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Surface structures on cleaved silicon by scanning tunnelling microscopy

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Abstract. Scanning tunnelling microscopy observations on cleaved Si surfaces in ultra-high vacuum have revealed several new features. These include much deeper measured valleys between the 2×1 rows, and occurrences of chain bridging. The higher resolution surface profile data are readily compatible with the three-bond scission model but are difficult to reconcile with a modified Pandey chain model. Several surface structures are possible.

1. Introduction

There have been a number of studies with scanning tunnelling microscopy (STM) of the surfaces of silicon obtained by cleavage at room temperature in ultra-high vacuum (UHV) [1–11]. Si cleaves preferentially along (111) planes and shows by low energy electron diffraction (LEED) a 2×1 reconstruction [12, 13]. Such a reconstruction has been observed quite clearly by STM [1–11]. In addition, the STM studies have shown the presence of adatoms on cleaved, uncontaminated surfaces, as well as regions of disorder [1], antiphase boundaries [5, 10] and areas of apparently different structure [7–9].

The nature of the 2×1 reconstruction has been investigated extensively [13, 14]. A number of authors have favoured a surface chain model based on one originally proposed by Pandey [15], but modified to possess considerable row buckling [16–18], which we call the modified Pandey (MP) model. This involves single-bond (shuffle plane) (111) cleavage. However, it has been argued that this structure is not in accord with crack healing data [19, 20], or the lateral onset of a heat-induced 5×5 structure adjoining the 2×1 [21], as well as other criticisms [13]. Strong evidence in favour of the MP model was adduced from considerable dispersion observed in the Γ–J direction in angle-resolved photoemission measurements [22, 23]. Nevertheless, two groups had reported an additional relatively flat band [24–27] which is in accord with an alternative model featuring surface chains and based on the cleavage passing through the three-bond glide (111) plane, called the three-bond scission (TBS) model [13]. A 'reverse-tilt' MP model has also been proposed [28].

The two structures are shown schematically in figure 1. Both feature corrugation of the surface into rows due to the presence of atom chains, leading to changes observed upon varying the tip voltage from positive to negative [2].

A feature that could distinguish between TBS and MP structures is the depth of the atomic valley between surface chains, which is theoretically about 0.13 nm for MP, but considerably more, about 0.225 nm, for TBS, both numbers depending on the precise coordinates of atomic nuclei including the amount of chain buckling assumed. Models are shown in figure 1.

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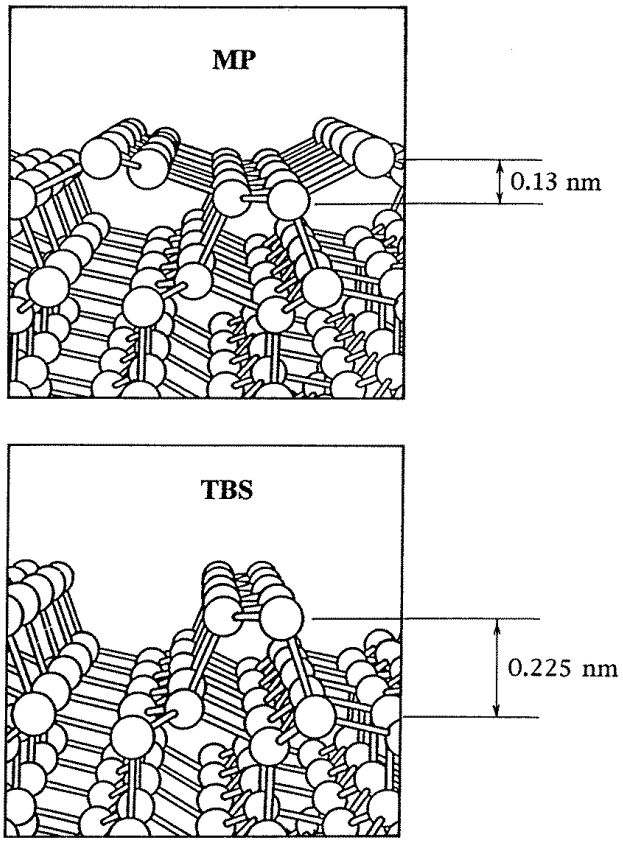


Figure 1. Schematic oblique-view diagrams of MP and TBS surface structures on cleaved Si.

