

## Structure determination of the Si(111)-(2×1) surface with channeling and blocking

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The structure of the cleaved Si(111)-(2×1) surface has been determined with medium-energy ion scattering using the effects of channeling and blocking. The basic structure arrived at is the  $\pi$ -bonded chain model, modified by a tilt in the first- and second-layer chains, of 0.3 (+0.35, -0.45 Å) and -0.15 (+0.25, -0.15 Å), respectively. The first-layer chain is not relaxed significantly. We find that strong enhancement of surface thermal vibrations is needed to obtain good agreement with experimental results. The structural parameters determined do not depend on the detailed choice of vibration amplitudes.

Medium-energy ion scattering combined with the effects of channeling and blocking was the first structure-sensitive technique to show that the structure of the cleaved Si(111)-(2×1) surface is best described by the  $\pi$ -bonded chain model proposed by Pandey.<sup>1,2</sup> Feder, using LEED (low-energy electron diffraction) *IV* analysis to study this same surface, concluded that the chain model was refuted by LEED, and he presented support for the buckling model.<sup>3</sup> Similarly, Liu, Cook, Jona, and Marcus concluded that the chain model did not pass the LEED test.<sup>4</sup> More recently, reevaluation of the LEED data by Feder and Mönch led to the conclusion that buckling (either on the ideal surface, or in the  $\pi$ -bonded chain model) must be present.<sup>5</sup> In these LEED studies, subsurface displacements induced by the reordering of the surface atoms were not considered. On the basis of our ion scattering results, we concluded that such displacements are important and should be taken into account. Even so, some minor discrepancies remained between the experimental ion scattering results and the surface-blocking minima calculated for the  $\pi$ -bonded chain model, including subsurface displacements. We anticipated that minor refinements of the chain model would suffice to resolve these discrepancies.

In this Rapid Communication we show that—through a systematic search—we have found a structure that is in very good agreement with ion scattering results.

Figure 1 shows a surface-blocking profile<sup>6</sup> measured on a single domain Si(111)-(2×1) surface with 99.2-keV protons, in the scattering geometry shown in the insert. The ion beam was aligned with the  $[\bar{1}\bar{1}\bar{1}]$  channeling direction. Surface atoms cast a shadow cone, reducing the probability for atoms deeper in the crystal to be hit by the ion beam. The effectiveness of this shadowing phenomenon depends on the extent to which (small) static and/or dynamic displacements from ideal positions occur, due to either surface reconstruction or surface thermal vibrations. If shadowing is perfect, only the first atom of each  $[\bar{1}\bar{1}\bar{1}]$  row can be hit by the ion beam, and the “number of atoms per row” visible to the ion beam is equal to one. If shadowing is not perfect, this number is larger. The surface peak intensities were converted to the number of atoms per row visible to ion beam and detector by comparison with a backscattering standard.<sup>6</sup> On the outgoing  $[11\bar{1}]$  direction we expect to find a strong surface-blocking minimum as is indeed ob-

served. Along this direction, ions scattered below the surface are blocked on their way to the vacuum by atoms closer to the surface. Similar blocking effects occur at smaller scattering angles, where more blocking minima are observed. Note, that the vertical scale in Fig. 1 is given in atoms per row and can be compared with calculated surface-blocking minima quantitatively. In a previous paper these experimental results have been compared with surface-blocking minima, calculated with a Monte Carlo simulation of the experiment, for various structure models. It was concluded that only the  $\pi$ -bonded chain model could be said to agree with the data, although there was no “perfect” agreement.<sup>1</sup>

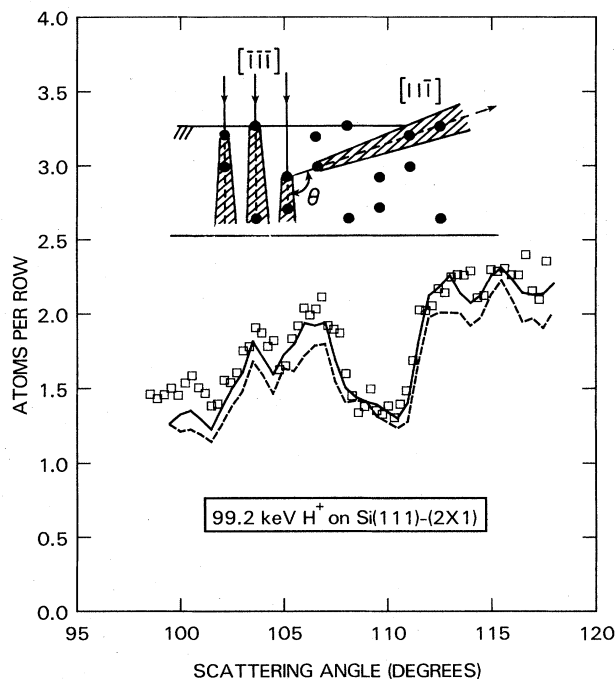


FIG. 1. Number of atoms per  $[\bar{1}\bar{1}\bar{1}]$  row, visible to ion beam and detector, plotted vs scattering angle. Data were taken on a single domain Si(111)-(2×1) surface in the scattering geometry shown in the insert. The solid and dashed lines are discussed in the text.

