# Real-Space Observation of π-Bonded Chains and Surface Disorder on Si(111)2×1

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Scanning tunneling microscopy is used to confirm the π-bonded chain structure of the Si(111)2×1 surface. Both the amplitude and voltage dependence of the vertical corrugation exclude the buckling model for the structure of this surface. Spectroscopic measurements of the tunneling current versus voltage identify a band gap for the 2×1 surface states. Spatial images of disorder-related states are obtained by tunneling at energies inside of this band gap.

The 2×1 reconstruction of the Si(111) crystal face has been the subject of numerous experimental and theoretical studies. It was originally thought that the reconstruction involved buckling of the surface atoms.[1] On the basis of a critical evaluation of experimental data and total-energy considerations, Pandey proposed a radically new "π-bonded chain model" for the Si(111) surface.[2] In this model, the (111) surface reconstructs to form zig-zag chains of atoms directed in the [01$\bar{1}$] direction. This structure has been confirmed by numerous subsequent experiments.[3] Defect-related states have been observed on the Si(111)2×1 surface, although the atomic structure of the defects was not known.[4] Here, we report the first scanning tunneling microscopy (STM)[5] study of the Si(111)2×1 surface. We observe a dominant [2$\bar{1}\bar{1}$] corrugation with an amplitude of 0.54 Å. This amplitude is inconsistent with atomic charge densities expected for a buckling-type surface structure. Furthermore, the voltage dependence of the corrugation is used to demonstrate that the observed charge densities are not enhanced by possible charge transfer between dangling bonds in the buckled geometry. Our results for the corrugation are consistent with a π-bonded surface structure. We also observe the well-known 0.45-eV band gap for the 2×1 surface states, and definitively establish the role of the surface states in the tunneling process. By acquiring images at voltages inside of this band gap, we are able to directly image disorder-related states on the surface.

The tunneling microscope used in this work is similar to that discussed by Binnig and Rohrer,[6] and is described in detail elsewhere.[7] Images were acquired with a constant tunneling current of 1 nA, and include data from both directions of a raster scan. We have studied both n- and p-type Si with dopant concentrations in the range $(9\times10^{14}$–$2\times10^{19})$ cm$^{-3}$, and the results presented here are practically independent of doping. Indium was used for back contacts, with a contact resistance of less than 100 Ω. The samples were cleaved *in situ* in the [2$\bar{1}\bar{1}$] direction, exposing a (111) crystal face. It is well known that such cleaved surfaces undergo a 2×1 reconstruction.

In Fig. 1 we present an STM image obtained with a sample voltage of +0.6 V relative to the probe tip. On the left-hand side of the image are the atomic rows of the 2×1 reconstruction. The lateral spacing between the rows is measured to be about 6.9 Å compared with an actual value of 6.65 Å for a periodicity of 2 unit cells; the difference between these values is presumably due to a small calibration error. The peak-to-valley corrugation amplitude for this [2$\bar{1}\bar{1}$] corrugation is measured from the image to be about 0.5 Å. The image of Fig. 1 actually displays exceptionally high resolution (as a result of a very sharp probe tip); most other images at a bias of +0.6 V have an [2$\bar{1}\bar{1}$] corrugation amplitude of typically 0.15 Å. From a Fourier analysis[8] of the ordered region on the left-hand side of
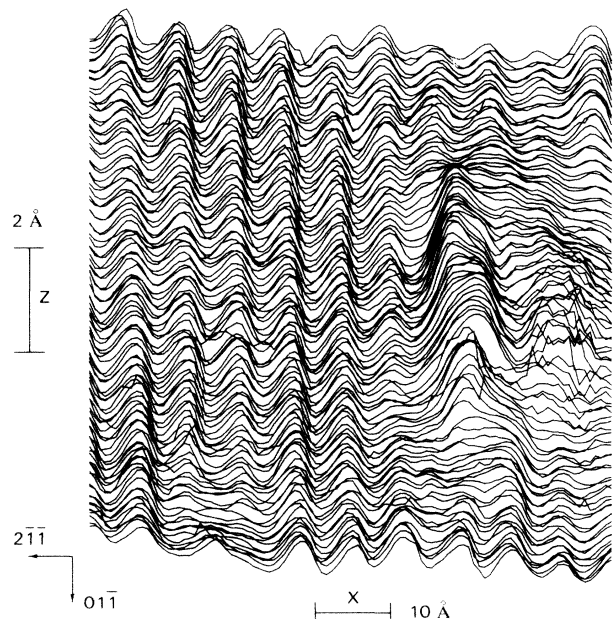


