Si(111)-(2×1) Surface: Buckling, Chains, or Molecules?

R. M. Tromp, L. Smit, and J. F. van der Veen
Fundamenteel Onderzoek der Materie–Institute for Atomic and Molecular Physics,
1098 SJ Amsterdam, The Netherlands

(Received 16 August 1983)

This Letter presents direct evidence for large displacements parallel to the surface of the atoms in the outer double layer of the cleaved Si(111)-(2 × 1) surface. This result excludes the buckling model for this surface reconstruction. Comparison of surface blocking patterns, obtained by medium-energy ion channeling and blocking, with computer simulations for the π-bonded chain model shows good agreement between experiment and model. The π-bonded molecule is not in agreement with the data.

PACS numbers: 68.20.+t

For many years there has been general agreement that the structure of the cleaved Si(111)-(2×1) surface is well described by the buckling model, proposed by Haneman.[1] In this model alternate rows of atoms are displaced up and down, doubling the periodicity of the surface unit cell. The displacements are primarily normal to the surface, and are very small parallel to the surface. Recently, however, Pandey[2] proposed a new model, in which the surface topology is changed to give rise to π-bonded chains running parallel to the surface. The formation of these chains causes large displacements of surface atoms along the [$\bar{1}\bar{1}2$] direction parallel to the surface, a feature which is strikingly different from the buckling model. Subsequently, Chadi[3] proposed a model in which π bonding occurs between pairs of atoms ("molecules") in the outer layer. In constrast to the π-bonded chain model the surface atoms in the molecule model are displaced out of the bulk ($\bar{1}10$) planes.

These new models were proposed on the basis of total-energy calculations.[2,4] Of the models now investigated the π-bonded chain model has the largest energy gain with respect to the bulklike surface. Recent angle-resolved photoemission data[5-7] and infrared absorption measurements[8,9] may be explained by this model, but these experiments alone have not unambiguously established the nature of the (2×1) surface reconstruction. The only structural technique used to study the π-bonded chain model is low-energy electron diffraction (LEED), yielding evidence in favor of the buckling model.[10] Moreover, in a recent paper Feder has shown that his data are inconsistent with the I-V curves calculated for the chain model.[11] In this LEED study the subsurface atoms were placed on bulklike positions, and strain-induced displacements were not considered.

In this paper we report on the study of cleaved, single-domain Si(111)-(2×1) surfaces with medium-energy ion scattering, combined with shadowing and blocking. It has been shown in previous work that this technique is very sensitive to the geometric structure of a solid surface. The technique can be used to determine displacements of surface atoms with respect to the atomic rows in the underlying bulk crystal. Comparison of experimental results with Monte Carlo computer simulations of the experiment for specific structure models allows distinction of these models on a quantitative basis.[12]

The inset of Fig. 1 shows a ($\bar{1}10$) scattering plane normal to the (111) surface of a bulklike Si

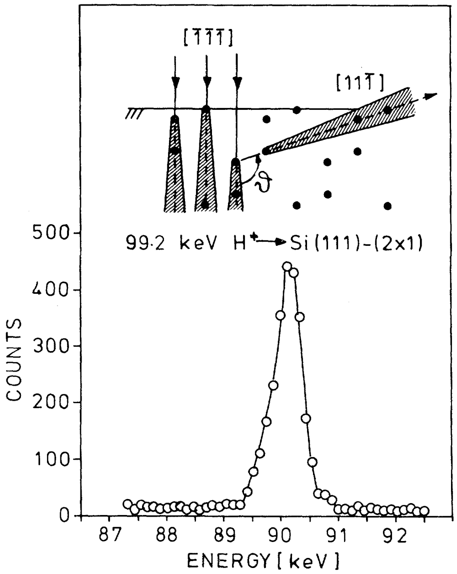

FIG. 1. Energy spectrum of protons with an initial energy of 99.2 keV, backscattered from a Si(111)-(2 × 1) surface in the geometry shown in the inset. $\theta = 109.6°$.

crystal. A 99.2-keV H^+ beam is aligned with the $[\bar{1}\bar{1}\bar{1}]$ direction. The first atom of each atomic row casts a shadow cone, reducing the probability of deeper atoms being hit by the ion beam. By definition the hitting probability of the first atom in each row is equal to 1. The sum of the hitting probabilities of the atoms along the row in the surface region is called the number of atoms per row. Shadowing of subsurface atoms is less effective if the atoms closer to the surface do not occupy their bulklike position, because of statistical thermal displacements, or because of static displacements as may occur in a reconstructed surface. Therefore such displacements influence the number of atoms per row visible to the ion beam.

