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Test of structural models for the Si{111}2×1 surface

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New low-energy electron diffraction (LEED) experiments and new calculations on Si{111}2×1 surfaces have produced the following results: (1) LEED intensity data from different surfaces cleaved in different directions in different experiments are reproduced well—thus, if two or more different 2×1 superstructures occur simultaneously on cleaved surfaces, their proportions are always the same; (2) LEED intensity calculations of different authors with different computer programs are reproducible—thus, confidence in the reliability of the calculations is confirmed; (3) the buckling model, the π-bonded chain model, the Seiwatz model, and the Chadi molecular model all fail the LEED test—thus, the Si{111}2×1 structural problem is still unsolved. A complete test of these models requires consideration of distortions in deeper atomic layers, so far unknown.

The atomic structure of a vacuum-cleaved Si{111} surface is the subject of a deep and unsettled controversy. Among the several different structural models that have been proposed for that surface, two have merged as prominent: the buckling model and the π-bonded chain model. The buckling model, which was introduced by Haneman[1] in 1961, involves raising and lowering alternate rows of atoms in the first surface layer, thereby reducing the symmetry of the system. However, recent total-energy calculations[2,3] have shown the buckling model to be unstable with respect to a nonbuckled and relaxed nonreconstructed (or 1×1) surface. The π-bonded chain model introduced by Pandey[2] produced an appreciable lowering of the total energy. In addition, Northrup and Cohen[3] showed that the energy barrier between buckled and π-bonded surfaces is surprisingly small (about 0.03 eV/atom) indicating that the chain structure can be obtained during cleavage without much increase of the total energy. The dispersion of the resulting surface state was calculated[2] to be in "remarkable agreement"[3] with angle-resolved photoemission measurements of Uhrberg, Hansson, Nicholls, and Flodstrom.[4]

Direct tests of the buckling and the chain model were carried out by Feder, Moench, and Auer[5] and by Feder,[6] respectively, with LEED (low-energy electron diffraction) intensity analysis. The results were reported as discriminating against the chain model in favor of the buckling model, in striking contrast to the total-energy calculations and the photoemission results mentioned above. Contradictory results of different photoemission experiments introduced additional complications: Himpsel, Heimann, and Eastman[7] found evidence for two surface dangling-bond bands, one dispersive and the other nearly dispersionless; Uhrberg *et al.*[4] observed the single highly dispersive band predicted by Pandey;[2] Petroff *et al.*[8] found a single dispersionless band. In an attempt at explaining this experimental irreproducibility Chadi[9] advanced the idea of a Si{111}2×1 surface having *two* distinct structures with chainlike and molecular types of π bonding, respectively, the occurrence of both bonding configurations in varying proportions providing an explanation for the contradictory photoemission results reported in the literature.

The work described in this paper originates from a desire to clarify the situation by repeating and extending the LEED tests done by Feder and co-workers.[5,6] In particular, the goals were (1) to carry out a new series of LEED experiments and collect a large intensity-data base; (2) to test experimental reproducibility by comparing results of different experiments with one another and with the original results of Moench and Auer;[10] (3) to do LEED intensity calculations for the buckling model and the chain model, and compare with the calculations of Feder and co-workers[5,6] and with the experimental data; and (4) to test other structural models for the Si{111}2×1 surface, namely, the molecular π-bonded model of Chadi[9] and the conjugated-chain model of Seiwatz.[11] A point not widely appreciated about LEED tests of specific structural models is that such tests require precise numerical definition of *all* structural parameters, i.e., specification of the coordinates of *all* atoms in the surface layers. Unfortunately, almost all proposers of new structural models do not quantify the parameters, so that the models are often imprecisely or at best incompletely defined. For this reason, the LEED tests carried out in this work were done for a range of parameter values in each model, although not all possible parameter combinations were covered. Nevertheless, a few results emerged that are new and seem worth reporting. These are as follows: (a) The experimental reproducibility was found to be good to excellent, thus making Chadi's suggestion of two distinct structures unlikely. (b) The calculational reproducibility was also found to be satisfactory, thus providing confidence about the accuracy of the theoretical calculations. (c) None of the structural models as defined passed the LEED test adequately—modifications and refinements of even the models, such as the π-bonded chain model, that have been found consistent with the results of other surface-sensitive techniques seem to be necessary. The overall conclusion is, therefore, that the Si{111}2×1 structural problem is still unsolved.

