

## An STM study of the chemisorption of $C_2H_4$ on $Si(001)(2 \times 1)$

A.J. Mayne <sup>a,b</sup>, A.R. Avery <sup>c</sup>, J. Knall <sup>a</sup>, T.S. Jones <sup>c</sup>, G.A.D. Briggs <sup>a</sup> and W.H. Weinberg <sup>d</sup>

<sup>a</sup> Department of Materials, Oxford University, Oxford OX1 3PH, UK

<sup>b</sup> Inorganic Chemistry Laboratory, Oxford University, Oxford OX1 3QR, UK

<sup>c</sup> Semiconductor IRC and Department of Chemistry, Imperial College, London SW7 2AY, UK

<sup>d</sup> QUEST and Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106, USA

Received 21 July 1992; accepted for publication 24 November 1992

The chemisorption of ethylene ( $C_2H_4$ ) on  $Si(001)(2 \times 1)$  at 300 K has been studied by scanning tunneling microscopy (STM) and spectroscopy (STS). Exposure of the surface to  $C_2H_4$  does not cause large scale rearrangement of the original Si surface atoms. The adsorption of individual molecules and changes in the local structure can, however, be observed. At low coverage, the  $C_2H_4$  molecules prefer to adsorb on alternate dimer sites creating either a local  $(2 \times 2)$  or  $c(2 \times 4)$  structure. The individual domains are relatively small ( $< 50 \text{ \AA}$ ) and the change in reconstruction cannot be detected by any diffraction technique. STS recorded from regions of the surface covered by adsorbates show the removal of the relatively weak  $\pi$ -bond formed by the dangling bonds and the participation of the dangling bond electrons in stronger  $sp^3$ -like bonds to the carbon atoms of the molecule after chemisorption. The  $(2 \times 1)$  dimer surface characteristic of clean  $Si(001)$  is restored upon heating the adsorbate covered surface. The pictures are consistent with a model in which the desorbed  $C_2H_4$  molecules leave restored dimers behind and the molecules which are left remain undissociated on the same type of dimer sites as before.

### 1. Introduction

There have been a number of studies of the interaction of both unsaturated and saturated hydrocarbons with Si surfaces. Although much of this has been stimulated by the technological importance of forming SiC films by chemical vapour deposition (CVD), there is also considerable interest in understanding the fundamental aspects of the adsorption of organic molecules on semiconductor surfaces. In general it has been shown that a carbon-carbon double (or triple) bond is essential for efficient reaction at the surface. On the  $Si(001)(2 \times 1)$  surface, for example, acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ) and propylene ( $C_3H_6$ ) all chemisorb on the surface, whereas neither methane ( $CH_4$ ), nor propane ( $C_3H_8$ ) undergo any form of reaction [1].

The adsorption of  $C_2H_4$  with  $Si(001)$  has been studied by several groups [2–5]. On clean  $Si(001)(2 \times 1)$ ,  $C_2H_4$  chemisorbs non-dissociatively throughout the temperature range 77–600

K [3]. Similar results have been obtained on the  $9^\circ$  vicinal (001) surface and also on the low index  $(001)-c(2 \times 4)$  surface [3]. It has been suggested, from high resolution electron energy loss spectroscopy (HREELS), that the adsorbed molecules adopt near  $sp^3$  hybridization and are di- $\sigma$  bonded (although this implies saturation of the dangling bonds and a remarkably long C–C bond length) [3]. At full coverage, it is believed that a single  $C_2H_4$  molecule bonds to each Si dimer site [4]. Isotopic mixing temperature-programmed desorption (TPD) studies (forming  $^{13}CH_2=^{12}CH_2$ ) demonstrated that less than 1% mixing of the isotopes occurred between 500 and 950 K thus eliminating the possibility of any surface dissociation and recombination processes taking place, such as  $2CH_{2(a)} \rightarrow C_2H_{4(a)} \rightarrow C_2H_{4(g)}$  [5]. The chemisorption of  $C_2H_4$  on  $Si(001)(2 \times 1)$  occurs via a mobile precursor mechanism. The activation energy difference for desorption and chemisorption from the precursor is  $2.9 \text{ kcal mol}^{-1}$  ( $0.13 \text{ eV/molecule}$ ) and the activation energy for de-

