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Reconstruction of Si(113) by adsorption of atomic hydrogen

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Abstract. The (113) face of Si is highly stable due to rehybridization of dangling bonds. We show that adsorbed atomic hydrogen upsets this stability. Structural models are provided for the resultant mixed 2×2 and 2×3 surface.

1. Introduction

With the characterization of many clean Si surfaces via scanning tunnelling microscopy (STM), attention has now turned to the effect of adsorbates. A number of studies with implications for heterogeneous reactions have recently appeared [1, 2]. STM is particularly useful since it provides direct information about both the electronic and topographic changes brought about by chemical reactions [3]. Atomic hydrogen is the simplest adsorption species and STM investigations of H-adsorption on the Si(100) [4] and Si(111) [5, 6] surfaces have already been reported. We have studied the adsorption of H on the relatively high index Si(113) surface using STM and current imaging tunnelling spectroscopy (CITS). Another study using low energy electron diffraction (LEED) has reported a transformation to a 3×1 -H structure [7]. Here we present preliminary results which show that H-adsorption at very low coverages induces a change in the surface reconstruction from 3×2 , found on the clean Si(113) surface [8], to a mixture of $2\times n$ domains. So far we have not observed a 3×1 -H structure using STM.

2. Experimental procedure

The experiments were performed in an Omicron ultra-high vacuum system with a base pressure of $\sim 1\times 10^{-10}$ Torr. Surface order and lack of contamination were confirmed by LEED and Auger electron spectroscopy respectively. The samples were 2×10^{18} cm $^{-3}$ Sb-doped Si(113) wafers. Exposure to atomic H was achieved by decomposing high purity H $_2$ on a 1700 K tungsten filament positioned 4 cm directly in front of the sample. The exact coverage of atomic H was not measured. Typical exposure conditions were 3 minutes with a H $_2$ pressure of 2×10^{-7} Torr. Assuming that one in four H $_2$ molecules striking the filament was dissociated [9] and a sample sticking coefficient of unity, we estimate from kinetic theory that our exposure conditions correspond to a coverage of approximately 2×10^{14} H atoms cm $^{-2}$. The sample temperature was held at about 650 K during exposure and also for 2-5 minutes afterwards to allow the surface to equilibrate prior to examination. We reproduced our results using a number of tips and samples.

3. Results

In figure 1 we present high resolution STM images of the surface before and after H-exposure. Both images were recorded at a constant tunnelling current I_t of 2 nA and a sample bias voltage V_S of -2 V which corresponds to imaging filled samples states. The $3\times$ periodicity in the $[\bar{1}10]$ direction of the clean surface has changed to a $2\times$ periodicity after exposure to H, which we also observed in LEED. In the $[33\bar{2}]$ direction the repeat distance of similar features apparent in figure 1(b) is either the same or 1.5 times that in figure 1(a) as indicated by the two dashed boxes A and B. We find that the surface has broken up into small A- or B-type domains leading to a variety of different boundaries. Heating the surface to 1100 K restored the clean 3×2 surface.

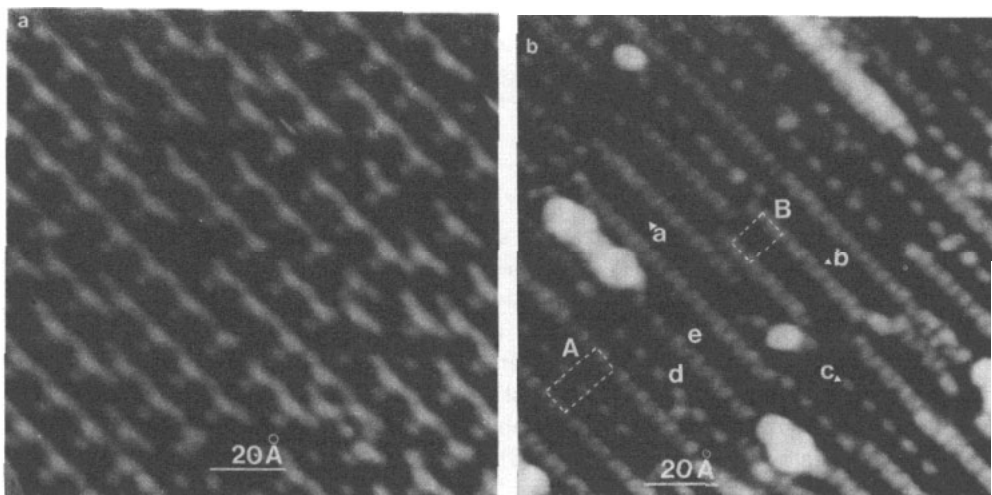


Figure 1. Filled state STM images of the Si(113) surface (a) before exposure and (b) after adsorption of approximately 2×10^{14} H atoms cm^{-2} . Both images were recorded with $I_t = 2$ nA and $V_S = -2$ V. The $[\bar{1}10]$ direction lies along the prominent rows.

