

## Surface chemistry of silicon-the behaviour of dangling bonds

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## Surface chemistry of silicon—the behaviour of dangling bonds

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**Abstract.** The role of surface dangling bonds in controlling the surface chemistry of Si(100) and Si(111) has been investigated using surface science methods. The adsorption and decomposition of acetylene on Si(100) has been shown to occur by means of a mobile precursor mechanism, leading to a di- $\sigma$  chemisorbed ethylenic species occupying Si dimer sites on Si(100). This species decomposes at elevated temperatures to produce adsorbed carbon and hydrogen (800 K) and then silicon carbide (1000 K).

The activity of Si(111) for the adsorption of species such as ammonia and atomic hydrogen can be significantly reduced by doping of the surface region with boron. It has been shown that subsurface boron significantly changes the structure of Si(111)-(7 $\times$ 7) to a  $\sqrt{3} \times \sqrt{3}$  R30° structure. In addition, the local doping of the surface reduces the chemical activity of the dangling bonds so that neither the dissociation of NH<sub>3</sub> nor the adsorption of atomic hydrogen will occur.

### 1. Introduction

The study of elementary surface chemical processes on semiconductor surfaces is currently a field in its infancy compared to similar investigations which have been carried out on metal surfaces in the last thirty years [1]. This is partly due to the overwhelming technological significance of surface chemistry to heterogeneous catalysis, as practised on metals since early in the nineteenth century [2]. However, today new technologies for the production of semiconductor materials and devices are providing a strong stimulus for fundamental investigations of chemistry on the surfaces of covalently bound solids.

The surface of a covalent solid projects dangling bonds into the vacuum, and these bonds act as free radical sites for inducing surface chemistry in molecules which adsorb on these sites. Recently, the scanning tunnelling microscope (STM) has been used effectively for imaging these dangling bonds, and beautiful examples of this can be found, for example, in the work of Demuth *et al* [3, 4] and Avouris *et al* [5-7] for the Si(100) and Si(111) surfaces respectively. In addition to imaging the dangling bonds, it has also been possible to measure the dangling bond local density of states, both filled and unfilled, by measuring the tunnelling current as a function of the electrical bias of the STM tip [3, 4]. A positive tip bias allows one to sample the filled dangling bond states; a negative bias samples the empty states. Using the STM, differing surface

reactivities of the various types of dangling bonds projecting from the Si(111)-(7×7) surface have been investigated with great effectiveness [5-7].

This paper is a review of our investigations of the reactivity of silicon surfaces with an organic molecule [8] and ammonia [9], and atomic hydrogen [10]. One reason for our interest in the bonding and reactivity of organic molecules with silicon has to do with the production of silicon carbide thin films on silicon surfaces by chemical vapor deposition (CVD) methods [11-13]. Silicon carbide films are grown in flow reactors by the interaction of organic molecules with hot silicon surfaces. The temperature of the CVD reactor is very high, and it is likely that gas phase free radical species are also involved in the silicon carbide deposition process [14], but these processes have not been investigated here.

Silicon carbide is a desired semiconductor material because of its wide bandgap (3.0 eV). This wide bandgap, contrasted to that of Si (1.1 eV), makes possible the fabrication of semiconductor devices from silicon carbide which are able to operate at high temperatures, as well as in the presence of high intensity radiation fields [15,16]. Thus, silicon carbide is a potential semiconductor of the future, and much interest already exists in its production and utilization as an electronic device material [17,18].

In this review, a representative study of the interaction of an interesting organic molecule, acetylene, with Si(100)-(2×1) will be presented. In addition, very recent studies using a surface dopant to effectively modify the reactivity of dangling bonds on Si(111) will be described.

## 2. The interaction of acetylene with Si(100)

The carbon-carbon triple bond in acetylene offers an excellent opportunity to examine chemical reactivity at a semiconductor surface, since the interaction of one-half filled silicon dangling bonds with the  $\pi$  electron system in acetylene should be effective in forming chemical bonds at the surface. Our inquiry is divided into four different categories:

1. The measurement of the absolute surface coverage of the saturated chemisorbed layer of  $C_2H_2$  on Si(100)-(2×1). How does this saturation coverage relate to the known dangling bond density on the clean surface?
2. The measurement of the kinetics and mechanism for the adsorption of  $C_2H_2$  on Si(100)-(2×1). By what kinetic process does  $C_2H_2$  seek dangling bond sites on the surface?
3. The determination of the mode of bonding of the  $C_2H_2$  molecule to the dangling bond sites. What is the structure of the chemisorbed species, and what are the energetics of bonding?
4. The use of electron energy loss spectroscopy to monitor the thermal degradation of chemisorbed  $C_2H_2$  to produce chemisorbed carbon on silicon which converts to silicon carbide at elevated temperatures.