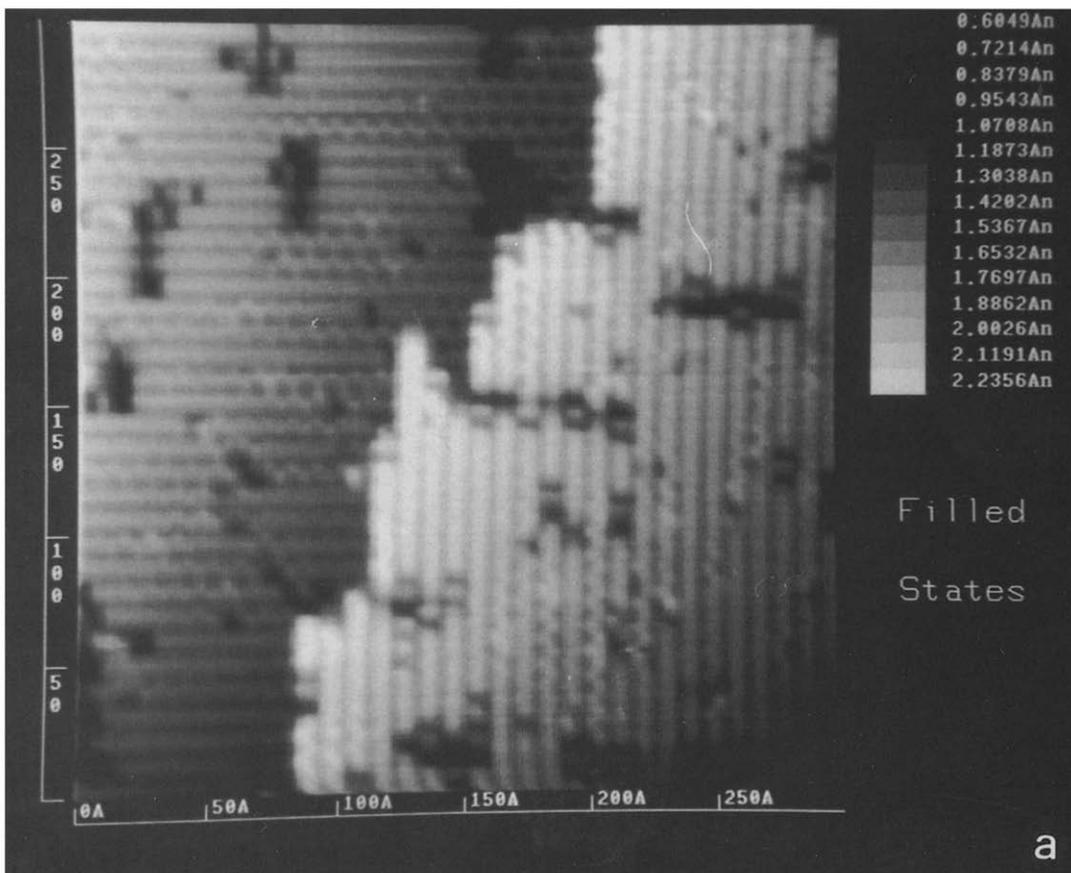


Fig. 1. Filled and empty states images of a clean  $Si(001)(2 \times 1)$  surface at a specimen bias and tunneling current of (a)  $-2$  V,  $1.0$  nA, and (b)  $+2$  V,  $1.0$  nA.

sorption from the chemisorbed state is only  $38 \text{ kcal mol}^{-1}$  ( $1.6 \text{ eV/molecule}$ ), sufficiently low to eliminate almost all dissociation before desorption [6]. Desorption occurs around  $550 \text{ K}$  with less than  $2\%$  of the molecules undergoing any dissociation. Consequently  $C_2H_4$  is not a good source of carbon for the formation of SiC by chemical vapour deposition.

None of these previous studies have examined the character and location of the *individual* molecules adsorbed on the Si surface. Scanning tunneling microscopy (STM) is a unique technique, providing real space information, for such a study. Although there have been many STM investigations of clean semiconductor surfaces [7], there are relatively few attempts in the literature to study molecular adsorbates [8]. In this paper

we present such a study for the adsorption of  $C_2H_4$  on  $Si(001)(2 \times 1)$ . This represents an ideal model adsorption system for study by STM because of the detailed information already available from other surface sensitive techniques.

## 2. Experimental

The experiments were carried out in a UHV chamber (base pressure  $< 2 \times 10^{-10} \text{ mbar}$ ) equipped with low energy electron diffraction (LEED), Auger electron spectroscopy, TPD and STM (Omicron). A fast entry load lock enabled efficient transfer of samples and tips. The tungsten tips were prepared by an electrochemical etching technique. The n-type ( $\rho = 0.02 \text{ } \Omega \cdot \text{m}$ )