The LEED experiments involved cleaving a suitable Si sample in ultrahigh vacuum (about 5×10^{-11} torr), identifying a sufficiently large flat area (1 mm^2 or more) on the cleaved surface as a single domain of the 2×1 superstruc-

ture, orienting such area with respect to the incident electron beam in such a way that the beam's angle of incidence θ and azimuth angle ϕ could be accurately measured, collecting intensity data for several diffracted beams for a range of incident-electron energies and for a few different values of the angles θ and ϕ. Several such experiments (i.e., several cleavages) were planned—in some experiments the cleavage direction was parallel, in others, perpendicular to a $\langle 211 \rangle$ direction. The azimuthal orientation of the resulting 2×1 structure varied from experiment to experiment. Furthermore, intensity data were collected not only immediately but at various time intervals (up to several hours) after cleavage. The intensities of several diffracted beams were measured rapidly and almost simultaneously with a data-acquisition system involving a television camera and a microcomputer. The experimental curves presented below are considered preliminary; they are not normalized to constant incident current and not corrected for contact-potential difference between cathode and sample— the experiments are still in progress at the time of writing. Nevertheless, we have acquired sufficient confidence in the validity of these preliminary data to use them for the tests and the arguments presented below.

The tests for experimental reproducibility involved comparing with one another LEED intensity spectra of corresponding beams as measured in different experiments. Eleven such spectra (6 integral order and 5 fractional order) at normal incidence were used from 3 different cleavages. The comparison between curves was done visually, and the results indicated good reproducibility for all spectra considered. Comparison of our data with the earlier data of Moench and Auer[10] was limited by the fact that only 2 spectra for normal incidence of the latter set are available in the literature: the $\bar{1}0$ and the $1\,\bar{1}/2$ beam.[12] Figures 1 and 2 show that the curves measured in two of our experiments (EXPT1 and EXPT2) and those published in the literature (FMA, MA EXPT1, and MA EXPT2) are in satisfactory agreement with one another. This observation, together with similar observations for 9 other beams, makes it unlikely that more than one structure exists on cleaved Si{111} surfaces. Since different samples, different cleavage directions, and different surface orientations were used in the experiments, we must conclude that, if Chadi's suggestion[9] of two different structures is correct, then the proportions of such structures were always very nearly the same in the experiments considered in this test.

The calculations of LEED intensities were done with the CHANGE computer program described elsewhere,[13] with 62 beams and 5 phase shifts, and the same potential and nonstructural parameters that were used in earlier Si calculations.[13,14] We tested four models: The buckling model as defined by Feder, Moench, and Auer,[5] the π-bonded chain model as described by Pandey,[2] the conjugated chain model as sketched by Seiwatz,[11] and the π-bonded molecular model as proposed by Chadi.[9] In all four cases at least two structural parameters were varied over a range of values.

Figure 3 depicts the buckling model: The version chosen by Feder, Moench, and Auer[5] has $b_1=0.15$ Å, $d_1=0.70$ Å (contracted 0.08 Å from the "bulk" value 0.78 Å), $d_2=2.27$ Å (contracted 0.08 Å from the bulk value 2.35 Å), and $L_2=0.10$ Å. Figure 1 exhibits the $\bar{1}0$ spectrum calculated by Feder, Moench, and Auer (curve labeled FMA THEOR) with these parameters. The curve labeled F is the

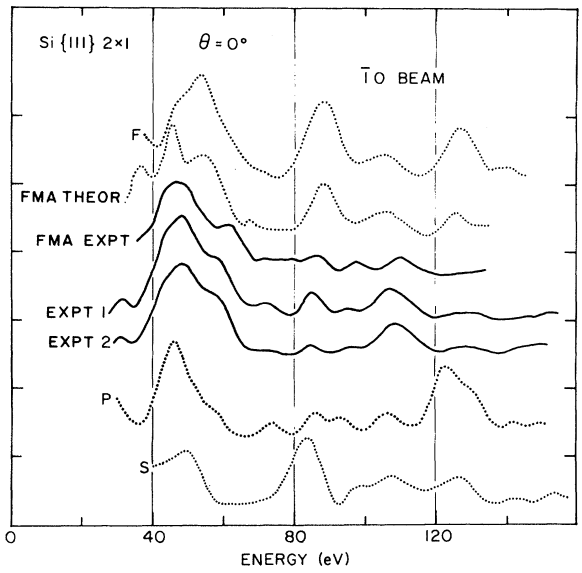

FIG. 1. Experimental (solid) and theoretical (dotted) $\bar{1}0$ spectra from Si{111}2×1. EXPT1 and EXPT2, present work, two different experiments (these curves not normalized); FMA EXPT, FMA THEOR, experimental and theoretical curves, respectively, published by Feder, Moench, and Auer (Ref. 5); F, P, S, theoretical curves for the models of Feder, Moench, and Auer (Ref. 5), Pandey (Ref. 2), and Seiwatz (Ref. 11), respectively.