Unfortunately, depth scans so far reported [1, 3, 9, 11] show corrugations across the rows of only 0.02 to 0.04 nm, the obtained depth resolution being limited by the sharpness of the STM tip. These measured corrugations are less than the theoretical values for either model. Therefore the models could not be distinguished by measured valley depths. In the course of our experiments we have, however, obtained on several occasions improved tip sharpness which provides values for the depth between rows which clearly distinguish between models.

Earlier LEED calculations [29, 30] had not given a convincing fit to LEED data for the MP models tested. Recently a renewed effort at fitting data has shown that while a reasonable fit is possible to a preferred data set using an adjusted MP model (but not the reverse tilt version), a significantly better fit is obtained by considering a mixture of both the MP and TBS models, and also other mixtures [31]. This has raised the possibility that the cleaved surface might possess more than one structure.

A row structure with spacing of 0.52 nm, different from that normally observed, has been reported for sections of closely spaced parallel terraces [7], and also an 8×1 structure if a different cleavage technique is used [11]. However, most areas seen by all STM authors show a parallel row structure of spacing approximately 0.65 nm, as expected from the LEED patterns.

As mentioned, the MP model is based on cleavage through the single-bond (111) surface, which may occur on regions that are different from those where cleavage might take place on

the three-bond plane, giving the TBS structure. If the two structures occur on different parts of the surface, with the regions separated by tear marks (multiple steps), it may be very difficult to determine by STM that they are different if the depth resolution is limited.

2. Experiment

Si wafers with (111) surfaces, thickness 0.45 mm, width 4 mm and length 26 mm were used. Most studies were carried out on boron-doped wafers of 0.001 Ω cm resistivity, but n-type samples of 2–8 Ω cm resistivity were also used to check that the results were general. In all, 28 cleavages were performed, of which half gave good topographs. A wafer strip was mounted horizontally in a small vice and cleaved in front of the horizontally mounted STM tip, then pushed through the vice for further cleavages. A multi-purpose arm was used both to perform cleavages by bending downwards the portion of specimen protruding through the vice, and also to push the specimen through for the next cleave. In addition, the arm could perform tip exchanges. The STM head was a Burleigh ARIS 4400 unit mounted in a UHV system that attained a pressure of lower than 6×10^{-11} Torr.

The STM tips were Pt–Ir alloy wires, electrochemically etched. Some oxidation might have occurred, but the topographs using these tips showed good resolution. On some occasions, 10 volt pulsing of the tip was carried out, but best resolution appeared to be obtained randomly. Most topographs were taken with a tip voltage of about +2 V relative to the surface, and current of about 6 nA for n-type samples, and at -0.8 to -2.2 V, with currents of several nA, for p-type samples. In order to obtain height data, constant current imaging was used. A given scan voltage and current were not varied during scans in order to avoid changing the conditions.

3. Results

Although regions of undistorted row structure existed, as shown in figure 2 (discussed below), many areas, particularly on the p-type samples, showed adatoms, each usually next to a vacancy, as shown in figure 3(a). Quite prevalent adatoms, as well as disorder, have been shown in all previous STM studies. In addition to disorder, surface vacancies and adatoms, other imperfections were noticeable. These included antiphase boundaries as reported already [10], plus chain-'bridging' phenomena as shown in figure 3(b), and also patches of lower height [32]. The height scale was calibrated at an atomic step, of known height 0.313 nm. The profile is shown in figure 4, giving a value of approximately 0.309 nm, confirming the instrument calibration. The measured step height did not change with mild filtering of the image, involving only plane removal and a 'morphological' noise filter.

Upon standing in vacuum for about an hour, no significant increase in adatoms was noted, consistent with the vacuum conditions, but the prevalence of chain-bridging regions, apparently always involving an adatom, appeared to increase. This could explain the weakening of half-integral-order LEED beams relative to the integral beams, which is observed when cleaved surfaces stand in high vacuum [33]. The row coherence areas reduce in size, thus affecting the fractional-order beams more than the integral beams, to which there are contributions from the sub-surface lattice.