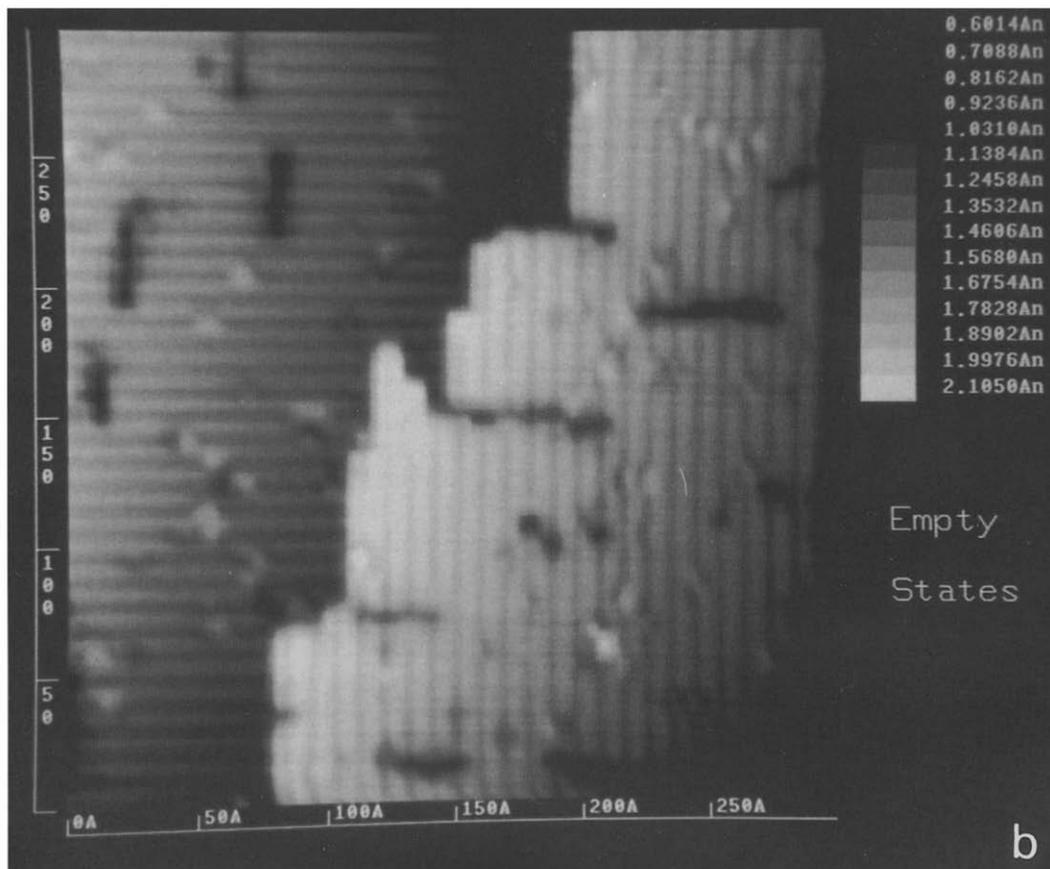


Fig. 1. Continued.

$Si(001)$  substrates were degreased and cleaned by a wet-chemical oxide etch-regrowth procedure prior to insertion in vacuum. Once under UHV, they were degassed by electron bombardment heating at  $650^\circ\text{C}$  and finally heated by direct heating to  $870^\circ\text{C}$  for  $\sim 2$  min in order to remove the surface oxide. Sample temperatures were measured using a pyrometer. The clean surface was characterised by the appearance of a two domain  $(2 \times 1)$  LEED pattern and the absence of any impurities in Auger. Adsorption studies were carried out by exposing the  $Si(001)(2 \times 1)$  surface to  $C_2H_4$  (Messer-Griesheim, 99.95% purity) at 300 K. Surface coverages were determined by TPD and with reference to previous studies of this adsorption system [6]. There were no apparent changes in the LEED pattern after adsorption.

The STM images shown in this paper were

taken at sample biases of  $+2$  and  $-2$  V, thus imaging both empty and filled states. One bias was used for the forward scan and the other for the reverse scan so that, except for a small amount of hysteresis, the two images can be compared directly. Typical tunneling currents were 1–2 nA. Scanning tunneling spectroscopy (STS) measurements were made by freezing the tip height and measuring  $I$  versus  $V$  over 51 steps from  $-2$  to  $+2$  V. Normalised conductivity  $(dI/dV)/(I/V)$  curves were calculated from  $I$  versus  $V$  data where  $I/V$  in the denominator has been broadened into the band gap [9].

### 3. Results and discussion

Fig. 1 shows both the filled and empty states STM topographs of clean  $Si(001)$  with the characteristic  $(2 \times 1)$  dimer reconstruction. In these par-

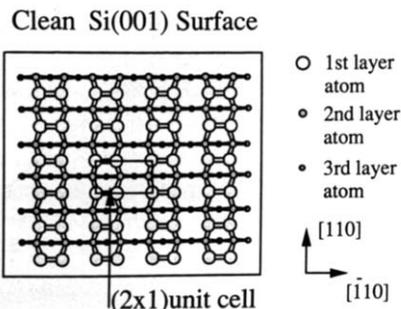


Fig. 2. The  $(2 \times 1)$  unit cell for clean  $Si(001)$  arising from the pairing of neighbouring surface Si atoms into dimers.

ticular images a step edge, a quarter of a lattice constant high, can easily be seen. This surface has been the subject of a number of detailed STM studies [10]. The  $(2 \times 1)$  periodicity arises from

the pairing of surface Si atoms into dimers in order to reduce the excess energy associated with the dangling bonds (fig. 2). The dimers tend to line up in straight rows, the most prominent defects on a low-index surface are not usually steps, but trenches of missing dimers which are irregular but roughly perpendicular to the dimer rows. In the image shown, the dimer rows change direction by  $90^\circ$  from the terrace above the step to the terrace below it. The “cigar” shaped appearance of the dimers in the filled states image (fig. 1a) is consistent with previous studies and arises because, at a sample bias of  $-2$  V, the image is associated with the  $\pi$ -bonding orbital of the rehybridized dangling bonds. The electron density of this orbital is localised between the Si atoms of the dimer. Some pictures seem to show

