Structure analysis of Si(111)2×1 with low-energy electron diffraction

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A structure analysis of the Si(111)2×1 surface is performed using extensive new low-energy electron-diffraction data (12 beams). Although the π-bonded chain model in its original form shows gross disagreement with low-energy electron diffraction, a modification of that structure gives moderate agreement. The major modifications are a buckling in the outer chain and an overall compression.

One of the unsolved problems in surface physics is the atomic structure of reconstructed semiconductor surfaces. So far, only the relaxed but unreconstructed (110)1×1 structures of some III-V compounds have been established conclusively[1] by agreement among several techniques, e.g., by LEED (low-energy electron diffraction), ion scattering, total energy calculations, and photoemission. A good candidate for solving a reconstructed structure is the cleaved Si(111)2×1 surface where a π-bonded chain reconstruction has been proposed[2] which gives the lowest total energy[3-5] of any structure calculated to date and also gives the best agreement with ion scattering,[6,7] optical absorption,[8] electron-energy-loss spectroscopy,[9] and photoemission[10] data, although some discrepancies remain. However, the chain model in its original form[2] has been found to be inconsistent[11] with LEED. The goal of our study is to determine if this inconsistency can be removed by using refined chain models and to find out which significant feature of the surface reconstruction is missing in the original model.

We have performed a LEED analysis using a Keating-type strain energy minimization[12] to take into account subsurface relaxation. By combining LEED with recent ion-scattering results we are able to utilize the strengths of both techniques, i.e., the straightforward interpretation of ion scattering (which provides the proper region of parameter space in which to find the best-fit parameters and helps avoid false fitting minima in LEED) and the high sensitivity of LEED to small atomic displacements. Our analysis uses extensive new LEED data and provides atomic coordinates down to the sixth layer. We show that the disagreement with LEED can be resolved and that moderate agreement can be achieved over a large set of integral and fractional order beams. Although the agreement is not good enough to consider the structure solved, we can show that significant changes have to be made in the original chain model which go beyond taking account of subsurface relaxation. The most salient features of our optimum structure are a buckling of ≈ 0.38 Å in the outer chain and an overall compression (the outer chain moves 0.2 Å inward). The amount of buckling is close to the extremal case where the down atom has planar sp^2 bond configuration in close similarity to the buckled (110)1×1 surfaces of III-V compounds.

The LEED data used in this analysis consists of 12

normal-incidence beams taken at room temperature [see Fig. 1(b)]. This new data base (see Ref. 13) is much larger than in previously published LEED studies of Si(111)2×1 and gives us confidence that the agreement is not a coincidence. The dynamical LEED program CHANGE[14] was used
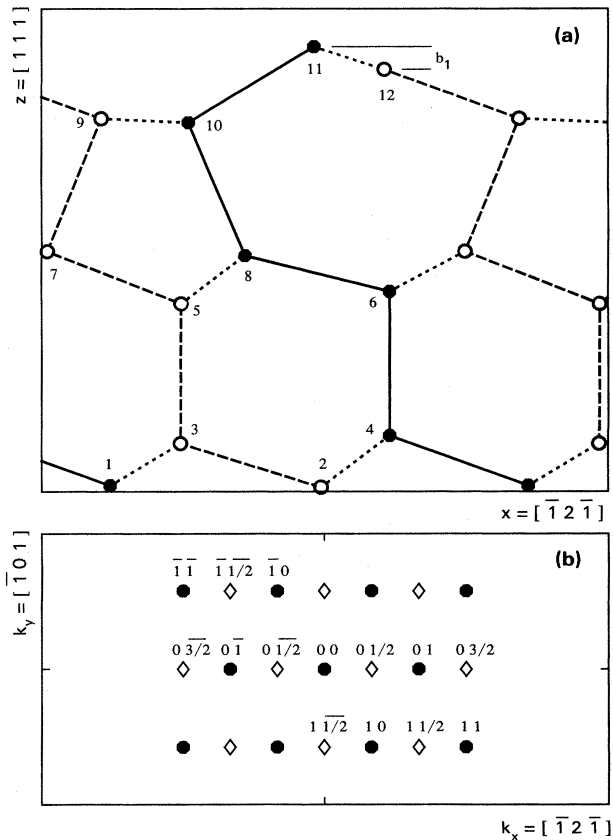

FIG. 1. (a) Side view looking along the chains of the optimized structure for Si(111)2×1. b_1 denotes the buckling of the outer chain. (b) Labeling of the LEED spots. Spots without labels are mirror symmetric to labeled spots via reflection at the ($\bar{1}01$) mirror plane.