4. Discussion

Figure 2 shows raw data scans of a defect-free 2×1 reconstruction on a (111) cleavage surface, plus profile scans along a [110] row, and also across the rows (of [112] type direction). Note that

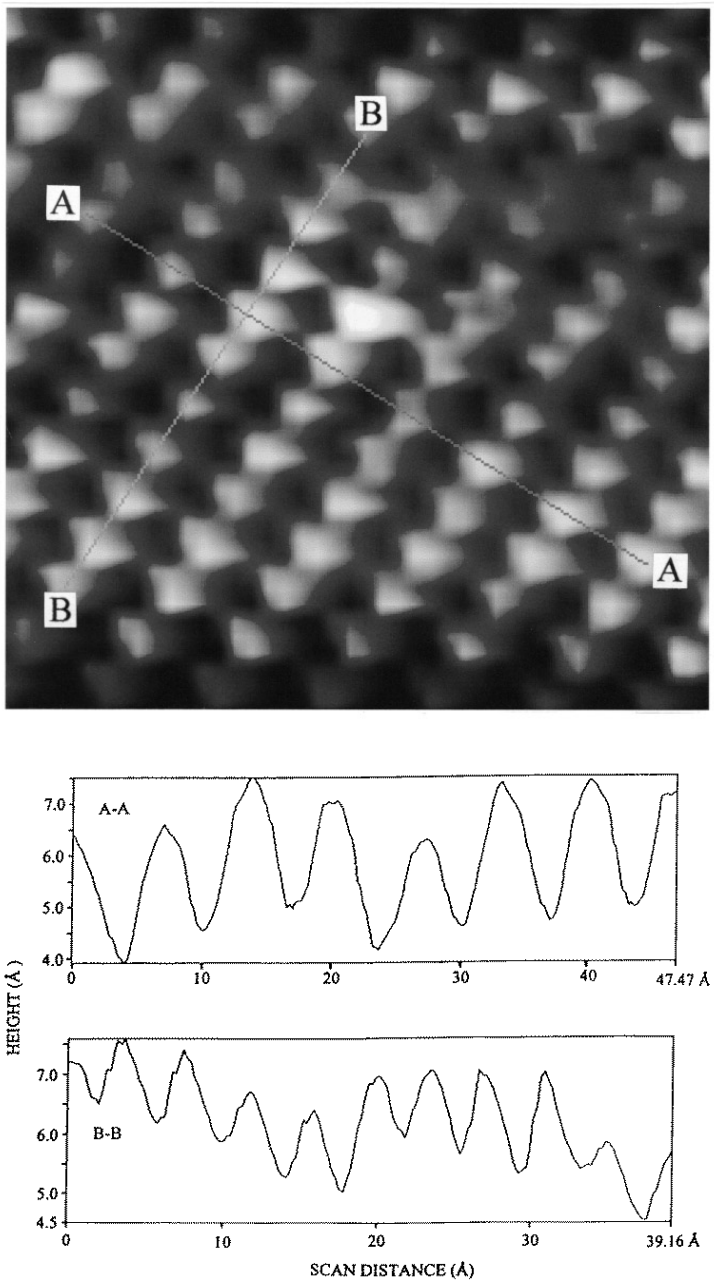
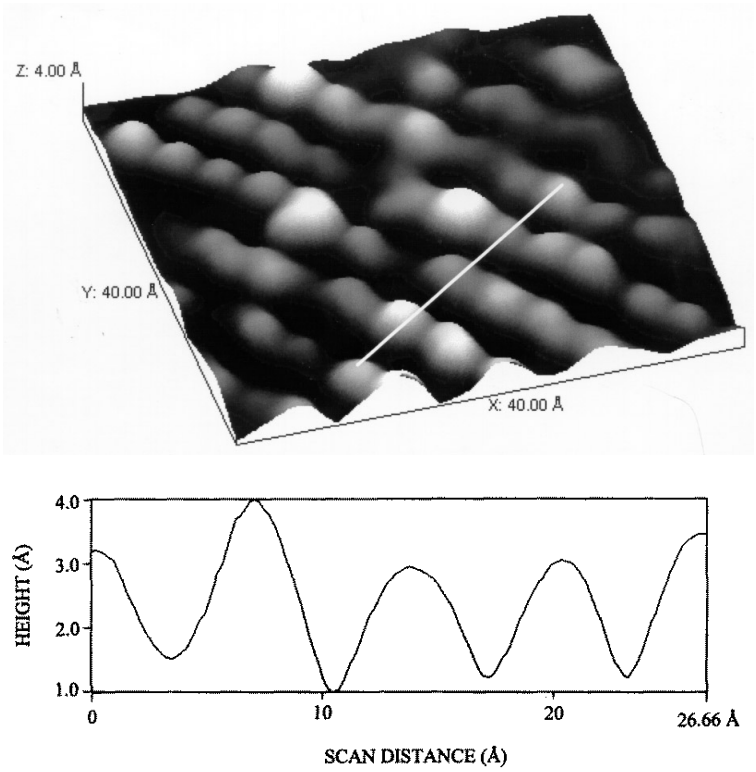
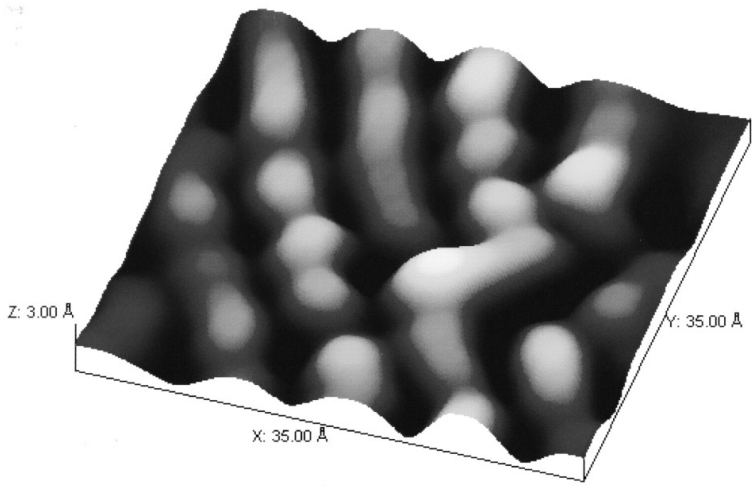