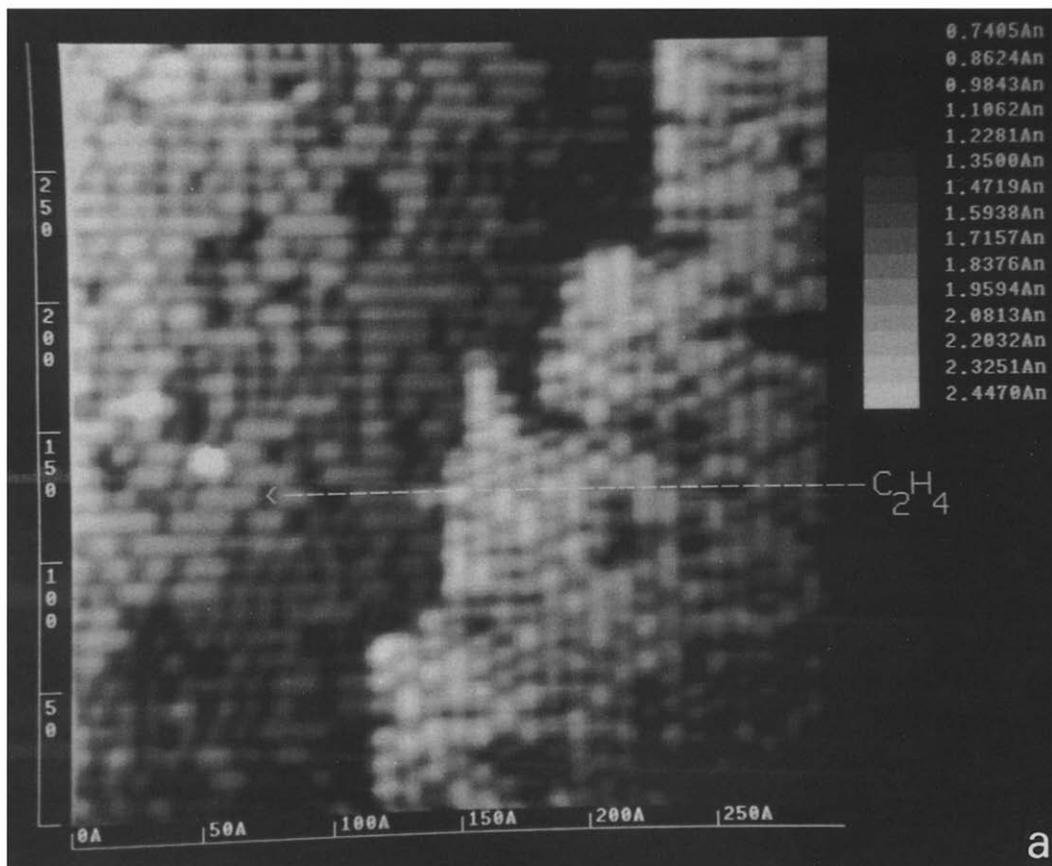


Fig. 3. Filled and empty states images of the  $Si(001)(2 \times 1)$  surface exposed to 2 L of  $C_2H_4$  recorded at a specimen bias and tunneling current of (a)  $-2$  V, 1.0 nA, and (b)  $+2$  V, 1.0 nA.

that the individual atoms of the dimer can be imaged at a negative sample bias [11]. We believe this to be a tip related effect since we have also obtained a similar image prior to a tip change midway through a scan. Although most of the rows in fig. 1a appear symmetrical, some of them show a zig-zag structure [10,12]. A recent STM study by Wolkow [13] has shown that images of the  $Si(001)(2 \times 1)$  surface taken at 120 K reveal an increasing number of buckled dimers compared to those recorded at 300 K in agreement with tight binding calculations [14].

Filled and empty state STM images of the  $Si(001)(2 \times 1)$  surface, that has been exposed to 2 L of  $C_2H_4$ , are shown in fig. 3. These images were recorded over essentially the same area of the surface as those shown in fig. 1 for the clean  $Si(001)(2 \times 1)$  surface. The same dimer positions

can be identified in both images using features in the step and missing dimers as reference points. Upon comparing both the filled and empty states images, both before and after adsorption, it can be seen that adsorption does not appear to cause large scale re-arrangement (i.e. displacements larger than interatomic distances) of the original Si surface atoms. The location of individual adsorbed molecules can, however, be observed. In the filled states image (fig. 3a), they appear as slightly shorter objects at the original dimer positions. In the empty states image (fig. 3b), they appear as bright objects on the dark rows between the brighter wider rows representing the antibonding orbitals of the Si dangling bond.

TPD measurements have shown that the adsorption and desorption of  $C_2H_4$  on  $Si(001)(2 \times 1)$  is a first-order process indicating insignifi-