### 2.1. Absolute coverage measurements

Figure 1 shows a schematic diagram of the ultrahigh vacuum apparatus employed to measure the kinetics of adsorption and the absolute surface coverage at any stage of adsorption [8b]. A collimated beam of adsorbate exits from a doser which contains a

### UHV System Used to Measure Absolute Coverages

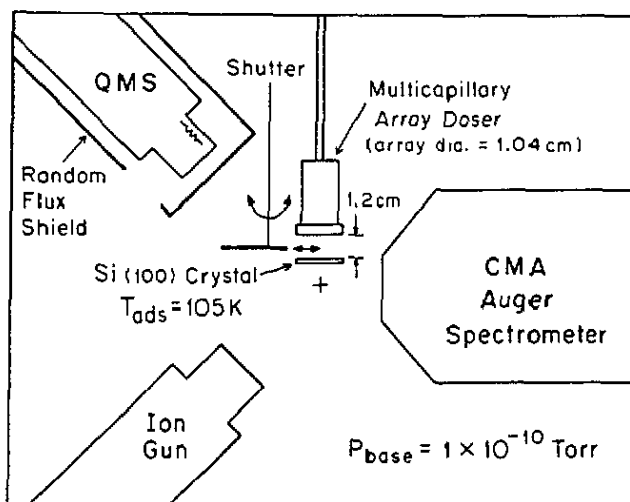


Figure 1. Top view of the ultrahigh vacuum apparatus used for absolute coverage and adsorption kinetic measurements [8b].

#### ADSORPTION OF $C_2H_2$ ON $Si(100)$ SURFACE AT 105K

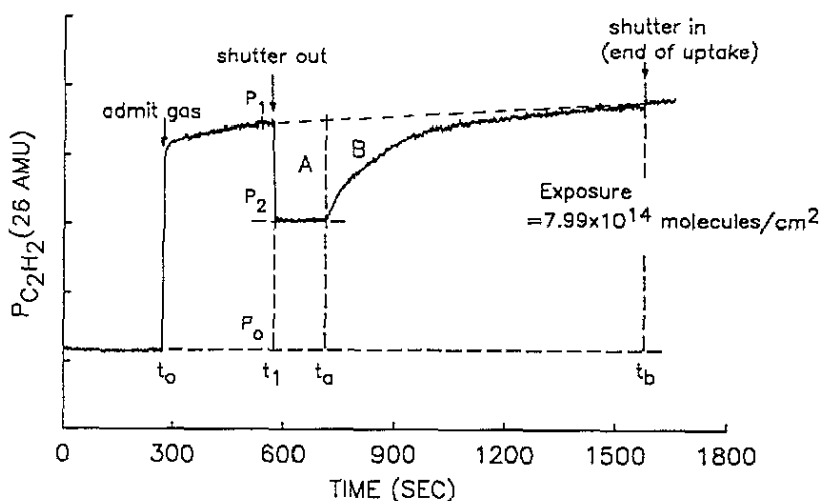


Figure 2. Kinetic uptake measurement of  $C_2H_2$  adsorption on  $Si(100)$  at 105K using the beam dosing technique with random flux detection [8a].

microchannelplate collimator array [19]. The doser also contains an internal pinhole aperture which has been calibrated accurately for its conductance for the adsorbate in question [8b]. In addition, the angular distribution of exiting gas from the collimator is accurately known by calculation [20, 21]. The cleaned silicon crystal is placed in a

known position relative to the doser, and a shutter is inserted between the doser and the crystal. After a flux of acetylene has been established through the doser into the system, the shutter is moved out of the beam, and adsorption begins to take place on the crystal. The gas molecules which miss the crystal, or which strike the crystal and do not adsorb, are measured with a shielded mass spectrometer which detects only the random flux of non-adsorbed gas. This method of measurement follows that of King and Wells [22] and of Madey [23].

Typical adsorption data for  $C_2H_2$  on  $Si(100)-(2 \times 1)$  are shown in figure 2. When the shutter is removed from its position between the doser and the crystal, the signal detected by the mass spectrometer decreases sharply by an amount  $\Delta_1$ , and with the crystal at 105 K,  $\Delta_1$  remains constant for a portion of the adsorption process. It may be shown, from the ratio  $(P_1 - P_2)/(P_1 - P_0)$ , that in this particular case the fraction of gas striking the crystal and adsorbing is 0.46. Since by calculation, the fraction of the gas intercepted by the crystal is  $0.45 \pm 0.01$ , it follows that the efficiency of adsorption of  $C_2H_2$  is initially unity at 105 K [8a]. By measuring the total integrated area of the uptake curve under the dashed baseline curve (area A + area B, figure 2), and by making a small experimental correction for adsorption at low efficiency after the uptake measurement has been completed [8b], it was possible to determine the total saturation coverage of  $C_2H_2$  on the  $Si(100)$  surface.  $N_{sat} = 2.54 \pm 0.11 \times 10^{14} \text{ cm}^{-2}$ . Other measurements of the yield of hydrogen as  $H_2$  (and as a 5% yield of undecomposed  $C_2H_2$ ) from the thermal desorption of the saturated  $C_2H_2$  layer on  $Si(100)$  yield  $N_{sat} = 2.8 \pm 0.3 \times 10^{14} \text{ C}_2\text{H}_2 \text{ cm}^{-2}$ .

