

# Atomically Resolved Determination of the Adsorption Sites as a Function of Temperature and Coverage: H<sub>2</sub>S on Si(111)-(7 × 7)

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Using a variable-temperature ultrahigh vacuum scanning tunneling microscope, we have studied the adsorption characteristics of H<sub>2</sub>S on Si(111)-(7 × 7). The data suggest that H<sub>2</sub>S adsorbs dissociatively at submonolayer coverage, from 50 to 300 K, with HS bonded to an adatom and H bonded to a rest atom. The adsorption is site selective, and the adsorption site preference is temperature dependent. At 50 K, the faulted center sites are most favored for adsorption, followed by unfaulted center sites, faulted corner sites, and unfaulted corner sites. As the temperature is increased, the differences between the faulted and unfaulted halves diminish, but the center sites remain more reactive than the corner sites. At room temperature, the ratio of adsorbates on center sites versus corner sites is 2:1. We present an explanation to account for the non-Langmuir kinetics involved in this system.

## I. Introduction

The dissociative adsorption of gas molecules on solid surfaces is a fundamental chemical reaction. The dissipation of the kinetic energy of the gas can involve energy transfer to the excited states of the solid, such as phonon and electronic excitations. Furthermore, the reactivity at the surface is influenced by the local properties of the surface. These local properties include the positions of the atoms at the surface, the electronic properties at different sites based on dangling bond configurations, and nonbulk collective effects, such as electronic surface states. By studying chemisorption at the atomic scale, we hope to understand the dynamics of the adsorption process and the effects of the local environment on this process.

The Si(111)-(7 × 7) surface provides an opportunity for studying the effects of the local environment on adsorption and dissociation. In the top (adatom) layer, the unit cell contains four different types of sites with dangling bonds, and the second (rest atom) layer also contains dangling bonds that are potentially reaction sites. The complexity of this surface makes it difficult to model theoretically, which emphasizes the need to investigate this surface experimentally. To elucidate the nature of the adsorption of H<sub>2</sub>S on silicon, we have performed our experiments at different temperatures and coverages. We will also suggest an explanation of the results. We hope that our data can spur *ab initio* theoretical studies of this system.

Our instrument is a homemade scanning tunneling microscope (STM) based on the Besocke design.<sup>1</sup> It is housed inside an ultrahigh vacuum (UHV) chamber with a base pressure of 3 × 10<sup>-11</sup> Torr. The STM and sample assembly is cooled with a continuous flow cryostat. The helium flow rate is adjustable, and the cold head can be heated. By setting the flow rate and controlling the heater with a temperature controller, the temperature can be held constant from 8 to 350 K to within 0.1 K. The silicon used in these experiments is cut from a p-type, boron-doped, 1 Ω cm, prime grade wafer. The sample is

mounted on a molybdenum sample holder. Both the sample and sample holder are outgassed at 1000 K for 10–12 h. The sample is further cleaned by repeated sputtering with 1 keV Ne<sup>+</sup> ions and annealing (1200–1500 K) cycles.

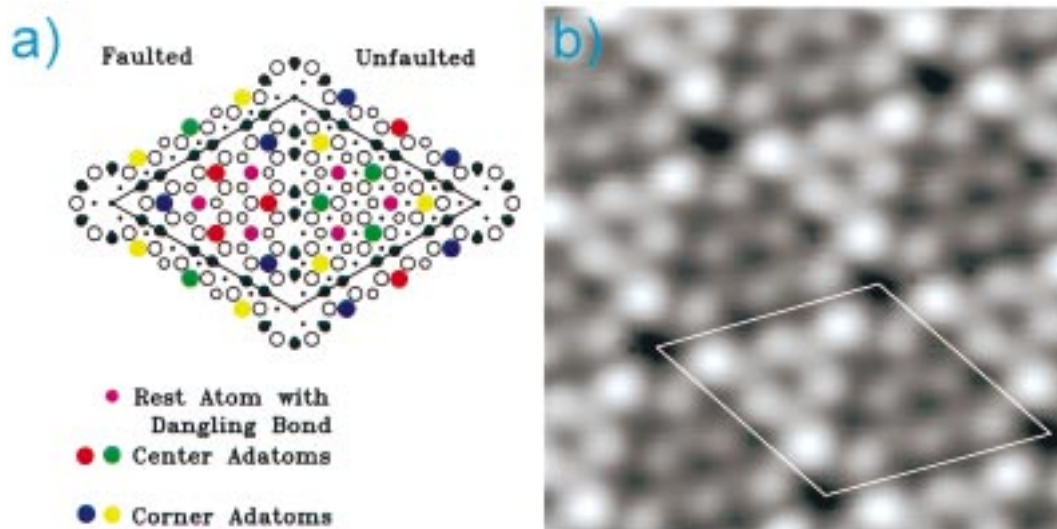
## II. Experimental Results

It is generally accepted that the initial adsorption of H<sub>2</sub>S on Si(111) is dissociative<sup>2</sup> even at low temperatures. Our experiments indicate that the adsorption characteristics change as a function of temperature and coverage. We will discuss the low-temperature results first and then describe the effects of increasing the sample temperature. We will denote the surface coverage as the percentage of adatoms that have adsorbates, because that is what we directly observe with the STM.

