times 1\text{):H}$ surface after 40 s of H_2 desorption at 720 K. (b) Probabilities of finding a second Cl atom at sites near the original S site (indicated by a green circle) obtained from 60 adsorption events on S sites. (c)–(i) Results of exposure to Cl_2 for a S site, showing 1, 2, 2, 2, 3, 4, and 5 Cl adatoms, respectively. The arrow points to the original S site in each case. (j) Three P sites on a $\text{Si}(100)\text{-(}2 \times 1\text{):H}$ surface after 120 s of H_2 desorption at 670 K. (k) The same area after Cl_2 exposure. Image sizes: $23 \text{ \AA} \times 23 \text{ \AA}$ (a, c–i), $63 \text{ \AA} \times 38 \text{ \AA}$ for (j, k). $I_t = 0.2 \text{ nA}$; $T = 300 \text{ K}$.

figure). These results are consistent with the observations described above and provide further evidence that large areas that are fully covered by the H resist are robust against both I_2 and Cl_2 attack. The diffuse boundary and extra Cl atoms must be associated with correlated reactions.

Figure 4 shows the details of the chain reactions. Figure 4(a) is a typical image of a S site. The seven pictures in Figs. 4(c)–4(i) are selected results obtained after exposure to Cl_2 ; an arrow indicates the location of the original isolated dangling bond in each case. For these seven cases, the final Cl adatom counts are 1, 2, 2, 2, 3, 4, and 5, respectively. The three cases with two Cl adatoms have different final geometries. An analysis of a large number of such events yields the probabilities of 55% for simple Cl-termination, 28% for termination with an additional Cl, and 17% for termination with two or more additional Cl. When Cl_2 is adsorbed on a single dangling bond, an abstract reaction takes place. Similar abstract reactions on the clean $\text{Si}(100)$ surface as a result of highly exothermic molecule-surface reactions have been identified.^{22,23} Hot atoms upon O_2 dissociation have also been observed to undergo a transient motion over a large distance.¹⁵ Similarly, the Cl radical that is left over from the reaction must be responsible for the formation of additional Cl termination in nearby areas through a chain reaction. An analysis of cases that involve just two Cl adatoms in the final state yields the statistics that are shown in Fig. 4(b). The

numbers in Fig. 4(b) are probabilities of finding a second Cl atom at sites near the original S site. Interestingly, the second Cl termination avoids the site neighboring the original dangling bond on the same dimer unit. The distance of the second Cl atom from the original dangling bond can be up to the third of the distance to the nearest neighbor [in the bottom right-hand corner in Fig. 4(b)]; this result is consistent with the propagation of a free Cl radical as an intermediate product in a multistep process.

Figure 4(j) shows an area that initially has three P sites; the image in Fig. 4(k) shows the results after exposure to Cl₂. An examination of many such pictures reveals that, in some cases, the P sites become simply terminated by a pair of Cl, perhaps because of either a simple pair adsorption process or two sequential abstractive reactions that involve one dangling bond at a time. However, in most cases, the results are more complicated, as discussed above, indicative of an abstractive process followed by chain reactions. Thus, simple pair adsorption of Cl₂ is possible, but it is a minor reaction channel.

The seemingly unusual results of Cl₂ adsorption are similar to those of the gas-phase chain reactions mentioned in the introduction. These reactions are consistent with the bond energetics on Si surfaces. The relevant bond energies are 2.4 eV for Cl₂, 3.8 eV for Si–Cl, 3.2 eV for Si–H, and 4.3 eV for H–Cl.²⁴ A Cl₂ molecule that impinges upon an isolated Si dangling bond can dissociate, based on energy considerations (2.4 eV < 3.8 eV), resulting in the bonding of a Cl atom to the Si. The remaining Cl radical can desorb into the vacuum, or it may propagate on the surface, bind with a H in the nearby masked area, and desorb as a HCl molecule; this resist-stripping process is again energetically favorable (4.3 eV > 3.2 eV). Thus, the result of the abstractive reaction of Cl₂ at a S site is either Cl-termination alone or Cl-termination plus the creation of a new Si dangling bond nearby. The latter can react with another incoming Cl₂ molecule, and the process can propagate for a few iterations, producing multiple Cl adatoms in the nearby area, as observed experimentally. The final reaction channel involves the formation of the HCl molecule in the intermediate step that does not desorb into vacuum but rebonds onto the bare surface (3.8 eV + 3.2 eV > 4.3 eV), resulting in a H-terminated site and a Cl-terminated site, if and only if dangling bonds are nearby to accommodate the reaction. This process is suppressed in small bare regions because of geometrical constraints, but effectively explains the finding of small admixtures of H-terminated sites in cases that involve larger bare regions, as presented in Figs. 2(c) and 2(f).

The relevant bond energies for I₂ adsorption are 1.5 eV for I₂, 2.3 eV for Si–I, 3.2 eV for Si–H, and 3.1 eV for H–I.²⁴ The energetics for the pair adsorption of an I₂ molecule are strongly favorable (2 × 2.3 eV ≫ 1.5 eV), and this process is the dominant observed process. While the dissociation of I₂ and its bonding to a single Si dangling bond are energetically permissible, (1.5 eV < 2.3 eV), the energy released in the abstractive reaction is much less than that in the corresponding Cl₂ case. This fact may suggest reduced reaction probability, as observed experimentally, but the activation barriers in the two cases may also differ. As noted in the

introduction, I₂ does not participate in free radical halogenation in organic chemistry because the overall reaction is thermodynamically unfavorable. In the present case of reactions on the Si(100) surface, a hot I atom cannot bind to a nearby H and desorb as a HI molecule based on energy considerations (3.1 eV < 3.2 eV). Thus, no cascading reactions are expected, and the observed lack of chain reactions for I₂ adsorption is consistent with the bond energetics. While energetics determine the available reaction channels, the reaction rates are determined by additional factors, such as the reaction barriers, which are not easy to predict without a detailed calculation.

IV. CONCLUSIONS

In summary, H on Si(100) is a robust resist against molecular Cl₂ and I₂ attack, and a straightforward processing pathway for precision adsorption on predefined bare regions is intuitively expected. However, the results are complicated and markedly different for the two model gases. Adsorption of I₂ generally results in under-filling because it is dominated by a pair process. Adsorption of Cl₂ is generally characterized by spillage and an ill-defined boundary. When the initial bare region is large, a small admixture of adsorbed H is also observed. The results can be understood in terms of the energetics of a reaction that involves chain propagation: an active surface bond is continually regenerated by the diffusion of free Cl radicals during Cl₂ abstractive adsorption. While the H resist is robust against Cl₂ attack, it is not robust against the Cl radicals attack. These detailed atomic processes are revealed by *in situ* observations of the reaction results for various active site patterns.

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