

## Surface Science Letters

## Site selective atomic chlorine adsorption on the Si(1 1 1)7×7 surface

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**Abstract**

The spontaneous dissociation of trichloroethylene molecules on the Si(1 1 1)7 × 7 surface was investigated using STM. Chlorine atoms were identified by using voltage dependent imaging and by observing voltage dependent tip-induced diffusion. At low coverage, we identify one chlorine that dissociates and binds to an adatom, leaving a nearby chlorovinyl group as the other product bound to the surface. Chlorine atoms show strong site selectivity for corner adatoms and some preference for the faulted half of the unit cell. This result differs significantly from previous studies of chlorine on this surface and a site-selective mobile precursor model is used to explain this discrepancy. The observed site-selectivity is consistent with the high electronegativity value for chlorine.

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Understanding the adsorption of atoms on very clean surfaces is one of the basic problems in surface science and it is reasonable to assume that differences in electronic structure among dangling bonds could result in site selectivity for adsorption. STM studies of adsorption on the Si(1 1 1)7 × 7 surface are ideal for testing this assumption because STM has high spatial resolution and because the well-understood surface has dangling bonds with widely-varying electronic structure. In particular, because of charge transfer processes, rest atom dangling bonds contain approximately 1.5–2.0 electrons, while corner adatom dangling bonds contain approximately 0.75 electrons and center adatoms contain approximately 0.5 electrons. There is also charge transfer from the unfaulted to the faulted half of the unit cell, adding even more richness to this system. A reasonable hypothesis is that, because of their large electronegativity, halogen atoms would have a preference for binding to dangling bonds with a local charge value near 1.0 electrons and therefore might chemisorb with higher frequency on top of the corner adatoms as compared to center adatoms. In support of this hypothesis, a

firm theoretical foundation has been established through the density functional based considerations of the Joannopoulos group [1]. Experiments, however, have not as yet provided a clear picture. A previous experimental study showed no preference for atomic chlorine for either corner or center adatoms [2]. Studies of molecular halogens showed a preference for center adatoms [3]. STM studies have shown site preferences for other molecules, O<sub>2</sub> [4,5], H<sub>2</sub>O [4], NH<sub>3</sub> [6] and chlorobenzene [7], for example, but until now no study has shown a simple result regarding the site preference of atoms. In this Letter, we present STM results showing that when the Si(1 1 1)7 × 7 surface is dosed with atomic chlorine coming from a dissociation reaction, there is a strong site selectivity towards adatoms with greater local charge.

Our studies were performed using a homebuilt STM operating at room temperature in a UHV chamber with base pressure <math>3 \times 10^{-11}</math> Torr. Reagent grade (Merck) trichloroethylene (99.5% purity) was placed in a quartz glass tube connected to a stainless steel gas line and was repeatedly degassed by freeze-pump-thaw cycles. The clean silicon sample was exposed by passing trichloroethylene (TCE) vapour into the main chamber from the gas line via a variable leak valve.

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The Si(111)7 × 7 surface was exposed to chlorine atoms through dissociation of a parent TCE molecule. Previous EELS and TDS studies have shown that TCE on Si(111)7 × 7 spontaneously dissociates at room temperature by losing one chlorine atom to the surface [8].