In general, we found that acquiring images of empty states ($V_S > 0$) was more difficult than for filled states ($V_S < 0$) and frequently resulted in a tip crash. Figure 2 shows two STM images of identical areas recorded at $V_S = -2$ V and $+2$ V respectively with $I_t = 2$ nA. These images were obtained under similar exposure conditions to figure 1(b). Although more disorder is present, we can identify two of the features also present in the earlier image. These are labelled 'b' and 'c' respectively and similarly in figure 1(b). We find that feature 'c' in figure 2(a) appears as two bright areas in figure 2(b) (marked ' c^{+2V} '), giving rise to an apparent $1\times$ periodicity in the $[\bar{1}10]$ direction, while feature 'b' is resolved as distinct rings in the empty state image.

Figure 3 shows normalized differential tunnelling conductance spectra for five different sites on the H-exposed surface, obtained by CITS. The stabilization voltage and current for feedback were -2 V and 2 nA respectively. For each spectrum the I-V characteristic was averaged over several equivalent sites. The five locations are marked in figure 1(b). All spectra show a state at approximately -1 V, though it appears as a weaker shoulder in spectra 'd' and 'e'. In addition, spectra 'a', 'b', 'd' and 'e' reveal a small state at around $+1.2$ V which does not appear in spectrum 'c'. None of these sites contributed to states in the band gap.

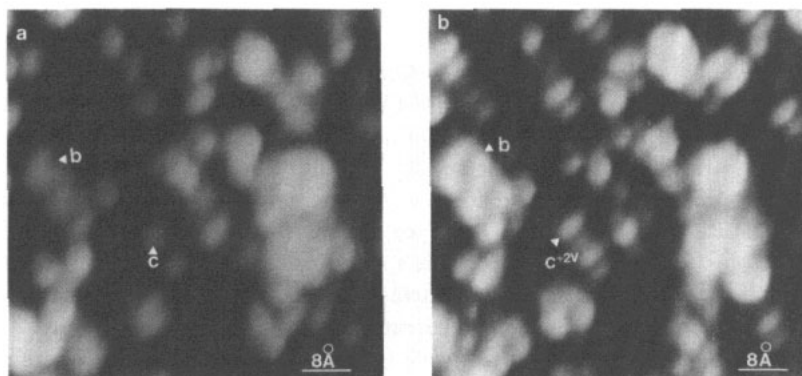


Figure 2. (a) Filled state STM image of the Si(113) surface recorded with $I_t = 2$ nA and $V_S = -2$ V after H-exposure. (b) Empty state STM image of the Si(113) surface recorded with $I_t = 2$ nA and $V_S = +2$ V after H-exposure. Both images are of exactly the same area and oriented in the same way as figure 1.

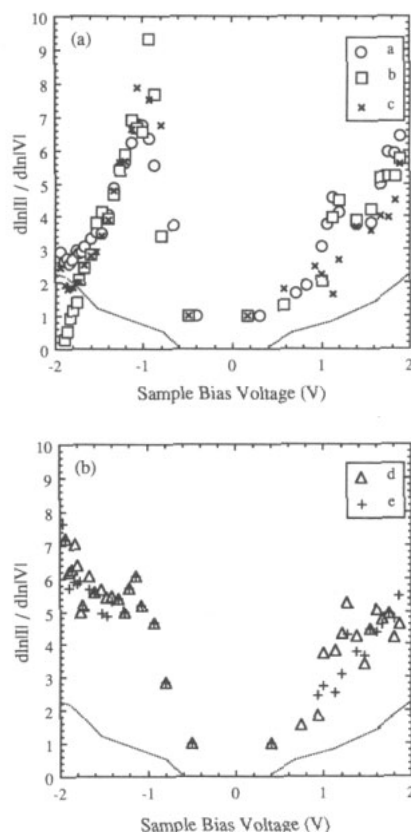


Figure 3. Tunnelling spectra, taken on the H-exposed Si(113) surface, at five different sites. The sites (labelled by letters) are shown in figure 1(b). The dotted lines are for reference and roughly follow the calculated silicon bulk density of states (see [3]).

4. Discussion

All the spectra shown in figure 3 differ from those obtained for the clean surface in having no electronic state at +0.4 V. This state has been shown to be strongly associated with atoms with single dangling bonds (DBs) surrounding the edges of the deep holes in the clean 3×2 surface [8]. A rehybridization of these atoms towards sp^2 has been proposed to account for the low energy of the clean surface [8]. Loss of the +0.4 V state for the H-exposed surface is consistent with a saturation of the DBs on these atoms, causing them to become sp^3 hybridized. Such a process would undermine the structural stability of a 3×2 surface so that some rearrangement of the surface atoms may be expected. Such a rearrangement is evident from figure 1.