Figure 1a shows the Si(111)-(7 × 7) reconstruction.<sup>3</sup> The topmost layer has 12 atoms in the unit cell, which, depending on their position, are called center or corner adatoms. The adatoms have a dangling bond, which is readily observed in STM images (Figure 1b). The unit cell has two halves, faulted and unfaulted, which refer to the faulted stacking of the adatom layer with respect to the fourth layer atoms. The stacking fault increases the local density of states in the faulted half of the unit cell,<sup>4</sup> as can be seen in the filled state STM images (Figure 1b). The second layer, called the rest atom layer, has six atoms with dangling bonds, as shown in Figure 1a. Note that each center adatom has two neighboring rest atoms with dangling bonds, whereas the corner adatoms have one. There are four inequivalent adatom sites: faulted/unfaulted center sites and faulted/unfaulted corner sites. The sticking probability of H<sub>2</sub>S on these sites changes as a function of temperature and coverage.

At 50 K, the low coverage regime is dominated by one species: HS adsorbed on faulted center adatom sites. At 2.3% coverage, 96% of the adsorbates were on faulted center sites, while the other 4% were on unfaulted center sites; there were no adsorbates on corner sites. We cannot see any atomic hydrogen, which is quite distinct when bonded to silicon adatoms. H reduces the local density of states (LDOS) and

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**Figure 1.** (a) Schematic drawing of the  $(7 \times 7)$  reconstructed Si(111) surface. The same color coding is used for the other figures. Note the position of the rest atoms with dangling bonds and the stacking fault. (b) Room-temperature STM image of the filled states (sample bias  $-2$  V, tunneling current,  $1$  nA) of Si(111)- $(7 \times 7)$ . The brighter half of the unit cell is the faulted half. The diamond outlines the  $(7 \times 7)$  unit cell.

appears like a missing adatom.<sup>5</sup> Even at higher coverage, there is no hydrogen bonded to the adatom layer. We propose that the hydrogen atoms are all adsorbed at the rest atoms adjacent to the HS adsorption sites. We will present evidence for this assignment and offer an explanation for this behavior. HS reduces the LDOS significantly, as it appears darker than the silicon atoms, even though it is above the surface (Figure 2a).

If two HS adsorbates are nearest neighbors, one in the faulted half, the other in the unfaulted half, the LDOS is further reduced (Figure 2b). Although the appearance of these darker neighboring sites could be interpreted as a different species, we verified by two different methods that the two molecules are HS. First, by successive in situ dosing, we found that sites with one adsorbate would turn darker if their nearest neighbor became occupied in the next dose. Second, we can dissociate HS molecules using the STM.<sup>6</sup> By dissociating each presumed HS molecule separately, we found features consistent with the reaction products being sulfur and hydrogen. If the two neighboring adsorbates are in the same half of the unit cell, the reduction in the LDOS is not as great (Figure 2c). From our dissociation experiments, it is clear that HS bonds with sulfur attached to silicon and the hydrogen is presumably on top of sulfur.

Given that the two neighboring HS molecules do not form a new species, that is, the major chemical bonds are not rearranged, we attribute the reduction in the LDOS to the dipole–dipole interaction between the two HS molecules. It is possible that the HS molecules bend slightly, so that the dipole moments are no longer parallel, thereby reducing the strain on the bonds by reducing the dipole–dipole force. Bending of the HS molecules would also explain the darker appearance in the STM images. We note that the distance between two center sites in opposite halves of the unit cell is  $6.7$  Å, and  $7.7$  Å for the same half of the unit cell. Since dipole–dipole interactions fall off as  $1/r^3$ , where  $r$  is the distance between the dipoles, the dipole force should be smaller in the same half of the unit cell. This is consistent with our interpretation of the STM images. Furthermore, the center-to-center distance of the two HS neighbors is  $0.3$  Å less than the silicon adatom distance ( $6.7$  Å), possibly signifying a shift in the atomic positions.