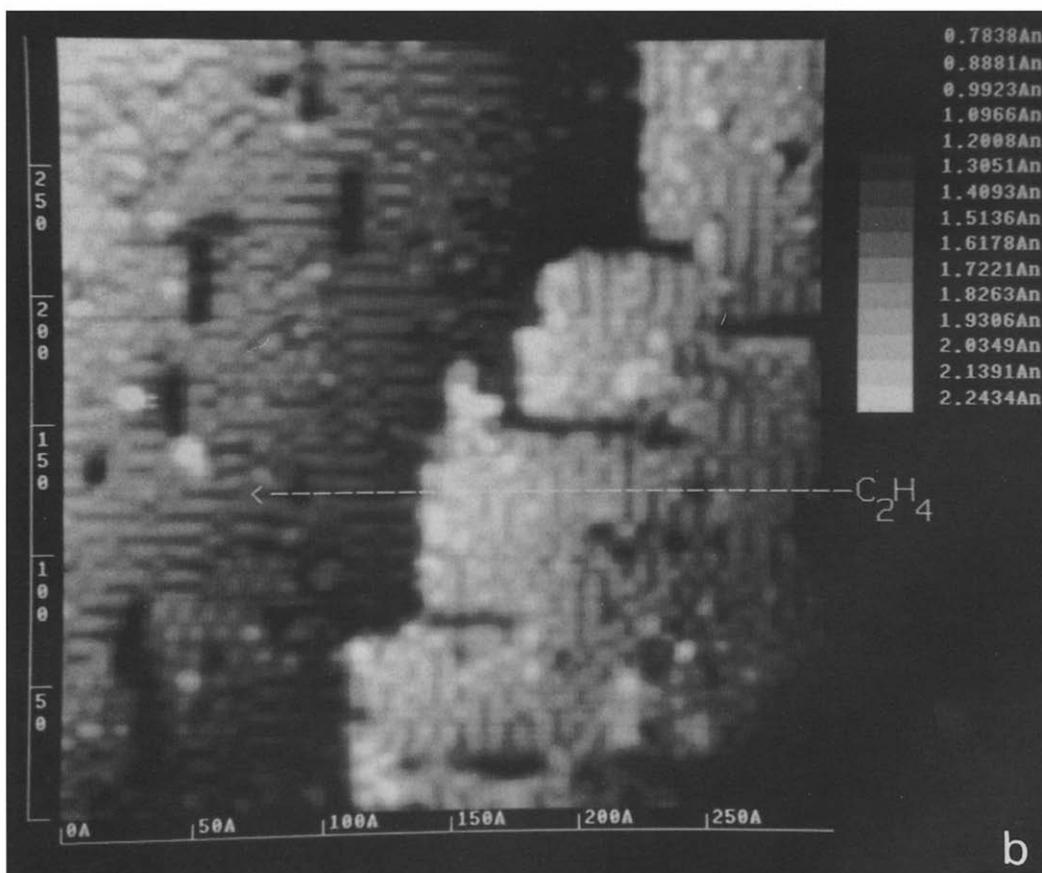


Fig. 3. Continued.

cant interaction between molecules [6]. This leads us to believe that each altered dimer site corresponds to the adsorption of one single molecule on top of the dimer. The most plausible orientation of the molecule would then be with the C–C bond axis aligned along the Si dimer axis. It is possible that the molecules insert into the dimer bond, cleaving it, forming a structure with  $sp^3$  hybridized C and Si atoms. Both the Si–Si  $\sigma$ -bond and the partial  $\pi$ -bond, formed by delocalisation of the remaining dangling bonds, would then be significantly disrupted [6]. A recent *ab initio* molecular dynamics calculation by Fisher et al. [15] supports the weakening of the dimer bond upon adsorption, although the increase in the Si–Si bond length is relatively small.

Despite the TPD results, the distribution of molecules on the surface does in fact indicate some interaction between the adsorbed molecules. This is evident in fig. 4 in areas which have a relatively high density of adsorbates. The molecules prefer to occupy every second rather than neighbouring dimers along a dimer row. This repulsive interaction may be an effect of local strain induced by the adsorption of the molecules and transmitted through the substrate to the neighbouring dimers. Depending on whether the molecules adsorb in a configuration where they line up next to each other across the dimer rows or not, they locally form a  $(2 \times 2)$  or  $c(2 \times 4)$  structure (fig. 5). The domains over which the structure remains the same are small ( $< 50$

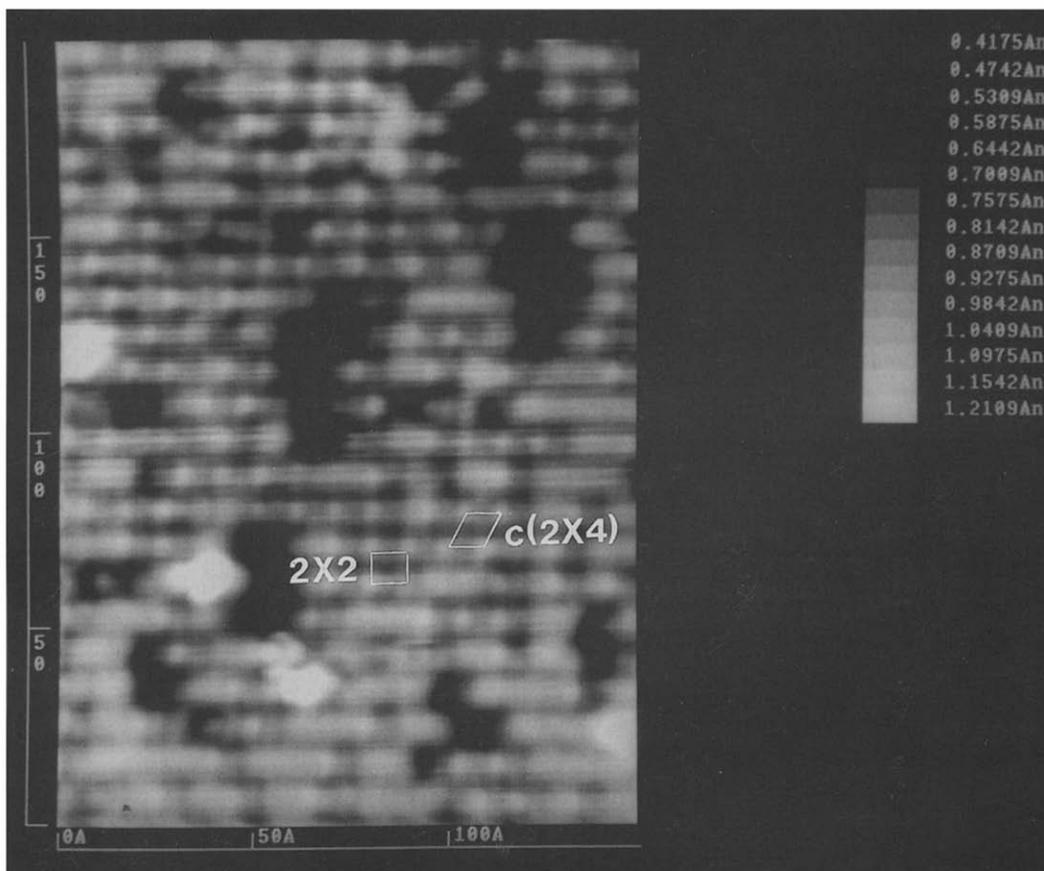


Fig. 4. A filled states image, recorded at a specimen bias of  $-2$  V and a tunneling current of  $1.0$  nA, of the  $Si(001)(2 \times 1)$  surface after exposure to  $2$  L of  $C_2H_4$  showing regions with both local  $(2 \times 2)$  and  $c(2 \times 4)$  structures.