FIG. 1. STM image of a cleaved Si(111) surface, acquired at a sample voltage of +0.6 V. The image extends laterally over an area of 70×70 Å$^2$, with the vertical height given by the scale on the left-hand side of the figure. The 2×1 π-bonded chains are seen at the left-hand side of the image, and a disordered region is seen on the right.

Fig. 1, we obtain a more quantitative value for the corrugation amplitude of 0.54 ± 0.05 Å, where the uncertainty reflects the variation in the amplitude across the image. An asymmetry in the corrugation is also clearly evident in Fig. 1 (the rows are steeper on the right-hand side than the left). This asymmetry results in a second-order Fourier component, with an amplitude of 0.07 ± 0.03 Å, and a phase angle of 95° ± 10° relative to the fundamental component. In the image of Fig. 1 we observe no [01$\bar{1}$] corrugation (i.e., corrugation along the rows) above our detection limit of 0.02 Å.

In the $\pi$-bonded chain model for the Si(111)2×1 surface, the top two layers of atoms form zig-zag "chains,"[2] with about 1 Å vertical separation between the top two atomic layers.[3] Such a structure is consistent with our STM observations; our maximum observed [2$\bar{1}\bar{1}$] corrugation amplitude of 0.54 Å is reduced from the atomic separation of 1 Å since STM samples the charge density at some distance away from the surface.[9,10] From charge-density calculations based on superposition of atomic charge,[9] we find that a corrugation amplitude of 0.54 Å corresponds to a distance of about 5 Å from the surface, which is consistent with that estimated from the magnitude of the tunneling current.[10] For the case of the buckling model of the Si(111) surface, the only row structure which arises in that model is due to alternating lines of raised and lowered atoms, with about 0.3 Å vertical separation between the atoms.[1,11] From our charge-density computations we find that this separation results in a corrugation amplitude of 0.19 Å at a distance of 5 Å from the surface. This amplitude is much too small to account for our observed value of 0.54 Å.

The above comparison between atomic positions and observed corrugation is based on the assumption that the surface charge density follows the atomic positions. Alternatively, the charge density observed by STM may reflect some purely electronic structure of the 2×1 surface states. For the buckling model, these surface states arise from dangling bonds on alternate rows of atoms, as shown in Fig. 2(a). If the charge transfer between rows is large, resulting in alternate rows of full and empty dangling bonds, then a large enhancement of the corrugation amplitude due to the surface states is possible. However, if this situation occurs in reality, then reversal of the polarity of the bias voltage will result in a reversal of the surface-state corrugation amplitude,[10] as pictured in Fig. 2(a). We have performed such an experiment, and the results are shown in Fig. 2(c). We plot a sequence of line scans, acquired over the same portion of the surface, in which the sample voltage was switched between +0.8 and −0.8 V between scans. No change in the sign of the corrugation is observed. Thus, if the surface structure is described by the buckling model, then either we are not sensitive to the surface states, or the charge transfer between dangling bonds is small. In either
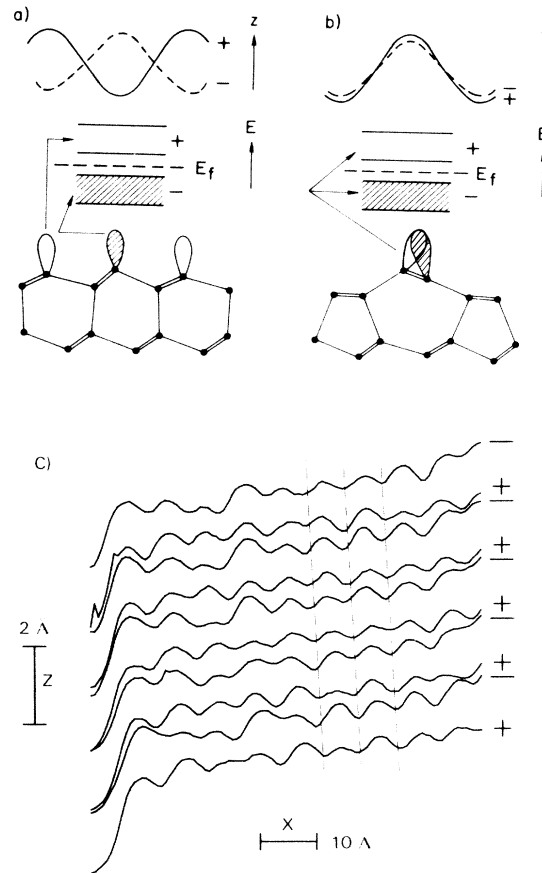