For the STM technique, identifying the products of dissociative adsorption generally poses a challenging problem. Fortunately in this case we are able to identify the chlorine atoms by making use of the significant body of work that has been reported concerning the chemisorption of halogens to silicon. Two facts are generally well known about STM of halogens on the Si(111) and (100) surfaces: one is a pronounced variability in topographs, with applied voltage, of the brightness of adsorbed halogens [9–15]. In particular, on Si(111)7 × 7, below (above) a sample voltage of ~1.5 V chlorine atoms appear dim (bright) compared to areas of clean silicon [14,15]. This general phenomenon, which involves an anti-bonding  $\sigma^*$  state, is now so well understood that Cl, Br and I can be distinguished on the Si(100) surface [13]. The other important fact is that tunneling electrons from the STM can induce diffusion of adsorbed halogen atoms [9,12,15–17]. Moreover, the tip-induced diffusion of atomic chlorine on Si(111)7 × 7 can be achieved even when the tip is not right above the chlorine atom, i.e., the effect can extend out as far as 30 nm or so from the affected atom. This type of tip-induced desorption is unusual. There are many reported cases of highly-localized tip-induced diffusion/desorption/dissociation (see Refs. [18–21] for a few) but only one other example of this non-localized diffusion is known [22]. The tip-induced diffusion is highly bias-dependent. Below certain threshold values, both occupied and unoccupied state imaging of Cl on silicon can be accomplished in a benign manner. Because of this established knowledge we feel confident in using the voltage-dependent imaging in conjunction with tip-induced diffusion studies to conclusively identify chlorine atoms from the TCE dissociation.

In Fig. 1(a–c) we present empty state STM topographs showing the dissociation products of various TCE molecules on the Si(111)7 × 7 surface. Our procedure, immediately after dosing, always involves imaging at bias values around +1.5 V. With the bias value in this range we are confident that the tip is not inducing any kind of chemical dissociation. We found when imaging in the range of about +1.4–+2.1 V sample bias, that the products of the spontaneous dissociation always consisted of bright features (substantially brighter than unreacted adatoms) and dark features that resemble missing adatoms. In Fig. 1(a), taken at +2.0 V sample bias, the bright features are very prominent, with an apparent height of 1.2 Å greater than the unreacted adatoms. In Fig. 1(b), taken at +1.7 V sample bias after a very low dose of TCE, a single bright feature is prominent, with an apparent height 0.9 Å greater than the unreacted adatoms. In the topograph in Fig. 1(c), taken at +1.0 V, there are no features with apparent height greater than the adatoms, i.e., features that are bright at >+1.4 V are imaged at +1.0 V with apparent