to calculate intensity spectra of some 200 structures, which include the chain structures proposed in the literature.[2-4] The eight z coordinates [see Fig. 1(a)] of all atoms down to the fourth layer were optimized. Four of these coordinates are restricted to a relatively narrow range (± 0.1 Å) in order to keep reasonable bond lengths between layers 2 and 3 and layers 4 and 5. Even so, the number of parameters to be optimized is much larger than for conventional LEED studies of metal surfaces or GaAs(110) because the topological changes in the surface layer (≈ 1 Å) are large and propagate deeply into the lattice (e.g., ≈ 0.1 Å in the fifth layer). The fifth and sixth layer z and all the x coordinates were determined by a Keating-like strain energy minimization,[12] since they have a minor influence on the LEED beams. The y coordinates were frozen at the mirror plane positions. After a reasonable fit was achieved for the less sensitive LEED beams, all parameters were varied systematically to obtain the final structure by optimizing the Zanazzi-Jona R factor.[15] Other parameters of our LEED calculation were an imaginary part $\beta = 3.5$ eV of the poten-

TABLE I. Atomic positions (in Å) for the optimized Si(111)2×1 chain structure. The coordinates x, y, and z refer to the $[\bar{1}2\bar{1}]$, $[\bar{1}01]$, and $[111]$ directions (see Fig. 1) with the origin at a third layer atom of the truncated bulk lattice. The atom numbers refer to Fig. 1(a).

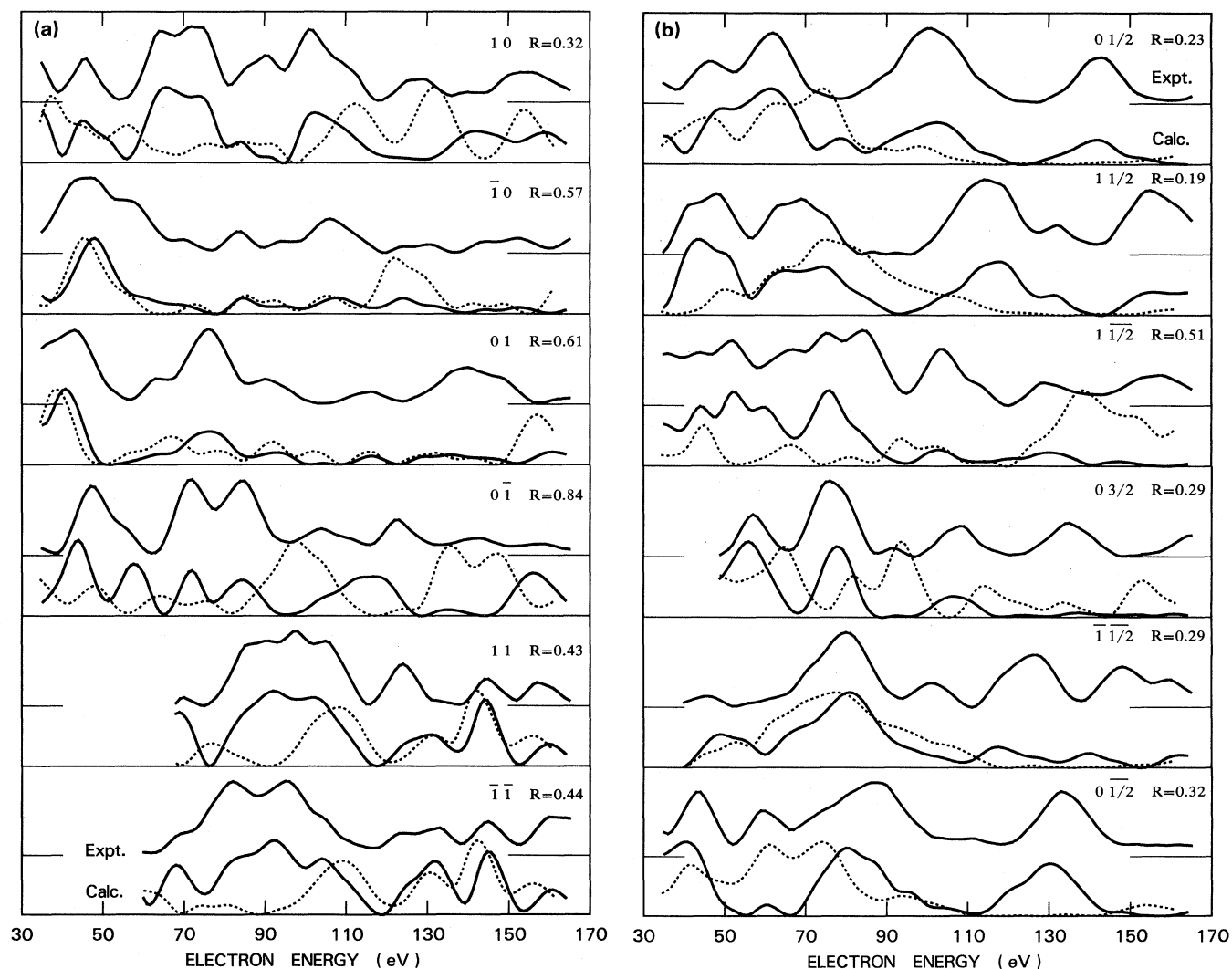| NR	X	Y	Z
1	1.09	1.92	−3.90
2	4.45	0.0	−3.93
3	2.21	0.0	−3.21
4	5.54	1.92	−3.08
5	2.22	0.0	−0.89
6	5.54	1.92	−0.69
7	0.09	0.0	−0.02
8	3.24	1.92	−0.09
9	0.95	0.0	2.18
10	2.34	1.92	2.11
11	4.34	1.92	3.37
12	5.46	0.0	2.99