If the  $Si(100)-(2 \times 1)$  crystal were perfect, it would expose  $3.4 \times 10^{14} \text{ Si}(100)$  dimer sites  $\text{cm}^{-2}$ . However, it is well known from STM experiments that at least 5–10% of a typical  $Si(100)-(2 \times 1)$  surface is defective [3,24], and defect sites do not adsorb unsaturated hydrocarbon molecules [25]. On this basis, one estimates that the saturation coverage of  $C_2H_2$  is about  $0.87 \pm 0.17 \text{ C}_2\text{H}_2/\text{Si}_2$  site. It is therefore likely that, given the errors in the measurement, each  $Si_2$  dimer site adsorbs a single  $C_2H_2$  molecule.

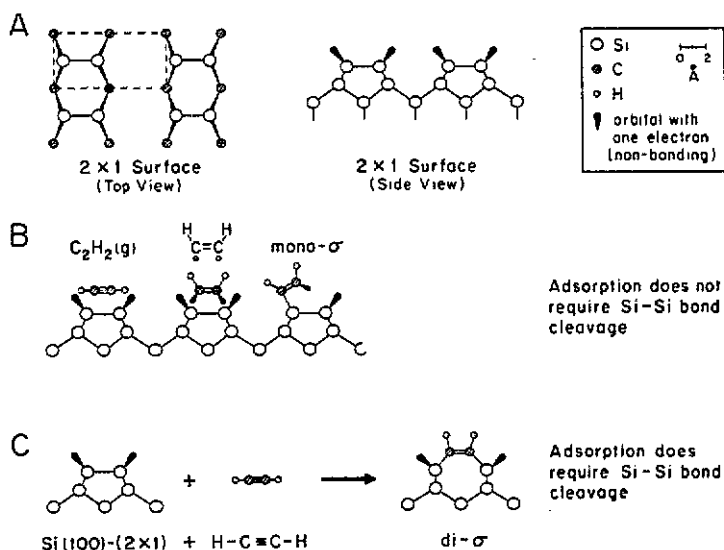


Figure 3. Various bonding modes for  $C_2H_2$  adsorption on the  $Si(100)-(2 \times 1)$  surface [8a].

Figure 3 shows possible modes of bonding of  $C_2H_2$  to  $Si_2$  dimer sites on  $Si(100)-(2 \times 1)$ . The top section, (A), shows a top view and a side view of the symmetrical dimer sites on the  $Si(100)-(2 \times 1)$  surface, where projecting dangling bonds are shown in black in the side view. Two possible modes of bonding of  $C_2H_2$  are shown in sections (B) and (C) of figure 3. Mono- $\sigma$  bonding (section B) involves attachment to a single Si dangling bond with the production of an anchored radical species and retention of the Si-Si dimer bond. Di- $\sigma$  bonding (section C) involves the breaking of a Si-Si dimer bond with the attachment of an anchored ethylenic species to the Si atoms involved in the original  $Si_2$  dimer site. If mono- $\sigma$  bonding were present, it is barely possible sterically to have a saturation coverage of two  $C_2H_2/Si_2$  site [8a]. However, for di- $\sigma$  bonding, the saturation coverage would be one  $C_2H_2/Si_2$  dimer site, in agreement with the experimental results above.

Thermodynamic arguments, involving the activation energy measured for acetylene thermal desorption ( $46 \text{ kcal mol}^{-1}$  at zero coverage) and the calculated strength of the C-Si bond(s) in the mono- and di- $\sigma$  bonding structures, clearly indicate that the mono- $\sigma$  structure is energetically disfavoured compared to the di- $\sigma$  structure [8a].

We therefore conclude, based on absolute coverage measurements of two types, and on energetic considerations, that the  $Si(100)$  dimer sites are the bonding sites for a single acetylene molecule which adsorbs in di- $\sigma$  fashion as an ethylenic species as shown in figure 3(c).

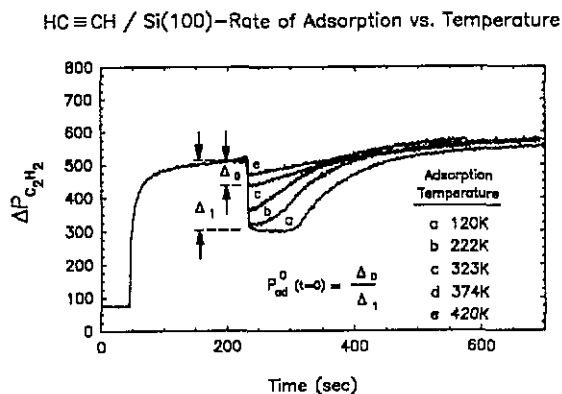


Figure 4. Rate of adsorption of  $C_2H_2$  on  $Si(100)-(2 \times 1)$  as a function of crystal temperature [8a].