The state at about -1 V in figure 3 is seen on the clean surface where it also appears strongest on the bright features in the filled state images [8]. This suggests that similar structural units may be present on the clean and H-exposed surfaces and that many of the DBs on atoms uppermost in the surface are probably still unsaturated after H-exposure. This is also expected, as less than one monolayer of H has been adsorbed.

In figure 4 we present ball-and-stick models of the surface, based on our data. The dashed boxes on the models correspond to the dashed boxes in figure 1(b). Most of the features present in figure 1(b), including boundaries, can be accounted for in terms of the structural units shown in figures 4(b) and 4(c), which are labelled accordingly. The empty state image [figure 2(b)] provides further evidence for this structural assignment. The apparent $1 \times$ periodicity is consistent with imaging the DBs marked 'c^{+2V}' in figure 4(b), while the observed rings are compatible with the antibonding states of the tetramers marked 'b' in figures 4(b) and (c).

For the 2×2 cell shown in figure 4(c), our estimate of the surface coverage of H corresponds to saturating only two of the eight DBs, which supports the suggestion that many of the surface DBs are unsaturated. We observe from figure 1(b) that feature 'a' is frequently absent and also that there are marked dark regions either side of feature 'c'. Without better empty state images as well as data for other coverages it is difficult to make a definite statement about the preferred adsorption site for H. However, by comparison of the dark areas in figure 1(b) with figures 4(b) and 4(c), we speculate that there may be some preference for H to saturate (111)-type DBs rather than (100)-type DBs associated with surface dimers. We note that hydrogen desorption studies on Si(111) [9] and Si(100) [10] indicate that H atoms are more strongly bound on (111) sites than (100) sites since they desorb at higher temperatures.

The peak at +1.2 V in figure 3 occurs at the same energy as a peak assigned to a Si-H antibonding state by Hamers *et al* [3]. Our peak, however, is weaker and less broad; furthermore, it is also seen to occur at positions which may correspond to unsaturated DBs. Further experiments are needed to be able to assign this peak with confidence.

5. Conclusion

We have shown, using STM and CITS, that the stable 3×2 structure of clean Si(113) is altered by sub-monolayer adsorption of atomic hydrogen, and structural models have been provided for the observed 2×2 and 2×3 domains. The H is most likely adsorbed at DBs in the conduction band on the clean surface, which removes the 3×2 stability [8], and gives gross rearrangement of the surface. The adsorbed H appears to continue to prefer such sites which, on the (113) face, are mainly of (111)-type.

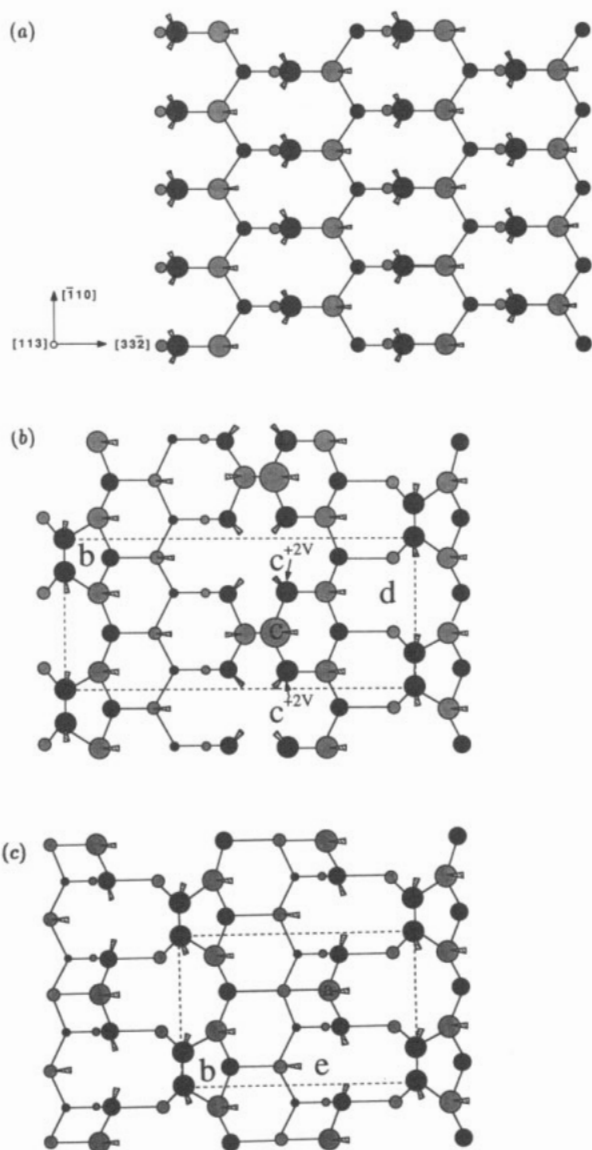


Figure 4. Ball-and-stick models showing (a) the bulk terminated Si(113) surface, (b) a 2×3 unit cell corresponding to box A in figure 1(b), and (c) a 2×2 unit cell corresponding to box B in figure 1(b).

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