FIG. 2. Comparison of normal incidence LEED intensity spectra (upper curves, short horizontal zero lines; see also Ref. 13) with calculations for the optimized Si(111)2×1 structure (lower full curves, long zero lines) and for the original Pandey model (Ref. 2) (dotted curves, long zero lines). All curves are normalized to the same height. R factors are given for individual beams of the optimized structure.

tial, a constant potential of −10 eV between the muffin-tin spheres, and a rms vibration amplitude of 0.1 Å (0.3 Å for the outermost chain). The extra surface vibration amplitude did not change the R factor of our optimum structure but gave somewhat better visual agreement. Comparable vibration amplitudes were found with ion scattering[7] (0.28 Å for the outer chain, 0.21 Å for the inner chain, and 0.13 Å in the bulk). A large enhancement of vibrations in the outer chain can be expected, since there exist extra vibration modes that involve mostly bond bending and little bond stretching. For the chain models derived from theory we used bulk vibration amplitudes (using enhanced surface vibrations did not change the conclusions).

The coordinates of 12 atoms in six layers and a side view of the optimized structure are given in Table I and Fig. 1(a), respectively. The corresponding calculated $I(V)$ curves are shown together with the data in Fig. 2 as full lines. Most of the major observed features are reproduced by the calculation for the optimized structure, whereas only about two beams can be matched by the original Pandey model (dotted lines in Fig. 2). This is reflected in the R factors ($R = 0.42$ for the optimized structure and $R = 0.92$ for the original Pandey model). The most important parameters making agreement with LEED possible are a buckling b_1 of the outer chain [see Fig. 1(a)] and an overall compression. A buckling of this type ($b_1 \approx 0.2$ Å) has been found by Northrup and Cohen[4,16] from total energy calculations and appears in recent LEED work.[17] Our optimized structure has a strong buckling $b_1 = 0.38 \pm 0.08$ Å (the original Pandey model[2] has $b_1 = 0.0$ Å and a recent optimized structure given by Pandey[18] has $b_1 = 0.09$ Å). The sign of the buckling is uniquely determined [see Fig. 1(a)]. The ion-scattering analysis[7] also gives an optimum fit for a fair amount of buckling ($b_1 = 0.3$ Å) but the uncertainty ($+0.35$ Å, -0.45 Å) is too large to discriminate buckled from nonbuckled structures. The overall expansion (compression) of the model by Northrup and Cohen is about the same as in our optimum LEED structure, the original Pandey model and the ion-scattering model are expanded, and the new Pandey model is compressed.

Subsurface relaxation plays an additional role in improving the agreement with LEED. For example, a strain energy minimization[12] improves the R factor from 0.92 to 0.65 for the original Pandey model. The largest effect of subsurface relaxation is a buckling of 0.2–0.3 Å in the fourth layer that is driven by bond angle changes of third layer atoms. The Keating strain minimization introduces a small (less than 0.1 Å) buckling in the inner chain opposite to that of the outer chain if the outer chain is assumed buckled. However, our best LEED fit gives an inner chain buckling of 0.07 Å in the same direction as for the outer chain, in agreement with predictions by a recent total energy calculation by Pandey[18] and ion-scattering results.[7]

We have tested other currently available chain models derived from total energy calculations[4,18] and from ion scattering[7] and find that they give significantly poorer agreement with LEED than the optimum structure (both visual inspection and R factor analysis come to the same conclusion). We obtain $R = 0.66$ for the structure given by Northrup and Cohen,[4] $R = 1.01$ for a recent optimized structure given by Pandey,[18] and $R = 0.70$ for the structure that gives the best fit with ion scattering (which has relatively large error bars). The differences between these structures are largest for the outer chain (± 0.3 Å) and become smaller for the inner chain and deeper layers (less than ± 0.1 Å). The optimum chain model is likely to reside within these bounds. The LEED spectra are sensitive to displacements of about ± 0.08 Å perpendicular to the surface. Although the question whether or not the structure of Si(111)2×1 has been solved at the sensitivity level of LEED remains open, we conclude that most of the discrepancy between current models for Si(111)2×1 and LEED can be resolved by modifications to the chain model.

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