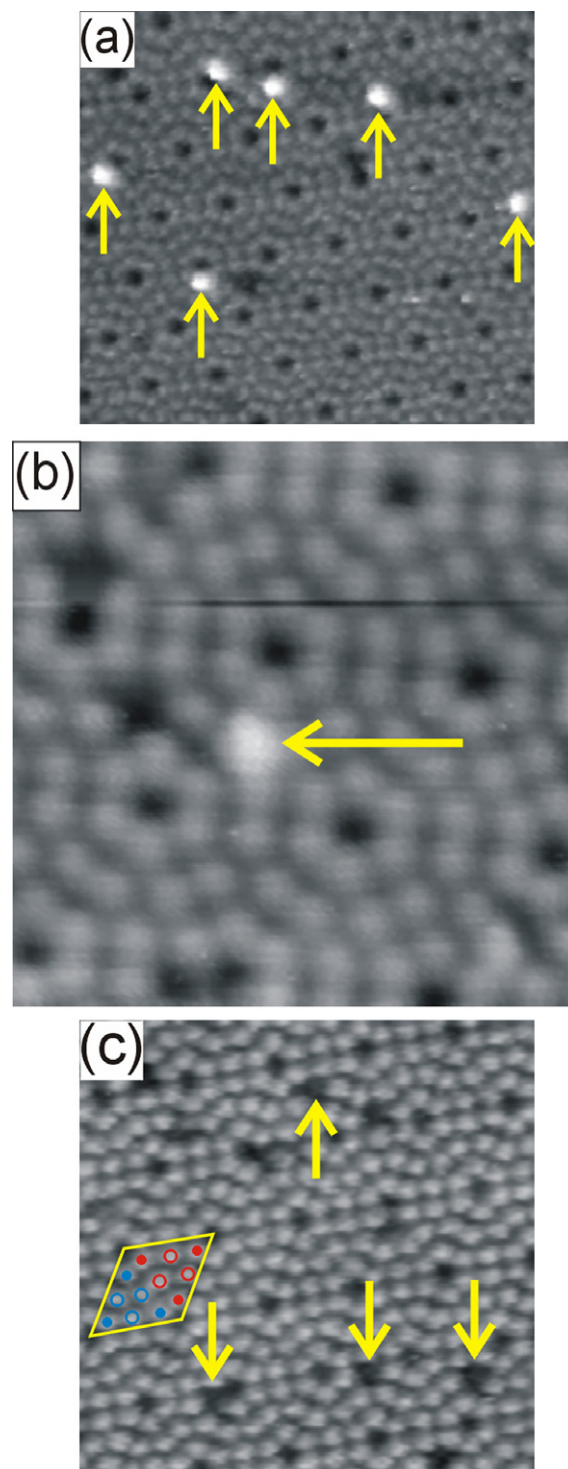


Fig. 1. Empty state STM topographs of TCE dosed Si(111)7 × 7 surface at (a) +2.0 V, (b) +1.7 V and (c) +1.0 V sample bias. Chemisorbed chlorine atoms, indicated with arrows, appear as (a, b) bright and (c) grey features on top of adatoms depending on the applied bias. Scanning was performed at 100 pA tunnel current. One unit cell is outlined in yellow. Filled (open) circles label corner (middle) adatoms and red (blue) markers denote (un)faulted adatoms. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

heights slightly lower than unreacted adatoms, i.e., as grey features.

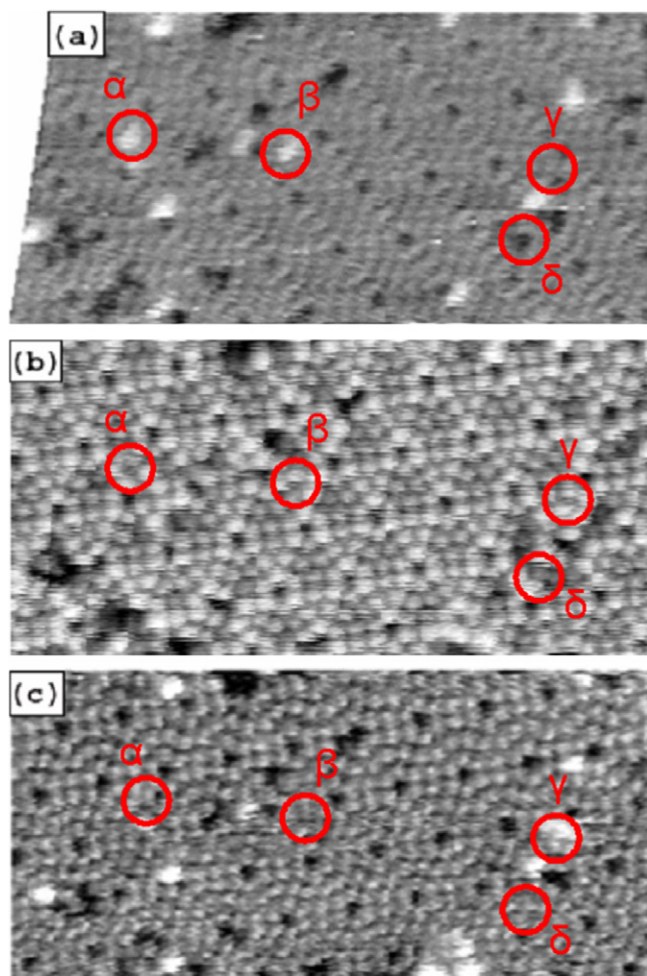


Fig. 2. Topographs over the same area taken at (a) +1.5 V, (b)  $-2.0$  V and (c) +1.5 V. Image (b) was taken after (a) and before (c). Comparison of (a) and (c) show that a significant number of chlorine diffusion events took place during the  $-2.0$  V treatment. In the occupied states topograph (c), the faulted half of the unit cell is brighter than the unfaulted half. Scanning was performed at tunnel currents of 120 pA for (a) and (b), and 200 pA for (c). Drift correction (and cropping) applied to these images gave rise to the slanted left side of (a).