In a reconstructed surface displacements of surface atoms from a bulklike position may be so large that these atoms do now shadow subsurface atoms. For example, in the π-bonded chain model not only the bulklike [111] rows of the underlying crystal are exposed to the ion beam, but also—as an extra—the displaced outer double layer of the crystal. By alignment of the ion beam along the $[\bar{1}\bar{1}\bar{1}]$ direction, as in Fig. 1, the number of atoms per $[\bar{1}\bar{1}\bar{1}]$ row displaced parallel to the surface can be determined in a backscattering experiment. For the buckling model, in which large parallel displacements do not occur, only the bulklike rows will be exposed to the ion beam, whereas in the π-bonded chain model (and in the π-bonded molecule model) one expects to see at least one extra double layer.

Further structural information may be obtained by detecting the yield of backscattered ions as a function of scattering angle, while keeping the direction of the incoming ion beam fixed along the $[\bar{1}\bar{1}\bar{1}]$ direction. Ions scattered below the surface can reach the vacuum, unless they are blocked on the outgoing path by an atom closer to the surface. In directions in which such blocking occurs, there is a minimum in the yield of backscattered ions, called a surface blocking minimum. In Fig. 1 one such direction is indicated along the $[\bar{1}\bar{1}\bar{1}]$ axis. Additional blocking minima may arise in a reconstructed surface. Thus, these surface blocking minima reveal the positions of the surface atoms.

For specific structural models the experiment may be simulated in a computer by Monte Carlo techniques. The number of atoms per row visible to both ion beam and detector can be calculated as function of scattering angle. The resulting blocking minima may be compared with measured surface blocking minima on an absolute basis. In the present study we have used a program in which a crystal is generated by repeating the surface unit cell parallel to the surface with periodic boundary conditions.[13] The ion is followed through the crystal along its path until it is backscattered towards the surface, or unitl it penetrates the crystal beyond the surface region where it no longer contributes to the surface backscattering yield. As a result of time reversibility the incident and outgoing paths can be treated separately with good accuracy. In the present simulations the finite opening angle of the analyzer outside the scattering plane has been taken into account.

Rectangular bars ($4\times10\times30$ mm^3) of float-zone Si(111) crystals were cleaved in the UHV scattering chamber in a special manipulator, designed for compatibility with the high-precision three-axis goniometer used for the ion scattering studies. On one long side of the Si bars grooves were cut, 0.5 mm wide and 1.5 mm deep. The other long side of the bar was polished. The crystals were cleaved in the $[\bar{1}\bar{1}2]$ direction. Cleavage along the $[\bar{1}10]$ direction was attempted first, but single-domain cleaves could not be obtained with sufficient efficiency. Furthermore, cleavage along this direction often resulted in a high density of defects in a region extending over tens of angstroms into the crystal, as could be judged from energy spectra of backscattered ions. This severe damage never occurred on crystals cleaved along the $[\bar{1}\bar{1}2]$ direction. After cleavage the sample holder and crystal were transferred from the special manipulator to the three-axis goniometer. The surface structure was inspected in the same UHV chamber with LEED prior to the ion-scattering experiments in order to select a suitable domain area on the surface. This inspection took only a few minutes, after which the ion-scattering experiments could be performed. The total duration of an experiment was typically 2–2.5 h, in a vacuum of less than 10^{-10} Torr with ion beam on target. After completion of the ion-scattering experiments, photographs were made of the LEED patterns on various positions on the surface.

Ions were simultaneously analyzed in energy and scattering angle with a toroidal electrostatic analyzer having an energy resolution of $\Delta E/E = 4\times10^{-3}$ and an angular resolution of 0.3°. Figure 1 shows an energy spectrum of 99.2-keV protons incident on a Si(111)-(2×1) surface along the $[\bar{1}\bar{1}\bar{1}]$ direction and leaving along the $[11\bar{1}]$ direction, at a scattering angle of 109.6°. The strong peak at 90.2 keV arises from backscattering of ions from the surface region and is shifted to an energy lower than the incident energy by the kinematical energy loss. At still lower backscattered energies (corresponding to greater depth) the intensity is very much reduced due to shadowing. The intensity in the sharp surface peak can be converted into the number of atoms per $[\bar{1}\bar{1}\bar{1}]$ row, visible to ion beam and detector, by comparison with the backscattering intensity from a well-known standard. The accuracy of this conversion is estimated to be ± 5%.