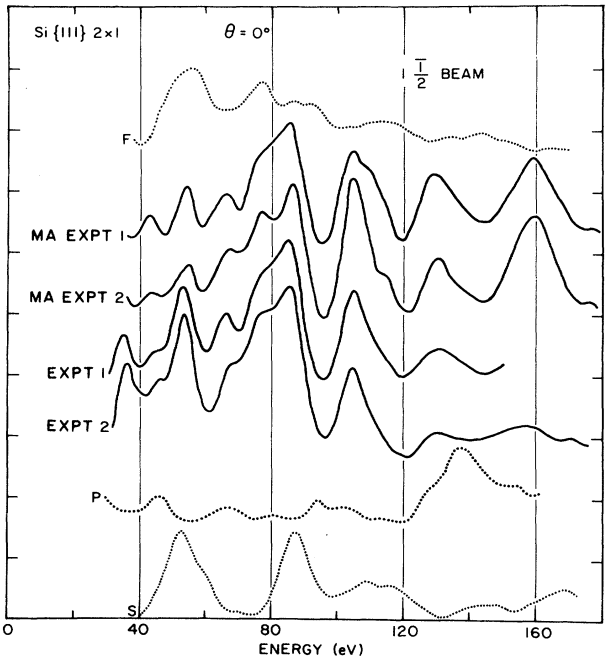

FIG. 2. Experimental (solid) and theoretical (dotted) $1\,\bar{1}/2$ spectra from Si{111}2×1. EXPT1 and EXPT2, present work, two different experiments (these curves not normalized); MA EXPT1, MA EXPT2, experimental curves of Moench and Auer (Ref. 10); F, P, S, theoretical curves for the models of Feder, Moench, and Auer (Ref. 5), Pandey (Ref. 2), and Seiwatz (Ref. 11), respectively.

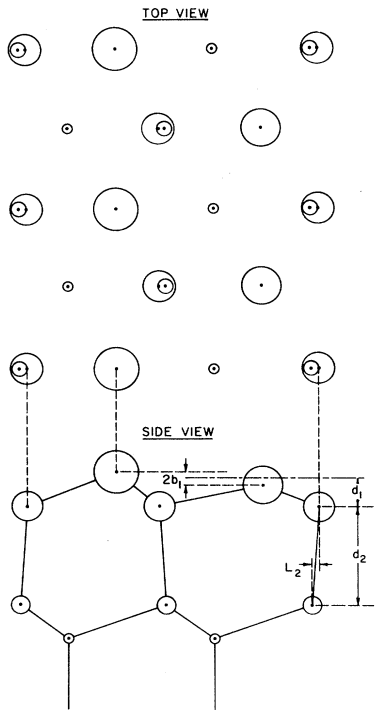

FIG. 3. Schematic top and side views of buckling model.

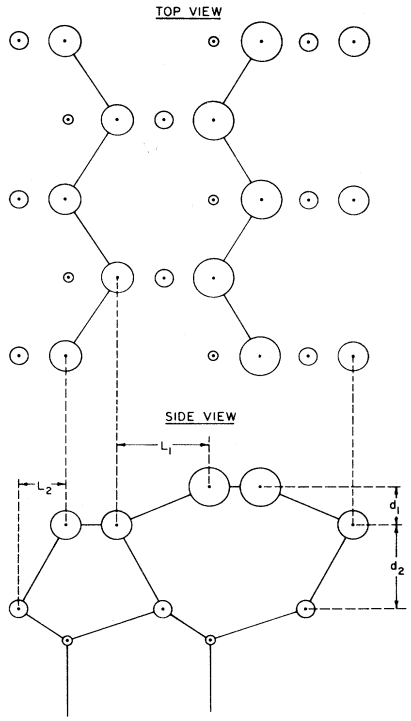

FIG. 4. Schematic top and side views of π-bonded chain model.