As we increased the coverage, the ratio of occupied faulted to occupied unfaulted center sites decreased. At 30% coverage,

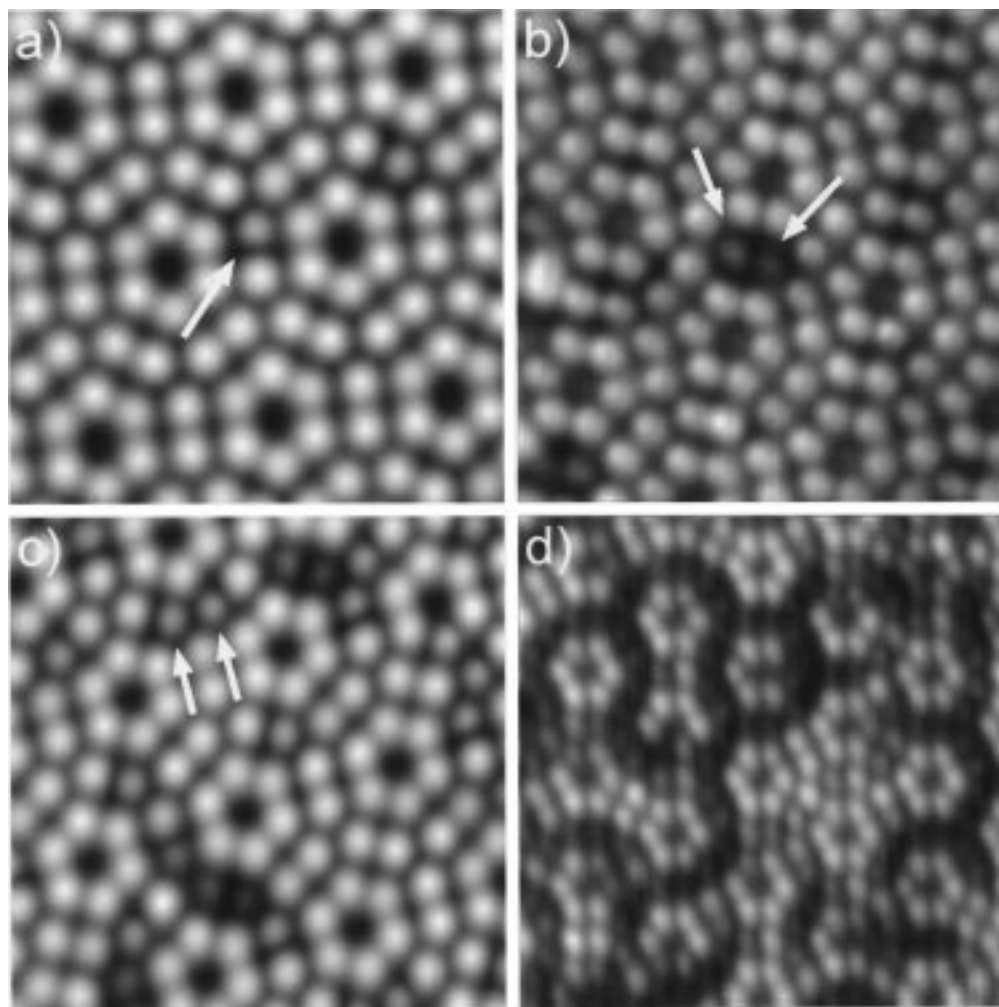
53% of the adsorbates were on faulted center sites, 30% were on unfaulted center sites, 15% were on faulted corner sites, and only 2% were on unfaulted corner sites. At first, we attributed the increase in unfaulted center site population to a simple saturation effect: the more faulted center sites had adsorbates, the less the probability of a new molecule sticking to these sites. But upon careful analysis, it became clear that there exists a nearest-neighbor interaction between adsorbates on faulted and unfaulted center sites that affects the sticking probability.

Figure 3d shows a typical scan at 50 K with 30% HS coverage. By combining statistics from several images, we found that in 254 unit cells, 474 ( $62\% \pm 3\%$ ) of faulted center sites have adsorbates and 275 (36%) of the unfaulted center sites have adsorbates. Each faulted center adatom has exactly one nearest-neighbor unfaulted center adatom. Therefore, if there were no interaction, we would expect about 170 (62%) of the adsorbates in the unfaulted half to have adsorbate neighbors in the faulted half. But 234 ( $85\% \pm 5.5\%$ ) of the adsorbates in the unfaulted half have neighbors in the faulted half. The probability of  $N$  unit cells with  $f$  occupied faulted center sites and  $u$  occupied unfaulted center sites to have  $u_n$  occupied unfaulted center sites with neighbors is given by

$$P(u_n) = \frac{\binom{f}{u_n} \binom{3N-f}{u-u_n}}{\binom{3N}{u}} \quad (1)$$

The probability of a random configuration of adsorbates with more than 203 (74%, which is two standard deviations from 85.5%) nearest-neighbor occupancy is given by  $\sum_{i=203}^{275} P(i)$ , which is less than  $10^{-6}$ . Although by looking at the image it is difficult to notice the change in sticking probability due to nearest-neighbor interaction, there is clear evidence for this effect. This interaction and the low probability of sticking to the corner adatoms produces chainlike structures that can be seen in Figure 2d.