Figure 2(a) shows the surface-blocking patterns obtained on single-domain Si(111)-(2×1) surfaces. The number of atoms per row is shown as function of scattering angle θ. The blocking minima shown are the result of experiments on four different crystals. The reproducibility from crystal to crystal was excellent and only the averaged data are shown to reduce statistical scatter in the data points. The data set represented by squares was measured with the H^+ beam aligned with the $[\bar{1}\bar{1}\bar{1}]$ direction and the analyzer detecting ions in the $(\bar{1}10)$ plane, as in Fig. 1. At $\theta = 109.48°$ a deep surface blocking minimum is observed along the outgoing $[11\bar{1}]$ direction. At smaller scattering angles several, partly overlapping, minima give rise to an overall reduction of the number of atoms per row. At higher scattering angles ($113° < \theta < 118°$) the number of atoms per row is fairly constant. The other set of data (triangles) was obtained with the ion beam channeling in the $[\bar{1}\bar{1}\bar{1}]$ direction, but in a scattering plane normal to the surface making an angle of 2° with the $(\bar{1}10)$ plane. This geometry is obtained from the one in Fig. 1 by rotating the crystal by 2° around its normal. In this rotated scattering plane the channeling conditions remain fixed, but atoms residing in the $(\bar{1}10)$ plane are no longer expected to give rise to blocking in the outgoing trajectories. Indeed, the major minimum at 109.5° and the overlapping minima at smaller scattering angles are completely absent in this geometry.

In the rotated geometry the measured number of atoms per row is higher than that calculated for a bulklike surface by 0.8–0.9 atoms per row, or 2.4–2.7 monolayers (1 monolayer $= 7.83 \times 10^{14}$ atoms/cm^2). Thus, 2.4–2.7 monolayers of silicon are displaced over such a large distance parallel to the surface that they do not shadow the atoms in the underlying bulk crystal. This experimental observation excludes all structural models for the (2×1) surface in which the atoms are not displaced parallel to the surface (i.e., buckling models). For $113° < \theta < 118°$ the yield in the $(\bar{1}10)$ scattering plane is found to be 0.3 atoms per row lower than in the 2° rotated plane. This lowering indicates that in the $(\bar{1}10)$ plane surface blocking occurs in this range of scattering angles. Thus, surface atoms are displaced parallel to the surface, but can still be found in the $(\bar{1}10)$ planes, where they give rise to blocking. Therefore, models in which the surface atoms are displaced parallel to the surface, but out of the $(\bar{1}10)$ planes (i.e., the π-bonded molecule model) are inconsistent with the experimental results.

In order to justify these qualitative conclusions

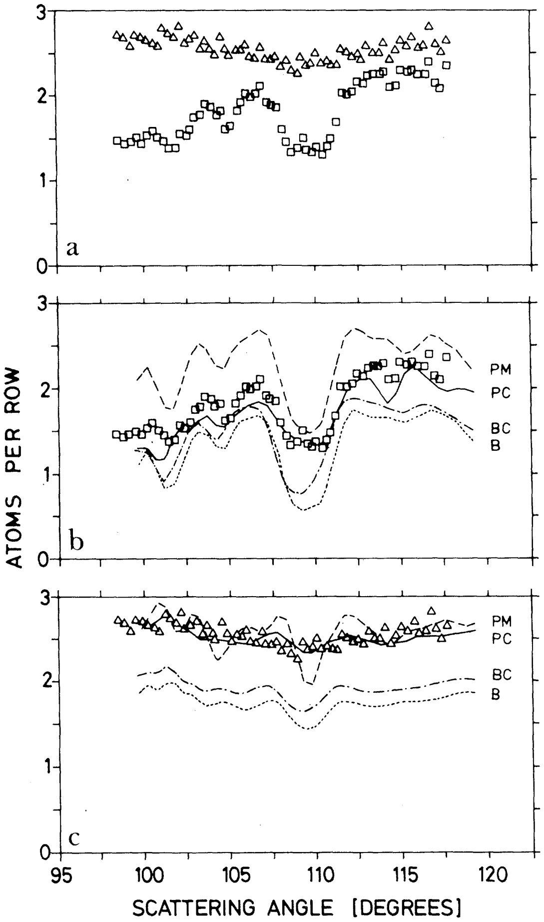

FIG. 2. (a) Surface-blocking profiles measured on the Si(111)-(2×1) surface. The data were taken in the geometry shown in Fig. 1 (squares) and in the rotated geometry (triangles) (see text). (b) and (c) The same data (a), and calculated surface-blocking profiles for a bulklike surface (B), a buckled surface (BC), the π-bonded chain model (PC), and the π-bonded molecule model (PM), for the two different backscattering geometries.