Tip-induced diffusion results are displayed in Fig. 2(a–c). In Fig. 2(a) and (c) the topographs were taken at +1.5 V at which the imaging is generally extremely stable as far as adsorbate diffusion is concerned. At a sample bias value of  $-2.0$  V, the scanning of the STM tip in the vicinity of the chlorines causes them to diffuse to either nearby adatoms or to desorb from the surface. The rings labeled  $\alpha$  all encircle the same adatom. In Fig. 2(a) this adatom has a chlorine atom bound to it, while in (c) it is free of the chlorine atom. The rings labeled  $\beta$  also display a similar phenomenon while the  $\gamma$  series of rings encircle an adatom that was initially unreacted and finished in a chlorine bound state. Our observations are consistent with the reported threshold voltage of about  $-1.5$  V with a peak at  $-2.0$  V of tip-induced diffusion of atomic chlorine [16]. During the scans at  $-2.0$  V we rarely saw the telltale sign of extremely localized tip-induced desorption/diffusion,

i.e., truncation of the diffusing feature during the topography scan [21]. This observation is consistent with the rare form of diffusion reported in Refs. [16,17]. We have also observed very active tip-induced diffusion at bias values of +2.4 V and +2.7 V and we have even some diffusion at +2.1 V. These observations are also consistent with reports of an electron injection effect, with a similar bias threshold, on atomic chlorine [15,17].

As the bright features in Fig. 1 look like chlorine atoms and move like chlorine atoms, the clear interpretation of our results is to identify, with a high level of confidence, these bright features as individual chlorine atoms bonded on top of adatoms. With these pieces of evidence we also confirm the previous reports [8] that the TCE molecule dissociates by losing a chlorine atom. It appears that the rest of the molecule, a dichlorovinyl radical, stays intact and attaches to a nearby binding site. This chlorovinyl group would then be responsible for the dark features in the topographs of Fig. 1. This conclusion is supported by our observations of roughly the same number of bright features as dark ones at bias values in the +1.5–+2.0 V range. Leung's group has reported that one chlorine dissociates from the TCE molecule and that the C–C double bond remains intact after binding into one of two possible, and as yet indistinguishable, adspecies; 1,2 and 2,2 dichlorovinyl [8]. Evidence for tip-induced desorption of these chlorovinyl groups at  $-2.0$  V is denoted by the set of  $\delta$  rings of Fig. 2 [23].

The dissociative adsorption of TCE results in a relatively easy way to dose the Si(1 1 1) $7 \times 7$  surface with atomic chlorine. We find that the rest of the TCE parent molecule chemisorbs on average a distance of about 30 Å from the chlorine atoms, well enough away so that no residual interaction is left with the parent. We stress that this is not an STM diffusion-induced result, i.e., this separation of products occurs very soon after the TCE molecule reaches the surface. At very low dosing levels we can often identify with some confidence the actual product pairs from the dissociation of a single TCE molecule. For example, in Fig. 1(b), the dark feature on the next-nearest adatom to the Cl marked with an arrow is most likely the corresponding chlorovinyl group. At low TCE doses, the result of this dissociative chemistry is a surface with adsorbed atomic chlorine suitable for basic surface studies.

After proper identification of the chlorine atoms, addressing the basic hypothesis of this Letter was a straightforward matter of counting chlorine atoms in the STM images taken at sample bias values in the +1.7–+2.0 V range. This bias range lies well below the threshold for tip-induced diffusion of chlorine, ensuring that the accumulated statistics do not incorporate any tip-induced effects. We distinguished between chlorines attached to center or corner adatoms and whether they were located in the faulted or unfaulted halves of the unit cell. The results for three hundred counts are displayed in Table 1. The clear result is a favouring of corner adatoms: we found that overall, chlorines chemisorbed to corner adatoms  $2.9 \pm 0.3$