Figure 3a,b show typical scanned images of  $\text{H}_2\text{S}$  adsorbed on silicon at 200 K. At low coverage, there are many more unfaulted center site adsorbates at 200 K as compared to 50 K, with more adsorbates on corner sites as well. At near saturation dosage, there are equal number of adsorbates on faulted and



**Figure 2.** Effects of coverage on adsorbate appearance. (a) At low coverage, the single adsorbate appears slightly darker than the Si adatoms. (b) Two neighboring adsorbates, one on each half of the unit cell, appear much darker than the single adsorbate. (c) Two neighboring adsorbates in the same half of the unit cell. These appear only slightly darker than the single adsorbate. (d) High coverage (47%) limit. The appearance of chainlike structures results from the preference of neighboring adsorbates to be on two different halves of the unit cell. Images scanned at 200 K, with 1 V sample bias and 0.1 nA tunneling current.

unfaulted center sites, as one would expect. When the experiment is performed at 300 K (Figure 3c), the same trend continues: more adsorbates bond to corner sites and unfaulted center sites. At coverages of 30% and above, the ratio of adsorbates on center sites to adsorbates on corner sites is 2:1. Figure 4 summarizes the site specific sticking probability as a function of coverage and temperature.

### III. Adsorption Geometry

It is clear from our experimental results that H<sub>2</sub>S adsorption on Si(111)-(7 × 7) does not follow simple Langmuir kinetics. We are studying this system on the atomic scale, and we would like to understand the adsorption characteristics from a dynamic point of view. Given the complex nature of the (7 × 7) silicon surface reconstruction, the adsorption geometry is of particular importance. By knowing the adsorption geometry, we can predict the maximum coverage and verify the prediction experimentally.

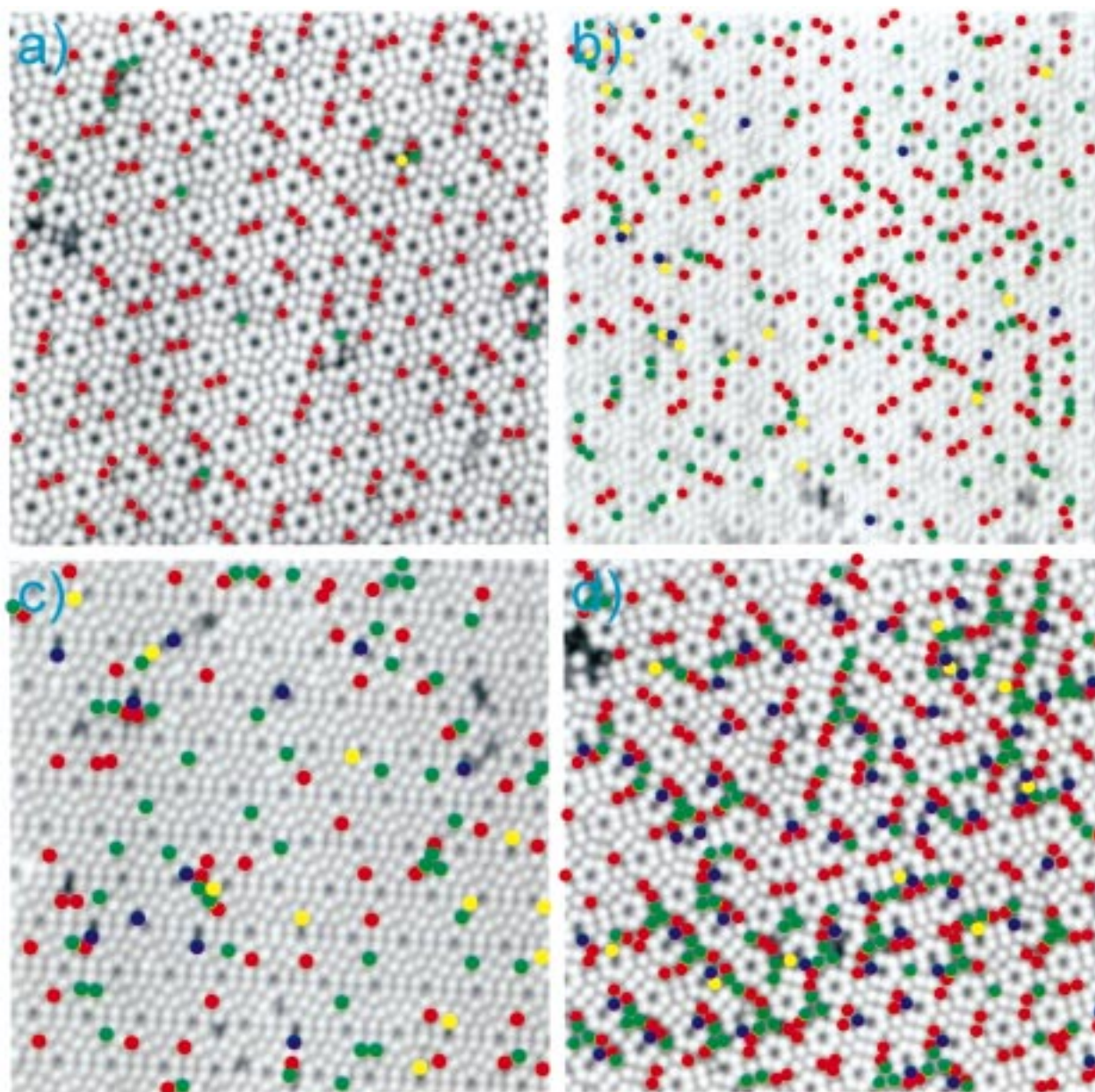
From previous experiments, we know that the submonolayer adsorption is dissociative.<sup>2</sup> We do not observe any hydrogen bonded to the adatom layer, even though atomic hydrogen bonds strongly to both the rest atoms and adatoms on silicon.<sup>5</sup> We can also dissociate the HS fragment further with the STM.<sup>6</sup> We