FIG. 2. Schematic view of the 2×1 surface states for (a) the buckling model and (b) the $\pi$-bonded chain model. Dangling bonds on the surface result in two bands of surface states above and below the Fermi level ($E_F$). The corrugation ($z$) of these bands can be measured separately with positive or negative voltages. (c) Experimental results for the corrugation. The sample voltage was switched between +0.8 and −0.8 V on successive line scans. A monatomic step is observed at the left-hand edge of the scans, and serves as a convenient spatial reference point.

case, the resulting charge density seen by STM will follow the atomic positions. However, we found above that such a charge density is inconsistent with the observed corrugation amplitude. Therefore, our STM results definitively exclude the buckling model as a possible structure for the Si(111)2×1 surface. Returning to the $\pi$-bonded chain model, the surface states which occur in that case are the occupied bonding $\pi$ states or the unoccupied antibonding $\pi^*$ states, and the difference between these states only involves a phase factor *along* the chains. Thus, as pictured in Fig. 2(b), reversal of the polarity of the voltage will not produce a large effect on the corrugation, in agreement with the experimental results shown in Fig. 2(c).

The role of the 2×1 surface states in the tunneling process can be established from the voltage depen-

dence of the tunneling current. In Fig. 3 we show the tunneling current versus voltage, acquired with a fixed tip-sample separation and at a sample location which displayed well-ordered 2×1 corrugation. The current exhibits a flat spot with width of 0.45 ±0.05 V, centered at −0.05 V. From its width and location in voltage we can identify this feature as arising from the 0.45-eV gap which is known to occur in the spectrum of 2×1 surface states.[12] The location of the bulk band gap relative to the Fermi level (0 V) as determined from photoemission[13] is also shown in Fig. 3. We see that for voltages in the range 0.2–0.7 V, the tunneling is occurring within the bulk band gap, and thus it is occurring via the 2×1 surface states themselves.

The occurrence of a band gap for the 2×1 surface states produces dramatic effects on the STM images. In particular, at voltages corresponding to energies just inside the band gap we observe an enhancement of certain types of disorder-related features in the images, as shown in the images of Figs. 4(d)–4(f). These images were taken successively, but are displaced relative to each other by about 15 Å per image because of drift of the STM. The arrows on the images indicate the same actual surface location, as determined from an accurate drift-rate calibration described in detail elsewhere.[7] Images 4(d) and 4(f) were taken at biases of −0.4 and −0.6 V, respectively, and appear quite similar. Image 4(e) was taken at a bias of −0.2 V and looks significantly different. In particular, in the low-bias image the chain marked by an arrow has a much larger STM signal than its neighbors. This enhanced STM signal of ∼1 Å cannot be due to atomic topography alone since it is not seen at the higher voltages. Rather, the enhanced features arise from charge densities of some disorder-related state on the chains. From Fig. 3 we see that a voltage of −0.2 V corre-