### 2.2. Kinetics of acetylene adsorption on $Si(100)-(2 \times 1)$

Figure 4 shows the uptake curves measured at various crystal temperatures in the range 120–420 K. At 120 K, the initial reaction probability is unity over a wide initial coverage range, and then the reaction probability falls below unity as the coverage increases further. At higher substrate temperatures, the initial reaction probability systematically decreases as the temperature increases. This type of behaviour is indicative of the involvement of a mobile precursor mechanism for acetylene adsorption, and a negative activation energy for adsorption [26,8a].

In this mechanism, the incoming molecule experiences a weakly attractive potential well which involves primarily van der Waals bonding of the molecule to the surface,

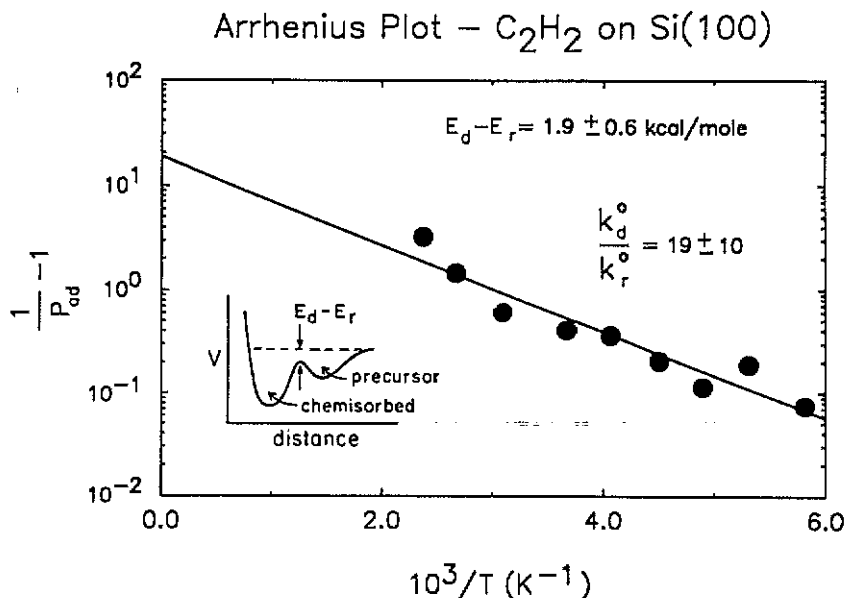


Figure 5. Arrhenius plot for C<sub>2</sub>H<sub>2</sub> adsorption on Si(100)-(2×1) [8a].

either above filled sites, or possibly also above empty adsorption sites. This potential well is schematically shown in the inset to figure 5. It is the surface migration of this precursor which feeds the chemisorption process. In the precursor state, the molecule can either adsorb more strongly as a chemisorbed species by passage over the barrier with a rate constant,  $k_r$ , or it can desorb into the gas phase with a rate constant,  $k_d$ . A simple steady state treatment of this situation yields an expression for the probability of adsorption (at zero coverage),  $P_{\text{ads}}^0$ , which involves only the ratio of the two rate constants,  $k_r$  and  $k_d$ , as shown in equation (1)

$$P_{\text{ads}}^0 = \frac{1}{1 + k_d/k_r} \quad (1)$$

By measuring  $P_{\text{ads}}^0$  from curves such as those shown in figure 4 as a function of temperature, it is possible to determine the ratio  $k_d/k_r$ , and hence to estimate ( $E_d - E_r$ ), the difference in barrier heights from the precursor to the desorbing species and to the chemisorbed species. A plot of these data is shown in figure 5, where the difference in activation energies is measured to be  $1.9 \pm 0.6 \text{ kcal mol}^{-1}$ . In addition, the ratio of the pre-exponential factors,  $\nu_d/\nu_r = 19$ , may also be estimated by a long extrapolation.

This analysis indicates two features of the adsorption of acetylene on Si(100)-(2×1):

1. The reaction occurs via a mobile precursor mechanism in which the activation energy for chemisorption from the precursor is less than that for desorption (negative activation energy mechanism), causing the initial probability of surface reaction to *decrease* as the temperature is raised.
2. The first order pre-exponential factor for precursor desorption exceeds that for chemisorption from the precursor species. This suggests that the activation entropy for desorption exceeds that for adsorption. This is reasonable, since the

activated complex for adsorption on the  $\text{Si}_2$  dimer sites will probably be more sterically ordered than the activated complex through which desorption occurs.