have never observed more than one hydrogen after the STM-induced dissociation, which provides further evidence for the dissociative adsorption of H<sub>2</sub>S, to form HS and H at and below 300 K.

With a sharp tip, we consistently observe an asymmetry in the scanned images. Figure 5a shows an example of two adsorbates, bonded to the surface at the same relative location in two different unit cells. Since center adatoms have two neighboring rest atoms (Figure 1a), it should be possible for H<sub>2</sub>S to dissociate, with the hydrogen atom attached to either of these rest atoms. From the line profiles (Figure 5c,d), we can see that the upper adsorbate has an asymmetry associated with the left rest atom, whereas the bottom adsorbate has the same asymmetry on the right side. The false color image (Figure 5b) also reveals this asymmetry. We note that this cannot be a tip effect, because the adsorbates are in the same relative position in the unit cell. We attribute this asymmetry to the hydrogen atom adsorbed at one of the two possible rest atom sites.

The adsorption of H<sub>2</sub>S depends critically on the rest atom—adatom pair. Since there are only three rest atoms in each half of the unit cell, the maximum number of adsorbates in each half is three. Therefore, the maximum coverage is 50%. Figure 3d shows 30% H<sub>2</sub>S coverage at 50 K. There are no unit cells with more than three adsorbates in each half. This fact also





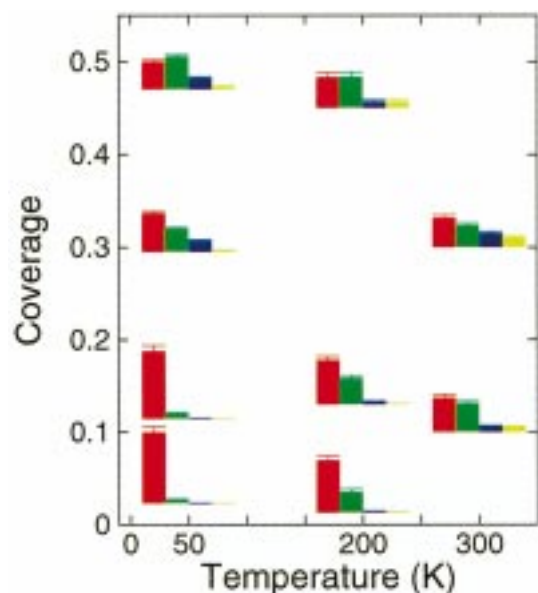
**Figure 3.** 10% HS coverage at (a) 50 K, (b) 200 K, and (c) 300 K, respectively. (d) 30% HS coverage at 50 K. The color coding is the same as in Figure 1a. Images scanned at 1 V sample bias and 0.1 nA tunneling current.

explains the adsorption behavior at high coverage and low temperature, where fewer faulted center sites are occupied compared to unfaulted center sites even though the low-coverage adsorption probability is much higher for faulted sites. Since the adsorption on a corner site inhibits adsorption on a center site in the same unit cell, and also because the adsorption probability is higher for faulted corner sites, near saturation coverage, more faulted center sites can no longer act as adsorption sites compared to the unfaulted center sites. At high dosage,  $\text{H}_2\text{S}$  is known to form molecular multilayers,<sup>2</sup> which are difficult to observe with the STM, as the molecules are either partially mobile or interact with the tip. Heavy dosing also often leads to an unstable STM tip, owing to the molecules being adsorbed on the tip. The maximum coverage we have been able to observe is 47%, which is consistent with our prediction of 50%.