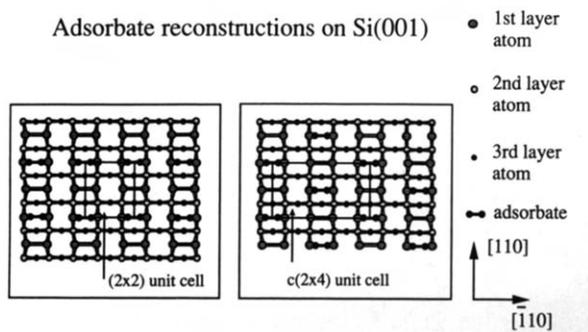


Fig. 5. The  $(2 \times 2)$  and  $c(2 \times 4)$  unit cells for  $C_2H_4$  adsorbed on  $Si(001)(2 \times 1)$ .

Å) and only the diffraction spots common to both reconstructions are revealed in LEED. This alternate adsorption site picture is particularly clear in the filled states image shown in fig. 6, which was recorded after the surface had been exposed to 6 L of  $C_2H_4$ .

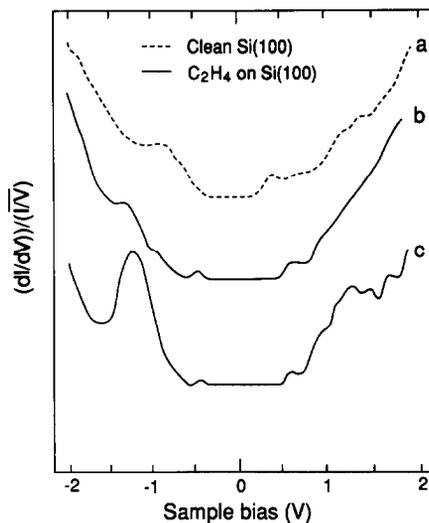


Fig. 7.  $dI/dV$  versus  $V$  tunneling spectra from a  $Si(001)(2 \times 1)$  surface spectra (a) before, and (b,c) after exposure to 16 L of  $C_2H_4$ . The spectra from the exposed surface were obtained (b) over adsorbed molecules, and (c) over free dimers.



Fig. 6. A filled states image, recorded at a specimen bias of  $-2$  V and a tunneling current of  $1.0$  nA, of the  $Si(001)(2 \times 1)$  surface after exposure to 6 L of  $C_2H_4$  showing clearly the alternate adsorption site picture.

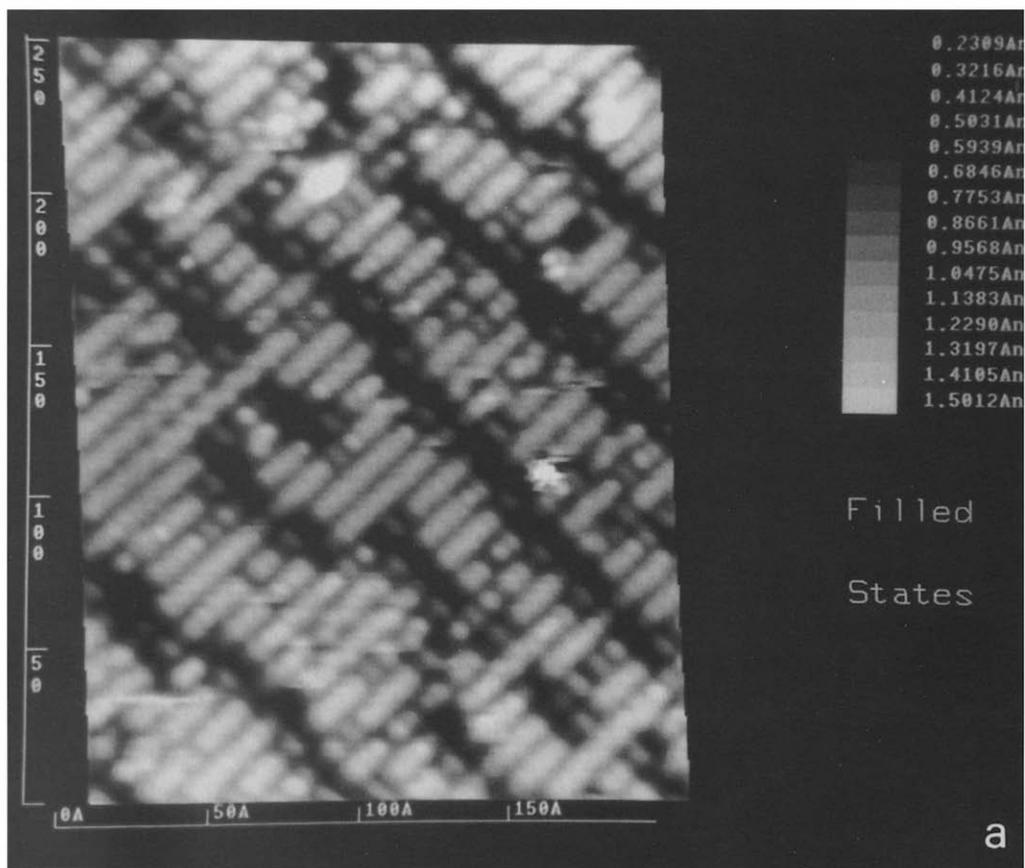


Fig. 8. Filled and empty states images of the  $C_2H_4$  covered  $Si(001)(2 \times 1)$  surface after partial thermal desorption recorded at a specimen bias and tunneling current of (a)  $-2$  V,  $1.0$  nA, and (b)  $+2$  V,  $1.0$  nA.