sponds to tunneling within the 2×1 surface-state gap. States inside the gap can only arise from disorder or defects on the surface, and thus it is precisely this type of disorder-related surface state which is imaged in Fig. 4(e). These states tend to propagate along the chains, and vary from chain to chain in a manner which appears to be related to the presence of nearby structural defects. This type of disorder is similar to that which occurs for the corrugation asymmetry seen in Fig. 1. There, the atomic rows in the center of the image, near the structural defect, are much more asymmetric than those in the upper left-hand corner. An asymmetry of the [$2\bar{1}\bar{1}$] corrugation probably arises from a tilt of the π-bonded chains. Thus, we
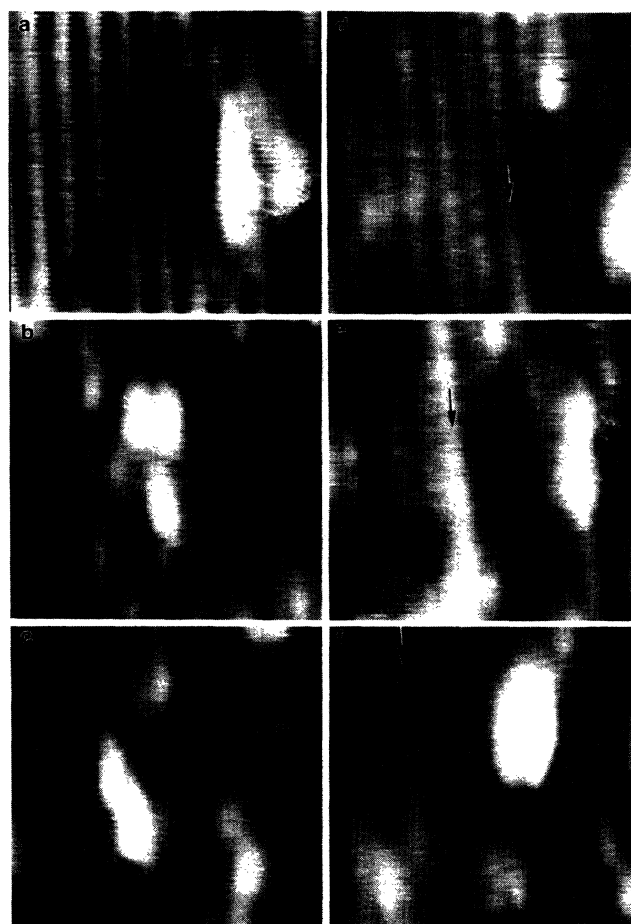


FIG. 4. Series of STM images taken at sample voltages of (a) +0.6, (b) +0.5, (c) −1.45, (d) −0.4, (e) −0.2, and (f) −0.6 V. All images extend laterally over an area of 70×70 Å², with topography given by a grey scale from 0 (black) to 1.5 Å (white). Crystallographic orientations are the same as shown in Fig. 1. The data in (a) are identical with that of Fig. 1. Images (b) and (c) illustrate types of surface disorder. Images (d)–(f) are a sequence of successive images; arrows indicate the same surface position on each image.
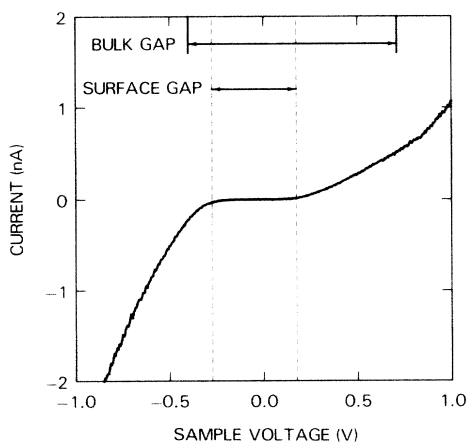


FIG. 3. Tunneling current as a function of sample voltage. The 0.45-V-wide flat spot in the current arises from a surface-state band gap, indicated together with the 1.1-V bulk band gap at the top of the figure.

suggest that the disorder-related states imaged in Fig. 4(e) result from some small tilt or translation of the chains in response to strain arising from a nearby structural defect.