We do not know of any theoretical studies of the adsorption of  $\text{H}_2\text{S}$  on  $\text{Si}(111)-(7 \times 7)$ . There is, however, an extended Huckel calculation<sup>7</sup> done for  $\text{H}_2\text{O}$  on  $\text{Si}(111)-(7 \times 7)$ , which is a very similar system. Results from this calculation suggest that

the lowest energy state for dissociative adsorption of  $\text{H}_2\text{O}$  is OH attached to center site and H bonded to a corner site. STM experiments with  $\text{H}_2\text{O}$  on  $\text{Si}(111)$  have shown that this is not the preferred bonding arrangement.<sup>8</sup>  $\text{H}_2\text{O}$  adsorbs much like  $\text{H}_2\text{S}$ . Even if the adsorption site is restricted to adatom–rest atom pairs, OH bonded to the rest atom is favored over H bonded to the rest atom in the theoretical results. The adsorption process is a nonequilibrium process that involves more than just final state energies. The adsorption geometry is better explained in terms of the local electronic properties of the surface and the kinetics of the adsorption process.

From theoretical calculations<sup>10</sup> and spectroscopy measurements,<sup>11</sup> it can be concluded that the rest atoms with a dangling bond have an excess of charge and can act as electron donors, whereas the adatoms have a charge deficit.  $\text{H}_2\text{S}$  is polarized with the sulfur atom having a slightly negative charge. One possible reaction pathway is for sulfur to bond to an adatom, which is likely due to the charge configuration of the reactants. One of the hydrogen atoms is then attracted to a nearby rest atom with excess charge and bonds to it.



**Figure 4.** Summary of the temperature and coverage dependence of the site selectivity. The height of the histogram represents the percentage of HS adsorbed on different sites. The sum of the four heights for each temperature and coverage is 100%. The color scheme is the same as in Figure 1a. The error bars start from the top of each histogram.

The rest atom–adatom pair act as molecular bond cleavers owing to their opposite charge states. This also explains the lack of hydrogen adsorbed on the adatom layer, which may be energetically favored. Therefore, the adsorption of H<sub>2</sub>S on the adatom layer is consistent with the electronic properties of the surface and the molecule. The adsorbate dissociation by the adatom–rest atom pair was suggested earlier for NH<sub>3</sub> on Si(111).<sup>12–14</sup>

#### IV. Adsorption Site Temperature Dependence

The preference of adsorbates for the faulted half of the (7 × 7) unit cell has been observed for many systems. These adsorbates include H,<sup>9</sup> O<sub>2</sub>,<sup>15</sup> Li,<sup>16</sup> P,<sup>17</sup> Cu,<sup>18</sup> Pb,<sup>19</sup> Ag,<sup>20,21</sup> Ti,<sup>22</sup> Pd,<sup>23</sup> C<sub>2</sub>H<sub>2</sub>,<sup>24</sup> C<sub>2</sub>H<sub>4</sub>,<sup>25</sup> and C<sub>60</sub>.<sup>26</sup> All but one<sup>21</sup> of the cited experiments are performed with STM's as the determination of site selectivity is difficult by other means. Furthermore, these experiments were performed at room temperature or higher, and the low-temperature dependence of this effect has not been explored. We have not found any references to adsorbates that prefer the unfaulted half of the unit cell.

The site preference of O<sub>2</sub> on Si has been explained in terms of the local properties of the surface.<sup>15</sup> O<sub>2</sub> prefers corner sites over center sites and also the faulted half over the unfaulted half. The LDOS on the Si(111)-(7 × 7) surface varies from site to site; the faulted half has a higher LDOS, and within each half the corner sites have higher LDOS than the center sites. O<sub>2</sub> becomes adsorbed through charge transfer and interaction with the electron–hole pairs in the S1 surface state. Therefore, O<sub>2</sub> has a higher probability of sticking to sites with higher LDOS. Although this is a reasonable explanation for O<sub>2</sub>, it does not fit our data for H<sub>2</sub>S. We do not see a preference for the corner sites, especially at low temperatures. Furthermore, we have not seen any change in the LDOS as a function of temperature as measured by the STM. Since the probability of adsorption to different sites is temperature dependent, we need a different explanation for our system.