STM images have also been recorded at higher exposures ( $> 6$  L) which indicate that molecules can adsorb on neighbouring dimers. Even after very large exposures ( $> 100$  L), however, the fraction of molecules on neighbouring dimers is still relatively small. Previous work has indicated that the saturation fractional coverage of  $C_2H_4$  is  $\sim 0.80$  molecules per Si dimer, i.e. per  $(1 \times 2)$  unit cell [6]. It has been suggested that this corresponds to one  $C_2H_4$  molecule per dimer on a perfect, defect-free  $Si(001)(2 \times 1)$  surface [6]. Work is currently in progress in which the STM is being used to try to understand the adsorption behaviour of the  $C_2H_4$  molecules at higher coverages and resolve this apparent discrepancy.

Tunneling spectra recorded at specific locations over the  $Si(001)(2 \times 1)$  surface after expo-

sure to  $16$  L of  $C_2H_4$  are shown in fig. 7 together with a spectrum measured over a Si dimer on a clean surface (fig. 7a). For the adsorbate covered surface, spectra were recorded over molecules (fig. 7b) and over free dimers (fig. 7c). The  $(dI/dV)/(I/V)$  curves approximate the local density of states. The clean dimer reconstructed surface exhibits a surface conductivity gap of  $\sim 0.8$  eV which is slightly smaller than the bulk band gap ( $1.1$  eV). The positions of the observed states below and above the gap are in agreement both with previous STS results [16] and photoemission and inverse photoemission [17,18] measurements which indicate states at  $-0.7$  and  $+0.3$  eV relative to the Fermi energy. In the spectrum recorded from adsorbed  $C_2H_4$  molecules (fig. 7b), there is a significant decrease in the intensity of the states

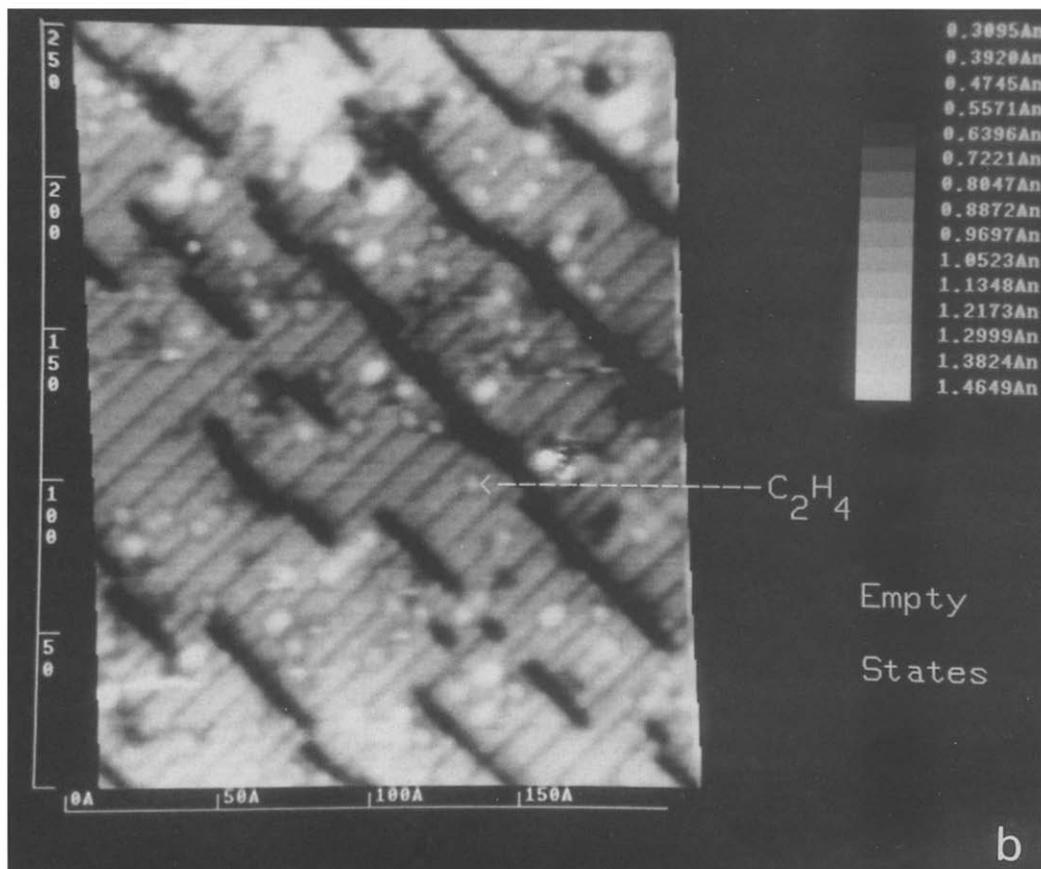


Fig. 8. Continued.

observed on the clean surface and both the highest filled and lowest empty states are further away from the Fermi level. This is consistent with the removal of the relatively weak  $\pi$ -bond formed by the dangling bonds and the participation of the dangling bond electrons in stronger  $sp^3$ -like bonds to the carbon atoms of the molecule after chemisorption. Spectra recorded over free Si dimers between two adsorbate molecules (fig. 7c) show that the energy of the highest filled states is reduced with respect to the dimers of the clean surface. This is consistent with the fact that adsorption onto a dimer next to an occupied dimer is less favourable.