In conclusion, we find that the magnitude and voltage dependence of the $[2\bar{1}\bar{1}]$ corrugation amplitude is consistent with the $\pi$-bonded chain model and inconsistent with the buckling model for the structure of the $Si(111)2\times1$ surface. By tunneling at voltages inside of the bulk band gap we establish the role of the $2\times1$ surface states in the tunneling process. Furthermore, by tunneling at voltages within the $2\times1$ surface-state gap, we directly image disorder-related states on the surface. These disorder-related surface states propagate along the chains, and we associate them with small tilts or translations of the chains in response to strain arising from nearby structural defects.

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[1]D. Haneman, Phys. Rev. 121, 1093 (1961), and Adv. Phys. 31, 165 (1982).

[2]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981), and 49, 223 (1982), and Proc. Indian Natl. Sci. Acad., Part A 51, 17 (1985).

[3]F. J. Himpsel, P. M. Marcus, R. Tromp, I. P. Batra, M. R. Cook, F. Jona, and H. Liu, Phys. Rev. B 30, 2257 (1984), and references contained therein.

[4]N. J. DiNardo, J. E. Demuth, W. A. Thompson, and Ph. Avouris, Phys. Rev. B 31, 4077 (1985).

[5]G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. 50, 120 (1983), and Surf. Sci. 131, L379 (1983).

[6]G. Binnig and H. Rohrer, Helv. Phys. Acta 55, 726 (1982).

[7]R. M. Feenstra, W. A. Thompson, and A. P. Fein, in Proceedings of the Thirty-Second American Vacuum Society National Symposium, J. Vac. Sci. Technol. A (to be published).

[8]Corrugation amplitudes are computed from the peak height in the Fourier transform multiplied by 4 (2 for peaks at positive and negative frequency, and 2 to arrive at peak-to-valley amplitudes).

[9]J. Tersoff and D. R. Hamann, Phys. Rev. Lett. 50, 1998 (1983), and Phys. Rev. B 31, 805 (1985).

[10]A. Baratoff, Physica (Amsterdam) 127B+C, 143 (1984).

[11]R. Feder, W. Mönch, and P. P. Auer, J. Phys. C 12, L179 (1979).

[12]G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

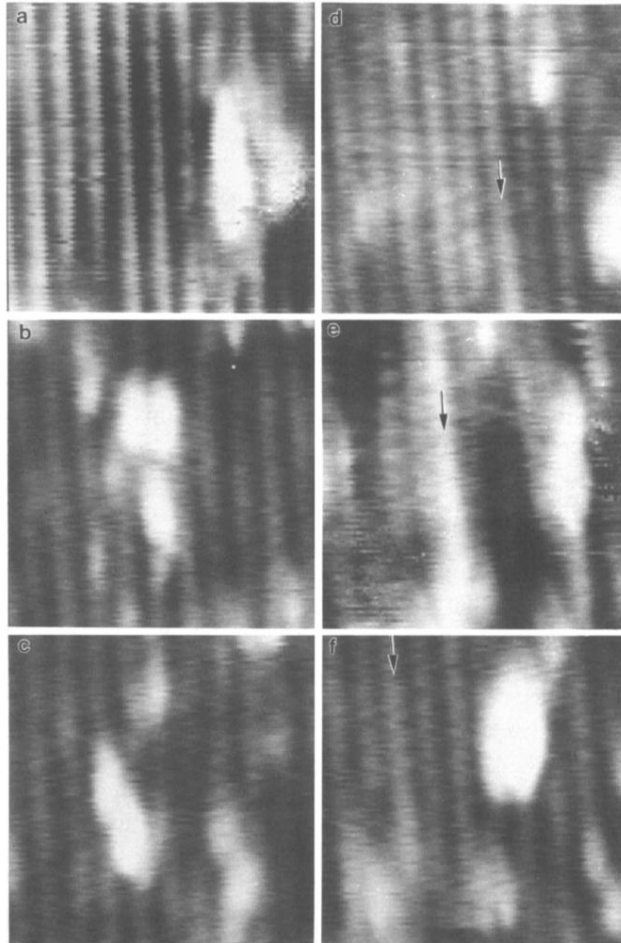[13]F. J. Himpsel, G. Hollinger, and R. A. Pollack, Phys. Rev. B 28, 7014 (1983).

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