A simple explanation for the adsorption behavior is a mobile precursor state, such as the precursor state observed for benzene

on Si(111).<sup>27</sup> The molecule adsorbs loosely on the surface and becomes thermally equilibrated with the surface. The molecule then dissociatively adsorbs on the basis of the temperature and the dissociation barrier at the different sites. At higher temperatures, higher energy barriers are more easily overcome, whereas at low temperatures only the lowest energy barriers are surmountable. The barrier to dissociation is site dependent. Given this explanation, we can conclude that the lowest energy barrier to dissociation is associated with the faulted center sites, followed by unfaulted center sites, faulted corner sites, and finally unfaulted corner sites.

We can estimate the difference between the energy barriers by assuming the same preexponential factor in Arrhenius law from which we obtain

$$R = f/u = e^{\Delta E/kT}, \quad \Delta E = E_u - E_f \quad (2)$$

where  $R$  is the ratio between the two populations,  $f$  is the number of adsorbates on the faulted center sites,  $u$  is the number of adsorbates on the unfaulted center sites,  $k$  is Boltzmann's constant,  $T$  is the temperature,  $E_f$  is the energy barrier at faulted center sites,  $E_u$  is the energy barrier at unfaulted center sites, and  $\Delta E$  is the energy difference. Using our low coverage (1–2%) results to avoid saturation and nearest-neighbor effects, we obtain  $\Delta E = 14 \pm 2$  meV at 50 K and  $\Delta E = 16 \pm 2$  meV at 200 K, which are in reasonable agreement with each other.

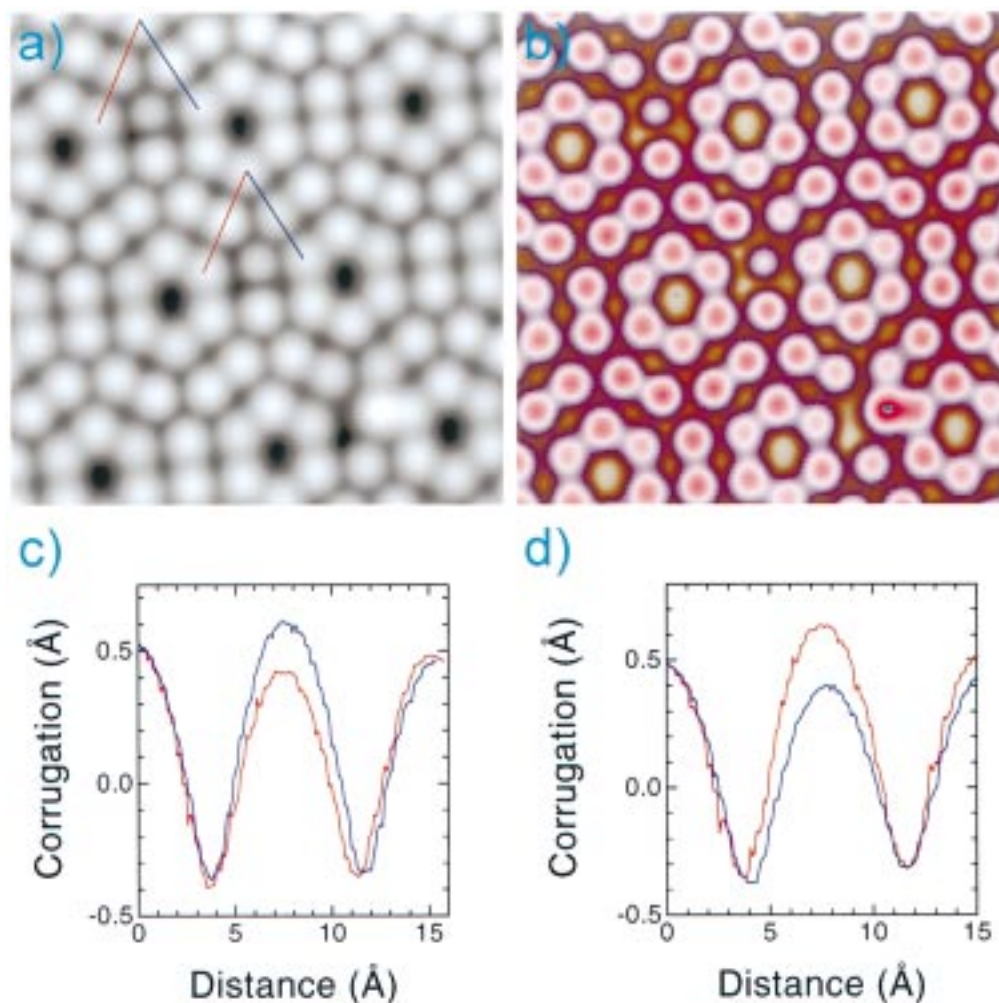
We note that at room temperature and moderate coverage, the ratio of the center site adsorbates to corner site adsorbates is 2:1. This ratio can be attributed to the fact that the corner adatoms have one neighboring rest atom, but center adatoms have two such neighbors and therefore the dissociation probability is twice as high at center sites. Although there is no evidence for a mobile precursor state, the adsorbate does not have to move far to find a suitable site. Every adatom on the silicon surface has a neighboring faulted center site adatom. The furthest an adsorbate would have to move to find a faulted center site is about 13 Å from the corner hole. It is also possible that a gas molecule will not adsorb if it cannot find a suitable site. Although that would change the overall sticking probability, we cannot measure the sticking probability accurately enough to notice a temperature dependence.