### 2.3. Thermal behaviour of chemisorbed acetylene

Using Auger spectroscopy, it was shown that only about 5% of a monolayer of chemisorbed acetylene desorbs as acetylene from  $\text{Si}(100)$ . The remaining 95% decomposes to produce chemisorbed carbon and hydrogen. The activation energy for acetylene desorption at zero coverage was estimated as  $46 \text{ kcal mol}^{-1}$  from the characteristics of the acetylene desorption trace at 750 K [8a]. In addition, no other hydrocarbon species are observed to desorb from the chemisorbed acetylene layer. Thus, the breaking of C-H and C=C bonds in the di- $\sigma$  adsorbate species are the primary chemical processes which occur upon heating to  $\sim 800 \text{ K}$ .

This C-H bond breaking process has been witnessed in HREELS studies of the vibrational spectrum of the species produced as adsorbed  $\text{C}_2\text{H}_2$  decomposes on  $\text{Si}(100)$ , and is shown in figure 6.

Figure 6 shows that on heating to 290 K and above, Si-H bonds form as a result of C-H bond scission in the acetylene-derived species. C-H bonds persist to 870 K or above. At 930 K, all C-H and Si-H bonds have been broken and all  $\text{H}_2$  has desorbed from the surface, and only the  $800 \text{ cm}^{-1}$  mode remains indicating the presence of  $\text{SiC}$  on the surface.

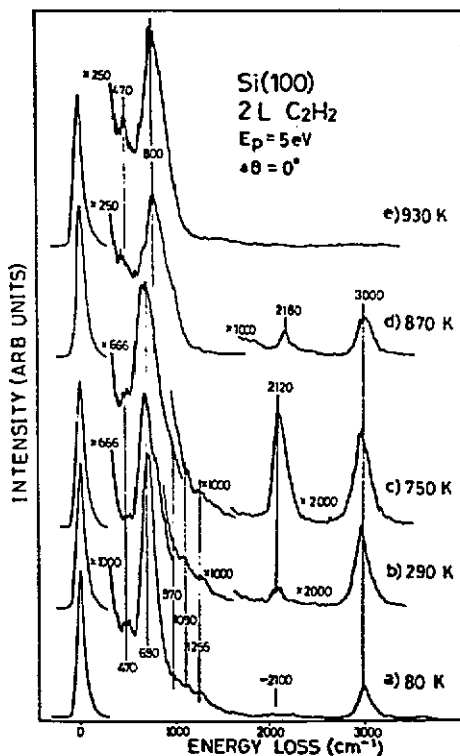


Figure 6. HREEL spectra in the specular mode for  $\text{C}_2\text{H}_2$  adsorbed on  $\text{Si}(100)-(2 \times 1)$  at 80 K, followed by heating to higher temperatures [27].



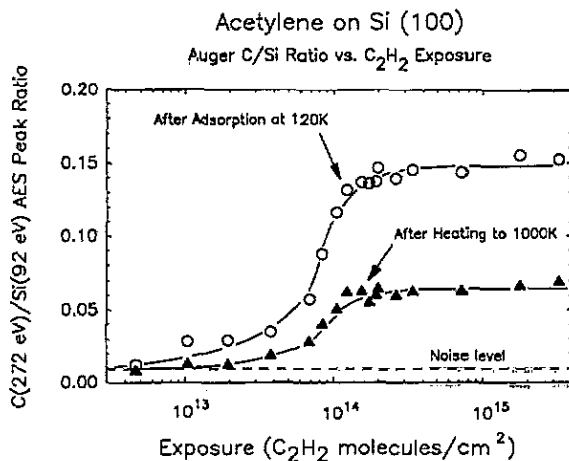


Figure 7. Auger intensity behaviour for carbon/Si(100) upon heating to 1000 K at various acetylene exposures [8a].

Studies of the intensity of the carbon Auger signal before and after heating to 1000 K are plotted for various C<sub>2</sub>H<sub>2</sub> exposures in figure 7. At all coverages, a ~ 60% decrease in the carbon Auger intensity is seen, which is probably indicative of carbon penetration into the silicon lattice at this temperature. Auxiliary studies have shown that a 26 eV plasmon loss feature, characteristic of SiC, forms from hydrocarbon species decomposing at 1000 K on Si(100) [13].

#### 2.4. Summary of the behaviour of acetylene on Si(100)—relationship to the chemical vapour deposition of silicon carbide

The chemisorption of acetylene on Si(100) occurs via the interaction of the dangling bonds at the silicon surface with the carbon-carbon triple bond in the acetylene. In contrast to this, the chemical interaction of alkanes, including the strained alkane, cyclopropane, does not occur on Si(100) at low temperatures; C-C and C-H bonds are completely unreactive [28]. Acetylene chemisorption occurs via a mobile precursor adsorption mechanism, in which a weakly-bound molecular precursor species migrates to unfilled Si<sub>2</sub> dimer sites where reaction occurs by way of di-σ bonding. Above about 300 K the di-σ-bound ethylenic species produced from acetylene begins to undergo C-H bond scission, producing Si-H bonds on the surface. By about 900 K, all C-H and Si-H bonds have been broken, and hydrogen has desorbed from the surface, leaving adsorbed carbon. This carbon penetrates into the silicon surface by 1000 K, forming a silicon carbide film.