result of our own calculation with the same parameters. Except for differences at low energies (< 50 eV), which are probably due to the use of different potentials, the agreement between the two calculations is satisfactory. We note also that the agreement between theory and experiment is perhaps acceptable. However, Fig. 2 shows that theory and experiment do *not* agree for the $1\,\bar{1}/2$ beam (the corresponding theoretical curve of FMA for this beam at normal incidence is not available). For the remaining 9 spectra tested (not shown) we also found no satisfactory correspondence between theory and experiment. This conclusion did not change when we varied the buckling parameter b_1 from 0.15 to 0.075 and 0.225 Å, and the bond length d_2 from 2.27 to 2.19 and 2.35 Å. The correspondence between theory and experiment was too poor to justify use of an r-factor[15] analysis. We must, therefore, disagree with the conclusion reached by Feder, Moench, and Auer[5]—the buckling model, as defined in Fig. 3 and above, does not pass the LEED test.

Figure 4 depicts the π-bonded chain model of Pandey.[2] The author's requirements for this model are that all bond lengths should be equal to the bulk value (2.35 Å) except along the upper chain where they are contracted by 0.1 Å. Hence, the parameters defined in Fig. 4 should be $d_1 = 1.14$ Å, $d_2 = 2.14$ Å, $L_1 = 2.06$ Å, and $L_2 = 0.99$ Å. The $\bar{1}0$ and $1\,\bar{1}/2$ LEED spectra calculated with these values are depicted as curves P in Figs. 1 and 2. We varied d_1 from 1.14 to 0.94 Å and d_2 from 2.14 to 1.94 Å, and found some slight improvement in the theory-experiment correspondence for some integral-order beams by using a contracted d_1 value. Unfortunately, the correspondence for all fractional-order

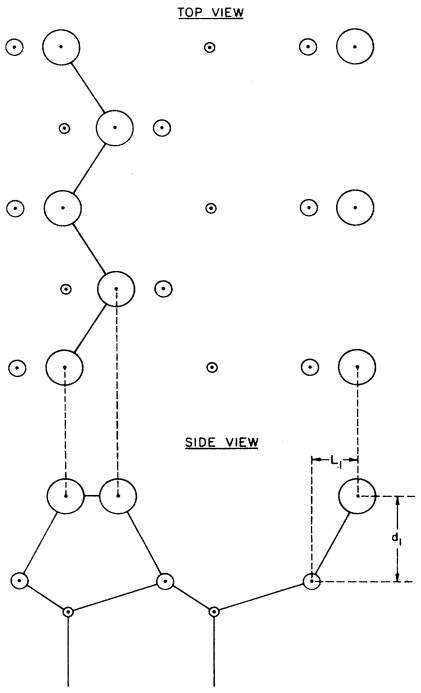

FIG. 5. Schematic top and side views of conjugated-chain model.

beams is always very poor and unacceptable. The conclusion is that the chain model as defined in Fig. 4 and above does not pass the LEED test.

The Seiwatz model[11] is quantified schematically in Fig. 5. The parameters defined in Fig. 5 were chosen as $L_1 = 1.07$ Å and d_1 varying from 1.89 to 2.09 to 2.29 Å. Correspondence of calculated with observed spectra was found to be very poor. A similar conclusion was drawn for a version of Chadi's molecular model exhibiting symmetrical and nonbuckled chains.

In summary, the work done so far has produced some positive and some negative results. (a) LEED intensity data from a cleaved Si{111} surface exhibiting a single-domain 2×1 structure are reproduced well from experiment to experiment. (b) The hypothesis of two 2×1 structures simultaneously present on the surface is rather improbable—conversely, if more than one structure is present, then the relative proportions of the occurring structures seem to be constant. (c) None of the models tested, in particular, the buckling and the π-bonded chain models, passes the LEED test: The structure of Si{111}2×1 is still unknown. It is possible, indeed probable, that distortions in deeper layers, not taken into account here, play an important role, as they do in the structure of Si{001}2×1.[14] If and when such distortions become quantitatively known, all the models tested in this work will have to be tested again.

Note added in proof. In later work Petroff and co-workers find both the dispersive and dispersionless band (F. Houzay, G. M. Guichar, R. Pinchaux, G. Jezequel, F. Solar, A. Barsky, P. Steiner, and Y. Petroff, in *Proceedings of the 2nd IUPAP Semiconductor Symposium, Surfaces and Interfaces, Physics and Electronics, Trieste, Italy, 1982* [Surf. Sci. (in press)]).

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