further, we have calculated surface blocking minima for a bulklike surface (B), a buckled surface[10] (BC), the π-bonded chain model (PC), and the π-bonded molecule model[3] (PM), all for the two experimental geometries of Fig. 2(a). The coordinates for the chain model were obtained by minimization of the elastic strain in the outer four layers of the crystal in a Keating formalism.[14,15] The bond length between atoms in the top chain was fixed at 2.25 Å.[2,4] In the simulations a one-dimensional rms thermal displacement of 0.075 Å (the bulk value) was used, while in the reconstructed surfaces the atoms in the outer double layer were given an enhanced amplitude of 0.11 Å. The results were not very sensitive to this surface enhancement. Correlations in the thermal motions are expected to have little effect and were not included.

The results are shown in Figs. 2(b) and 2(c). It is interesting to compare the experimental minimum at 109.5° with those calculated for the bulklike and the buckled surface. In these models the surface atoms occupy (nearly) bulklike positions and give rise to efficient blocking along this direction. In the experiment blocking is far less efficient, indicating that the surface atoms do not reside on such (nearly) bulklike positions as a result of a strong reconstruction of the surface. For the π-bonded chain model we find good agreement between experiments and simulations in both geometries. The results of these computer simulations confirm the conclusions based on the experimental observations and show that, of the models presently investigated, only the π-bonded chain model is consistent with the ion-scattering results.[16] The fact that the displacements parallel to the surface occur in more than two monolayers indicates that substrate (strain-induced) displacements play a role in this surface. It is likely that such displacements will influence the analysis of other experiments like LEED.

The authors would like to thank Dr. W. Mönch and Dr. G. V. Hansson for helpful suggestions concerning the art of cleaving silicon. The authors thank the Philips Research Laboratories in Eindhoven for their contribution.

This work was sponsored by the Fundamenteel Onderzoek der Materie–Institute for Atomic and Molecular Physics with financial support by the Nederlandse Organisatie Voor Zuiver-Wetenschappelijk Onderzoek.

---

[1] D. Haneman, Phys. Rev. 121, 1093 (1961).

[2] K. C. Pandey, Phys. Rev. Lett. 47, 913 (1981), and 49, 223 (1982).

[3] D. J. Chadi, Phys. Rev. B 26, 4762 (1982), and private communication.

[4] J. E. Northrup and M. L. Cohen, J. Vac. Sci. Technol. 21, 333 (1982).

[5] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. Lett. 48, 1032 (1982); G. V. Hansson, R. Z. Bachrach, R. S. Bauer, D. J. Chadi, and W. Göpel, Surf. Sci. 99, 13 (1980).

[6] F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B 24, 2003 (1981).

[7] F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, J. Vac. Sci. Technol. 18, 860 (1981).

[8] S. Nannarone, P. Chiaradia, F. Ciccacci, R. Memeo, P. Sassaroli, S. Selchi, and G. Chiarotti, Solid State Commun. 33, 593 (1980).

[9] J. Assmann and W. Mönch, Surf. Sci. 99, 34 (1980).

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

[11] R. Feder, Solid State Commun. 45, 51 (1983).

[12] R. M. Tromp, J. Vac. Sci. Technol. 1A, 1047 (1983).

[13] J. W. M. Frenken, R. M. Tromp, and J. F. van der Veen, to be published.

[14] P. N. Keating, Phys. Rev. 145, 637 (1966).

[15] J. A. Appelbaum and D. R. Hamann, Surf. Sci. 74, 21 (1978).

[16] Two minor differences between the simulations for the π-bonded chain model and the data remain. In Fig. 2(b) the calculated minimum at $\theta = 114°$ is slightly deeper and the calculated minima near 101° and 104.5° appear at slightly too small scattering angles. These differences indicate that minor modifications in the coordinates of the atoms in the chain model are necessary to obtain exact agreement with the data in Fig. 2(b). Further work on the chain model to clarify these issues is in progress.