One might ask whether this information is relevant to the growth of silicon carbide films on silicon, since it would be expected that the exposed silicon carbide surface, characteristic of a growing silicon carbide film, would exhibit a different reactivity from silicon, and hence our studies would apply only to the formation of the *first* atomic layer of carbon on silicon. This expectation is however not operative in the growth of silicon carbide films, since it has been found that a growing silicon carbide film is covered by a layer of elemental silicon throughout the growth process [13]. It is this outer layer of elemental silicon which continues to participate in the growth of the silicon carbide film, and presumably the surface chemistry found on Si(100) will,

to some degree, continue to operate on the *silicon* layer exposed on the surface of the growing silicon carbide film.

### 3. Boron passivation of silicon surface chemistry

#### 3.1. The effect of subsurface boron on the chemistry of silicon dangling bonds

Recently, a number of paper have appeared which have been concerned with the passivation of silicon surface chemistry by subsurface boron atoms [29–33]. The boron may be segregated to the subsurface region of Si(111) by diffusion from the bulk [31,32], or alternatively by the decomposition of decaborane on the surface, with diffusion into the subsurface region [29]. It is believed that the subsurface boron atoms incorporate substitutionally into the silicon lattice in the third silicon atom level from the surface [29], as shown in figure 8.

Since boron is a group III element, it acts as an electron acceptor atom in the silicon lattice, and by electron counting, it might be expected to remove electronic charge from the projecting Si dangling bond above it. The Si(111)-(7×7) surface reconstructs to a  $\sqrt{3} \times \sqrt{3}$ -R30° structure upon boron incorporation. Figure 8 also shows top and side views of the reconstructed Si(111)-B surface.

#### Structure of the B-modified ( $\sqrt{3} \times \sqrt{3}$ )R30 Si(111) Surface

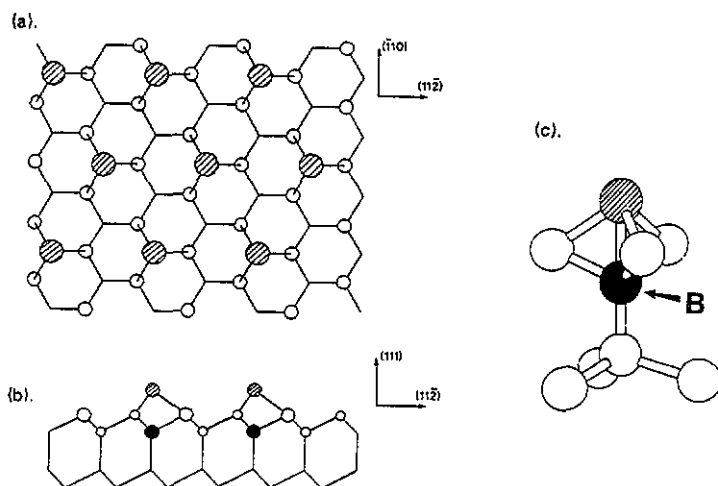


Figure 8. Location of subsurface boron in Si(111) [29].

#### 3.2. Passivation of Si(111) for ammonia dissociative chemisorption

The removal of electronic charge from the dangling bonds of Si(111) by underlying B impurity atoms was first reported to passivate the surface by Avouris *et al* [29,33], using the STM to measure the lack of chemical reactivity of the boron-passivated surface toward ammonia. We have examined this closely with HREELS and have made

Thermal Effects on an Intermediate Coverage  
 $\text{NH}_3/\text{Si}(111)-(7 \times 7)$  Layer