Figure 2. STM scan (5 nm × 5 nm) of defect-free region of vacuum-cleaved n-type Si surface. Tip voltage +2.06 V with respect to sample. Current 6.01 nA. The raw scan is shown, free from any computer filtering. Profile scans are shown across atomic rows A–A, and along the row B–B.

the scans shown represent original data without the application of noise filtering, which is usually performed to greatly improve the appearance of STM images. As seen, the maximum corrugation amplitude across the rows, line AA, is close to 0.25 nm. These values are consistent



(a)



(b)

Figure 3. (a) Oblique-view STM display showing adatom–vacancy pairs. The two prominent adatoms in the centre of the 4 nm × 4 nm scan have an associated vacancy in the adjoining row, on the left of the right hand adatom, and on the right of the left hand atom. A depth profile scan obtained from the original flat view topograph, along the white superimposed line, is also shown, displaying corrugation amplitudes of around 0.2 nm. Wafer is p-type, tip voltage −2.21 V, current 9.97 nA. (b) Oblique-view STM display, 3.5 nm × 3.5 nm, showing chain-bridging event, plus adatom and vacancy. Wafer is p-type, tip voltage is −0.79 V, current 3.62 nA.

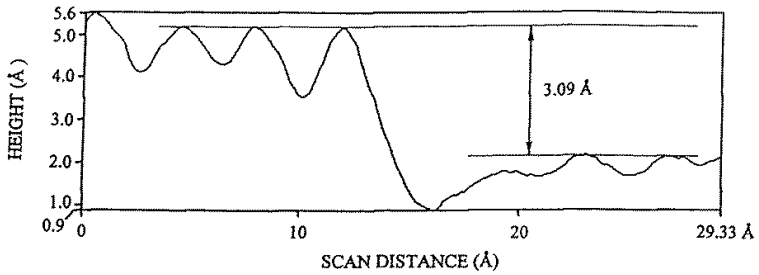


Figure 4. Profile of an atomic step, obtained from a scan subjected only to plane removal and morphological filtering. The raw data show the same step height.

with expectation (about 0.225 nm) from the TBS model, figure 1, but not from the MP model, which has a depth of about 0.13 nm from the upper buckled chain atom to the lower second layer atom [31]. The sharpness of the tip used for the data in figure 2 is also evident from the corrugation amplitude along the rows, line BB, of up to 0.11 nm in the raw data, much more than in previous reports [1, 3, 9, 11]. Of the 14 successful cleavage experiments, exceptionally good resolution as shown in figure 2 was obtained on three occasions, corresponding to different samples and tips. Thus the corrugation for the sample in figure 3(a), measured from the topograph, was about 0.2 nm. Because of different cleavage qualities and tip sharpnesses, it is not possible to give a reliable estimate of the prevalence of TBS regions on the cleaved surfaces.