Table 1  
Binding preference for chlorine atoms after dissociation from TCE molecules

| Adatom binding site | Chemisorbed chlorine atom fraction (%) |
|---------------------|--|
| Faulted corner      | 42 ± 3                                 |
| Unfaulted corner    | 32 ± 2                                 |
| Faulted center      | 15 ± 2                                 |
| Unfaulted center    | 10 ± 1                                 |

The counting statistics were extracted from topographs measured after TCE exposure levels near 1.1 L, the same level at which the topographs of Figs. 1(a,c) and 2 were measured. The pressure readings from our ionization gauge were not corrected for the ionization factor of TCE molecules.

times more frequently than to center adatoms. When comparing overall counts for the two halves of the unit cell we found a preference for the faulted half over the unfaulted half with a ratio of  $1.35 \pm 0.10$ . Both results support our conclusion that there is a selectivity for chlorine binding. In particular, there is a preference for binding at adatom sites with higher charge density.

This chemically intuitive result seems at first to be at odds with the previous study where atomic chlorine came directly from the gas phase and no adatom preference was found [2]. The most reasonable explanation is that upon reaching the surface from the gas phase, the chlorine atoms do not have opportunity to migrate laterally across the surface before chemisorption. This is reasonable given the high reactivity and symmetry (no steric hindrance) of a chlorine atom. The same holds true for the case of Si(111)7×7 exposed to gas-phase atomic hydrogen [24,25]. Very limited hot atom transport of chlorine atoms was found to be the case in the molecular chlorine study as well [3]. Chlorine atoms after Cl<sub>2</sub> dissociation rarely travel more than ~7 Å to the nearest adatom before binding. Kummel's group found that molecular chlorine has a tendency to dissociate above center adatoms, possibly because of the rather empty center adatom dangling bonds interacting strongly with a filled pair of doubly-degenerate molecular  $\pi^*$  states. The Kummel group also found that chlorine atoms from a given dissociation event almost always reacted with neighboring adatoms. Unlike the cases discussed in Refs. [2,3], in our study the chlorine atoms are given much more opportunity to bind to the adatoms with greater local charge.

It is unlikely that after the spontaneous TCE dissociation, a chlorine atom would travel 30 Å or more along the surface, given the extremely limited hot atom transport properties of chlorine, as discussed above. The more likely explanation involves a mobile precursor and that the TCE dissociation occurs much more frequently above corner adatoms than center adatoms (and somewhat more frequently in the faulted half of the unit cell than in the unfaulted half). This would mean that after dissociation, the hot dichlorovinyl radical travels ~30 Å before binding. It is difficult to comment on whether this travel distance is reasonable or not, since to our knowledge, the surface transport of such species has not yet been studied.

This precursor-mediated site selectivity could arise from any combination of the following two possible scenarios: the first is that the probability of a TCE dissociation event is greater when the precursor molecule is in the vicinity of a corner adatom, as compared to a center adatom. The high electron charge density above a faulted corner adatom, for example, could result in a lowering of the activation energy barrier for dissociative adsorption [10]. This makes perfect sense given the high electronegativity of chlorine. The second scenario is that before dissociation, as the TCE molecule diffuses across the surface in the precursor state, it spends more time above corner adatoms than the center ones. This second scenario is somewhat justified by the direct observation, using low temperature STM, that physisorbed benzene spends more time diffusing across the surface in a honeycomb-shaped region over the center adatoms, as compared to corner adatoms [26]. For the case of benzene there is about a 3:1 preference for chemisorption to center adatoms over corner adatoms, i.e., a preference for low-charge dangling bonds. As Wolkow's group pointed out, there is considerable corrugation in the van der Waals interaction potential for a semiconductor surface such as Si(111)7×7, as this interaction would be affected strongly by the local charge density. In the case of TCE it seems reasonable to conclude that there is a stronger van der Waals interaction above corner adatoms than elsewhere. One may even further speculate that it is the very presence of the strongly electronegative chlorine atoms in the TCE molecule that enhances this potential corrugation and hence the selectivity for corner adatoms.

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