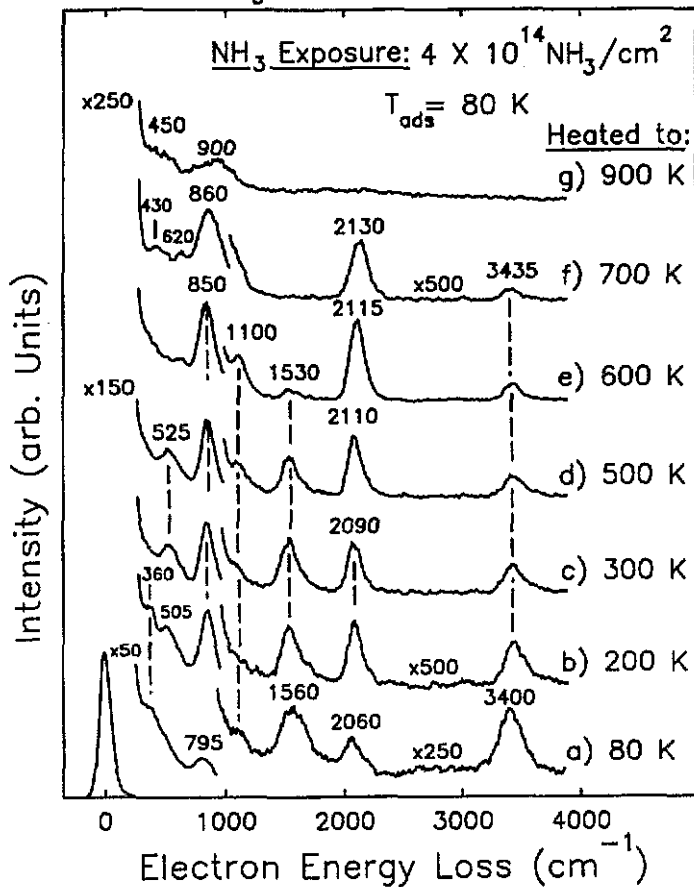


Figure 9. HREEL spectra in the specular mode for  $\text{NH}_3$  adsorption and decomposition on  $\text{Si}(111)-(7 \times 7)$  [9].

a comparison of the ammonia bonding and decomposition on  $\text{Si}(111)-(7 \times 7)$  [9] and on the  $\text{Si}(111)\text{-B}$  surface [34]. For  $\text{NH}_3$  on  $\text{Si}(111)-(7 \times 7)$ , evidence for the formation of  $\text{NH}_2(\text{a})$  and  $\text{H}(\text{a})$ , even at 80 K, is seen in figure 9. Here, at 80 K and above, a characteristic Si-H mode is observed at  $2070 \text{ cm}^{-1}$ , indicative of N-H bond scission. Other vibrational modes confirming the presence of  $\text{NH}_2(\text{a})$  species are observed at  $3435 \text{ cm}^{-1}$  and  $1530 \text{ cm}^{-1}$ .

In contrast to the behaviour of  $\text{NH}_3$  on  $\text{Si}(111)-(7 \times 7)$ , little decomposition of  $\text{NH}_3$  occurs on the  $\text{Si}(111)\text{-B}$  surface as shown in figure 10. Here it is seen that  $\text{NH}_3$  adsorbs molecularly at 80 K, giving N-H stretching modes at  $3325 \text{ cm}^{-1}$  and at  $2900 \text{ cm}^{-1}$ . We currently believe that the  $2900 \text{ cm}^{-1}$  mode is related to the formation of  $\text{NH}_3$  clusters on the passivated surface, even at submonolayer exposures [34]. This clustering tendency is present to a small degree at high  $\text{NH}_3$  exposures on the unpassivated  $\text{Si}(111)$  surface, for multilayer coverages where underlying  $\text{NH}_x(\text{a})$  species and  $\text{H}(\text{a})$  species have passivated the silicon surface also, and a weak  $2900 \text{ cm}^{-1}$  mode may also be seen in figure 9, as a result of  $\text{NH}_3$  clustering.

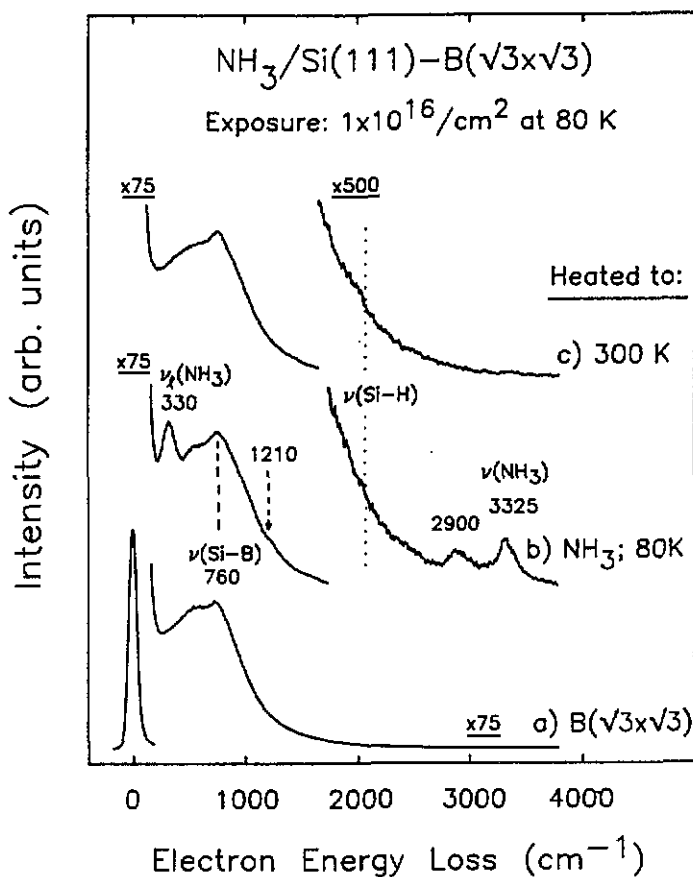
NH<sub>3</sub> Adsorption on Boron Modified Si(111)

Figure 10. HREEL spectra in the specular mode for ammonia adsorption on boron-modified Si(111) [34].