An important question is the reliability and significance of height measurements. STM senses contours of equal charge density outside the atom cores. Estimates of small height differences in STM studies are subject to many factors, discussed in some detail for the case of a 5×5 to 2×1 boundary [21], and the quantitative values observed can be affected by tip voltage and scanning conditions as seen from data in [3]. However, atomic steps of theoretical height difference 0.313 nm are readily measured and have been studied in detail [3]. Our instrument provided a correct value for the step height, as shown in figure 4.

Although the latter agreement lends confidence to the measurements, one may argue that measured heights within a given surface plane might be subject to distortion since the surface states being probed may be different on the different atomic levels. This is certainly true in the present case, because there are believed to be bonded p-type orbitals on the top (chain) atoms, and sp mixtures, perhaps sp^3 on the MP model, on the atoms between the chains. The height at which a given charge density occurs above an atomic nucleus for a p orbital and for an sp hybrid could differ by as much as about 0.05 nm ([21] and references therein). However, the required extra 0.12 nm for the MP model seems to be too large to be attainable by this argument.

One could also postulate the presence of 'anomalous' heights, as in the case of graphite [34]. However, the latter anomaly is well known to be related to the layer van der Waals structure of that material [34], so that tip interactions can have an effect. There have been no reports of anomalous heights for the case of silicon surfaces, although many STM height scans for various low-index surfaces have been shown and discussed (summarized in [34]). Therefore, the large value of the observed [112]-direction corrugation is very difficult to reconcile with the MP model, although it arises naturally from the TBS structure. In this connection we note that STM height scans performed across a 5×5 to 2×1 phase boundary [35] were consistent with the observed lateral space between the structures using the TBS model, but there was a 0.33 nm lateral anomaly if the MP model was used [21].

Barrier height and spectroscopic data from the same surface would be of interest, but were not taken in order not to vary the tip spacing and applied voltages, which would lose the particularly good scanning resolution of figure 2 and thus introduce indeterminacy.

The surfaces were not continually scanned, but only after intervals of several minutes so as to keep any scanned effects to a minimum. After about an hour and about eight scans, cross-row bridging effects were, as mentioned, noticeably more prevalent. It is possible that an adatom may be able to induce a cross-row structure.

It should be noted that cleavage is a relatively violent event, leading to the emission of atoms in the case of Ge [37], and of ions and electrons in Si [38], as well as luminescence of various kinds [39] and of small fragments that emit recombination radiation [40]. Even relatively flat areas show steps and other irregularities, as well as vacancies, adatoms (figure 3), disorder and low-height patches [32]. In experimental measurements on cleavage surfaces, techniques involving incident beams of light or of ions average over unknown fractions of imperfect surface which could account for differences in various results. LEED tends to be weighted by ordered regions more than ion and photon beam techniques, and for this reason may give more reliable information about the structure of clean, ordered parts of the cleavage surface. However, an assumption of a perfect single structure for calculations seems optimistic.

The true structure of a cleaved surface should be considered in conjunction with the ready conversion to other structures by annealing the surface at temperatures as low as 250 °C, depending on cleavage quality and heating times. (This literature is summarized in [33].) If the surface is cleaved at higher temperatures and quenched to room temperature in order to drastically reduce the effect of heating times, the 2×1 structure is found to exist up to 417 °C [33]. This is still relatively low, and points to the 2×1 structure being either metastable, or one where defects can readily initiate reconstructions.

In conclusion, we have found 2×1 surface structures featuring rows with valleys of measured depths of about 0.25 nm. The findings are readily consistent with the TBS model of the 2×1 surface structure, but require one to postulate extreme orbital differences between surface and second layer atoms in order to apply the MP model. LEED analysis [31] obtains improved agreement with experiment when mixtures of structures are considered. Therefore, although it is likely that we were observing a TBS region, one cannot rule out the possible existence of other regions with other structures.

Acknowledgments

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