When the  $Si(001)(2 \times 1)$  surface covered with  $C_2H_4$  is heated the molecules desorb intact [6]. We have performed experiments where the adsorbate covered sample was removed from the

STM and heated to partially or completely remove the adsorbed layer, the amount desorbed being monitored with the mass spectrometer [12]. STM images recorded after partial desorption (fig. 8) show that the desorbed  $C_2H_4$  leaves restored dimers behind and the molecules that are left on the surface remain undissociated on the same type of sites as prior to the heating of the sample.

#### 4. Conclusions

STM has been used to identify the adsorption of individual  $C_2H_4$  molecules on  $Si(001)(2 \times 1)$ . Although exposure of the surface to  $C_2H_4$  does not cause large scale rearrangement of the original Si surface atoms, changes in the local struc-

ture can be seen. The STM images support the model of a  $C_2H_4$  molecule adsorbed on top of a Si dimer. At coverages of less than one molecule per two surface dimers, the molecules prefer to occupy alternate sites along the dimer chain creating a mosaic structure with small domains of local  $(2 \times 2)$  or  $c(2 \times 4)$  ordering. Work is currently in progress aimed at understanding the adsorption behaviour at higher coverages. STS data recorded above adsorbed molecules show the removal of the relatively weak  $\pi$ -bond formed by the dangling bonds and the participation of the dangling bond electrons in stronger  $sp^3$ -like bonds to the carbon atoms after chemisorption. Partial desorption of the adsorbate-covered surface shows that the desorbed molecules leave restored dimers behind and the molecules which are left on the surface remain undissociated on the same type of sites as before. The  $(2 \times 1)$  dimer surface characteristic of clean  $Si(001)$  is restored upon complete desorption of the adsorbed layer.

### Acknowledgements

This work was supported by SERC grants GR/E 60185 and GR/H 20855. It is part of a collaboration, supported by NATO grant No. CRG910189, between QUEST at UCSB, and the Semiconductor IRC in London. The work at UCSB is supported by the NSF Science and Technology Centre for Quantized Electronic Structures, Grant No. DMR 91-20007. Discussions with Andrew Fisher, Adrian Sutton, Allen Hill and Bruce Joyce are gratefully acknowledged.

### References

- [1] M.J. Bozack, P.A. Taylor, W.J. Choyke and J.T. Yates, Jr., *Surf. Sci.* 177 (1986) L933.
- [2] F. Bozso, J.T. Yates, Jr. W.J. Choyke and L. Muehlhoff, *J. Appl. Phys.* 57 (1985) 2771.
- [3] J. Yoshinobu, H. Tsuda, M. Onchi and M. Nishijima, *J. Chem. Phys.* 87 (1987) 7332.
- [4] C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke and J.T. Yates, Jr., *J. Appl. Phys.* 67 (1990) 3693.
- [5] C.C. Cheng, W.J. Choyke and J.T. Yates, Jr., *Surf. Sci.* 231 (1990) 289.
- [6] L. Clemen, R.M. Wallace, P.A. Taylor, M.J. Dresser, W.J. Choyke, W.H. Weinberg and J.T. Yates, Jr., *Surf. Sci.* 268 (1992) 205.
- [7] See for example, R.J. Hamers, *Ann. Rev. Phys. Chem.* 40 (1989) 531.
- [8] Ph. Avouris, *J. Phys. Chem.* 94 (1990) 2246.
- [9] R.M. Feenstra, in: *Scanning Tunneling Microscopy and Related Methods*, Eds. R.J. Behm, N. García and H. Rohrer (Kluwer, Dordrecht, 1990) p. 211.
- [10] R.M. Tromp, R.J. Hamers and J.E. Demuth, *Phys. Rev. Lett.* 55 (1985) 1303; R.J. Hamers, R.M. Tromp and J.E. Demuth, *Phys. Rev. B* 34 (1986) 5343.
- [11] K. Sugihara, A. Sakai, Y. Kato, Y. Akama, N. Shoda, H. Tokumoto and M. Ono, *J. Vac. Sci. Technol. B* 9 (1991) 707.
- [12] G.A.D. Briggs, J. Knall, A.J. Mayne, T.S. Jones, W.H. Weinberg and A.R. Avery, *Nanotechnology*, in press.
- [13] R.A. Wolkow, *Phys. Rev. Lett.* 68 (1992) 2636.
- [14] D.J. Chadi, *Phys. Rev. Lett.* 43 (1979) 43.
- [15] A.J. Fisher, P.E. Blöchl and G.A.D. Briggs, to be published.
- [16] R.J. Hamers, Ph. Avouris and F. Bozso, *Phys. Rev. Lett.* 59 (1987) 2071.
- [17] F.J. Himpsel and T. Fauster, *J. Vac. Sci. Technol. A* 2 (1984) 815.
- [18] T. Fauster and F.J. Himpsel, *J. Vac. Sci. Technol. A* 1 (1983) 1111.