On heating the NH<sub>3</sub> layer to 300 K, desorption occurs without the formation of surface hydrogen or surface nitrogen species because of the passivation of the silicon surface by boron, as seen in figure 10 and confirmed with temperature programmed desorption and Auger spectroscopy [34].

### 3.3. Passivation of Si(111) for interaction with atomic hydrogen

An even more aggressive surface reactant than ammonia is atomic hydrogen. Atomic hydrogen is employed for the adsorption of hydrogen on silicon surfaces because molecular hydrogen is unreactive. The reaction of atomic hydrogen with Si(111) is so aggressive that it may be used to etch the surface, producing gas phase silane [35-37]. It was therefore of interest to determine whether boron doping of Si(111) would lead to a reduced tendency to adsorb atomic hydrogen and to form SiH<sub>4</sub> [10]. Experi-

HREELS Studies of Hydrogen Adsorption  
on Clean and B-Modified Si(111)

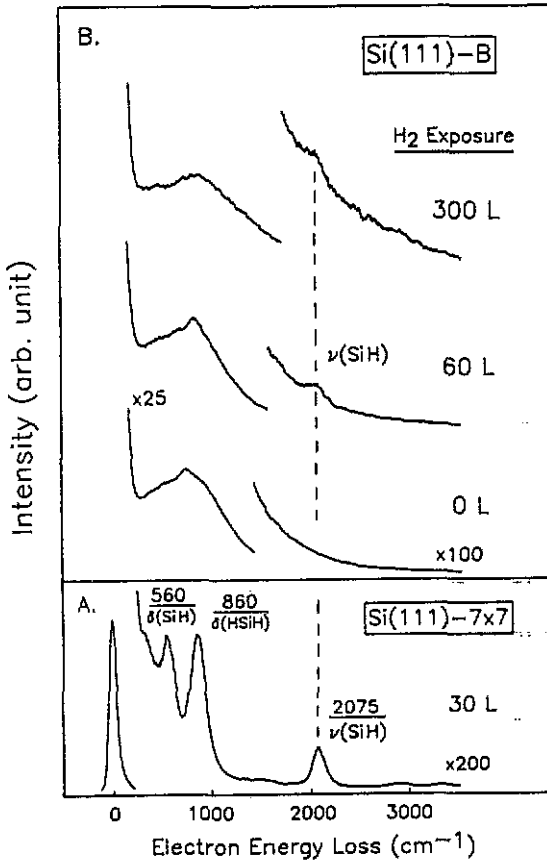


Figure 11. Comparison of HREELS behaviour of Si(111)-(7 $\times$ 7) and Si(111)-B toward atomic hydrogen [39].

ments involving the use of HREELS as a detector of hydrogen adsorption on Si(111) and on Si(111)-B clearly show that the reactivity of the boron-modified silicon surface is markedly reduced compared to Si(111)-(7 $\times$ 7). Figure 11 shows a comparison by HREELS of the two surfaces. A lower intensity of the Si-H mode for the boron-modified surface is observed, in comparison to the unmodified surface. The presence of some Si-H species on the boron-modified surface is probably due to the presence of undoped Si sites (defects in the  $\sqrt{3} \times \sqrt{3}$  R30° overlayer). The lower reactivity toward atomic hydrogen completely quenches the ability of the surface to be etched by atomic hydrogen, since no  $\text{SiH}_4$  is observed to thermally desorb at high atomic hydrogen exposures [10], in contrast to the behaviour of Si(111)-(7 $\times$ 7) [10]. Thus with spatial control of boron implantation into silicon, the passivation of atomic hydrogen etching might be useful in the processing of semiconductor devices.

#### 4. Conclusions

The involvement of dangling bonds in surface chemistry on covalently bonded substances has been investigated by various experimental methods. It has been found that silicon dangling bonds are capable, at low temperatures, of dissociating  $\pi$  bonds in hydrocarbon species and  $\sigma$  bonds in some molecules such as  $\text{NH}_3$ . The use of a group III subsurface dopant, like B, to passivate the surface chemistry of the silicon dangling bond has been demonstrated with reactive species such as  $\text{NH}_3$  and atomic hydrogen. It has been demonstrated that the chemisorption of reactive species often occurs by means of the initial production of a weakly-bound mobile precursor species.

#### Acknowledgments

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