Finally, we would like to explain the change in the sticking probability as a function of coverage. Like O<sub>2</sub>, H<sub>2</sub>S has a high electron affinity<sup>28</sup> and may become charged in the process of adsorbing. HS fragments already adsorbed on the surface act like dipoles, which can interact with the charged precursor. Electrostatic interaction between the adsorbate and the precursor may lead to a higher probability of dissociation near the adsorbate. One other possibility is for the adsorbate to lower the energy barrier to dissociation by changing the local properties of the surface. We can estimate the change in the energy barrier by modifying eq 1 to compensate for the expected unequal occupation of sites with and without neighbors

$$R = R_0 \frac{u_n}{u - u_n} = e^{\Delta \epsilon/kT}, \quad \Delta \epsilon = \epsilon - \epsilon_n \quad (3)$$

where  $u_n$  is the number of unfaulted center site adsorbates with neighbors in the faulted half,  $u$  is the total number of unfaulted center site adsorbates,  $R_0$  is the expected ratio of the two populations,  $\epsilon$  is the energy barrier for adsorbates without neighbors,  $\epsilon_n$  is the energy barrier for adsorbates with neighbors, and  $\Delta \epsilon$  is the energy difference. At 30% coverage, 62% of the faulted center sites have adsorbates and therefore  $R_0 = 0.38/0.62 = 0.61$ . Using  $u_n = 234$  and  $u = 275$ , we obtain  $\Delta \epsilon = 5.2 \pm 0.6$  meV.





**Figure 5.** (a) Gray scale STM image, with two adsorbates bonded to the same center adatom site in two different unit cells. (b) False color image of the same data. Note the asymmetry in the appearance of the neighboring adatoms to the adsorption site. (c) Profile cuts through the upper adsorbate position, as shown in (a). (d) Profile cuts through the lower adsorbate. Images scanned at 50 K with 1 V sample bias and 0.1 nA tunneling current.

This nearest-neighbor attraction is most pronounced between faulted and unfaulted center sites; otherwise, the change in adsorption behavior as a function of coverage would not be evident. It might seem unlikely that the probability of adsorption is higher on two center sites in opposite halves of the unit cell, as compared to two center sites in the faulted half of the unit cell. But by looking at the silicon rest atom positions, we can see that when a center site is bonded to an adsorbate, it automatically reduces the chances of one of the other center sites in the same half, because the other center site adatom now has only one unoccupied rest atom neighbor. It follows that the center site in the unfaulted half of the unit cell would be more favorable because it still has two rest atom neighbors to accommodate the H atom. If the attraction is electrostatic in nature, then the further distance of the sites in the same half of the unit cell may contribute to this effect as well.

## V. Conclusion

Further theoretical study of the dissociative adsorption of  $\text{H}_2\text{S}$  on  $\text{Si}(111)-(7 \times 7)$  is necessary for a better understanding of the physical phenomena underlying the observed behavior. Ab initio calculations, however, are very difficult to perform for this system. The reconstructed unit cell has over 100 atoms in

the first three layers, and any calculation would have to include additional layers in the bulk ( $1 \times 1$ ) configuration, which adds 49 atoms per layer. The sheer size of the problem makes it difficult to solve. Adding an impinging adsorbate to this system makes it an even more complex problem.

By varying the temperature, we can probe different aspects of the adsorption behavior. The site selectivity is more evident at low temperatures, and the determination of the small energy differences is only possible at low temperatures. Our estimates of energy barriers elucidate the effects of the local surface chemistry in the adsorption process.

We have studied the dissociative chemisorption of  $\text{H}_2\text{S}$  on  $\text{Si}(111)-(7 \times 7)$  from 50 to 300 K. The adsorption is both site selective and temperature dependent. We have determined the adsorption geometry by careful analysis of the data and by dissociating the HS fragment using the STM. The adsorption geometry is a consequence of the dangling bond structure on the reconstructed surface. HS bonds to the adatom sites, which have an abundance of electrons, and H bonds to the neighboring rest atom. To some extent, the adsorption preference for center adatoms is dictated by the surface reconstruction, because these sites have two neighboring rest atom dangling bonds. The temperature dependence of the adsorption site preference points to a thermally activated adsorption and dissociation process on different adatom sites.

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