Figure 2 shows a side view of the chain model. The figure indicates which structural parameters we have varied to improve the agreement with the experiment. We have considered a tilt of the top chain  $d_1$ , a tilt of the second layer chain  $d_2$ , and a relaxation of the top chain  $r_1$ . The atomic coordinates in the first five layers of the crystal were calculated by minimizing the total elastic energy in the crystal, in a Keating-type calculation,<sup>7,8</sup> with particular values of  $d_1$  and  $d_2$  imposed as boundary conditions and assuming that the Si-Si bond length in the top chain is 2.24 Å (Refs. 2 and 9). The resulting structures were defined as  $r_1=0$ . Relaxations of the top chain were considered by moving the top chain up and down rigidly, leaving all other coordinates unchanged. Surface-blocking minima have been calculated for  $r_1 = -0.3, 0.0,$  and  $+0.3$  Å for values of  $d_1$  and  $d_2$  ranging from  $-0.45$  to  $+0.6$  and  $-0.3$  to  $+0.3$  Å, respectively. For every blocking curve thus obtained, the normalized value of  $\chi^2$  was calculated. This quantity was defined as

$$\chi^2 = \frac{1}{n-m} \sum_{i=1}^n \frac{(wY_i^e - Y_i^c)^2}{\sigma_i^2},$$

where  $Y_i^e$  is the value of data point  $i$  (in atoms per row),  $Y_i^c$  the corresponding calculated value of point  $i$ ,  $\sigma_i$  the experimental (statistical) uncertainty of data point  $i$  (3%),  $w$  a scaling factor which must be in the range 0.95–1.05 and which reflects the experimental uncertainty in the calibration of the data,  $n$  the number of points, and  $m$  the number of fitting parameters.

Figure 3 shows the resulting contour plot of  $\chi^2$  as function of  $d_1$  and  $d_2$ . In every point, the lowest value of  $\chi^2$  with respect to  $r_1$  was used in this plot. One-dimensional (1D) rms thermal displacements were chosen to be 0.16, 0.125, 0.105, and 0.90 Å in the first four layers of the crystal and 0.075 Å in the deeper layers of the crystal (1 layer =  $7.83 \times 10^{14}$  atoms/cm<sup>2</sup>). In each point, the data were allowed to be scaled freely. The scaling factor always was in the experimental range 0.95–1.05. The contour plot shows a single minimum for  $d_1=0.3$  and  $d_2=-0.15$  Å. The

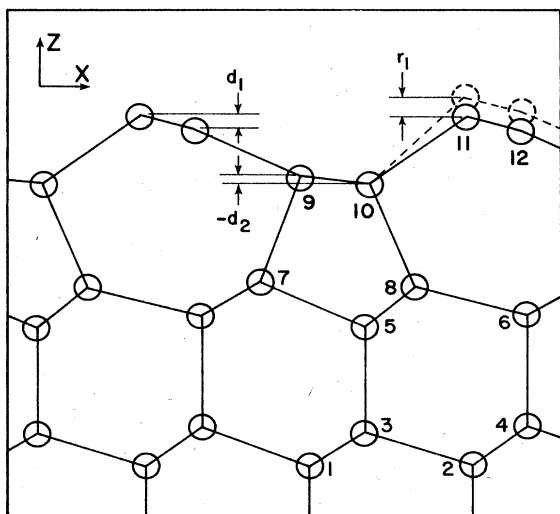


FIG. 2. Side view of the optimized chain model in  $[110]$  projection showing the parameters varied in the fitting procedure.  $d_1$ ,  $d_2$ , and  $r_1$  are defined as indicated by this figure.

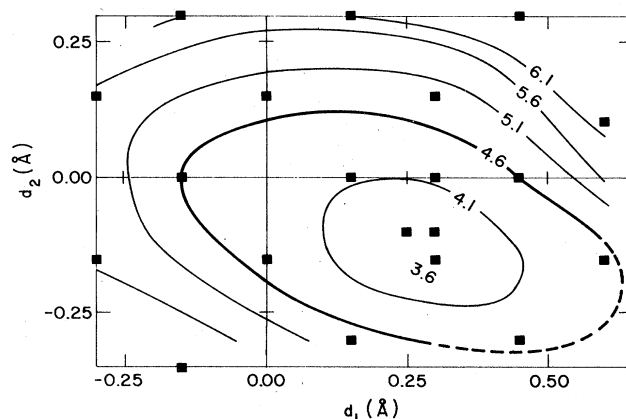


FIG. 3. Contours of constant  $\chi^2$  as function of  $d_1$  and  $d_2$ . In every point  $\chi^2$  was chosen to be minimum with respect to  $r_1$ . Vibration amplitudes are specified in the text. The full squares indicate for which points surface blocking minima have been calculated; the contours were obtained by interpolation. The dashed part of the heavy contour is an extrapolation.

heavy contour denotes an increase of one from the minimum value of  $\chi^2$ , and indicates the experimental uncertainty of the structural parameters.<sup>10</sup> Taking  $d_1=0.3$  and  $d_2=-0.15$  Å, we determine from a visual comparison of calculated blocking minima with the data that  $r_1=0.0 \pm 0.3$  Å. The values for the surface thermal vibration amplitudes are not the result of a unique determination. However, if much smaller enhancements are chosen, good agreement with experiment cannot be obtained. A contour plot similar to Fig. 3 was constructed with 1D rms thermal displacements of 0.11 Å in the outer two layers of the crystal and 0.075 Å in all deeper layers. The minimum in  $\chi^2$  occurred for similar values of  $d_1$  and  $d_2$ , with the same error bars, but with a scaling factor of the data that was consistently outside the experimental error bars. Also, the absolute value of  $\chi^2$  was not as good as in Fig. 3. The solid line in Fig. 1 gives the calculated blocking curve for the optimum structure of Fig. 3, the dashed line is for the same structure, but with the smaller vibration enhancements. Indeed, very good agreement with the data is now observed. The coordinates of this optimum structure are listed in Table I.

TABLE I. Coordinates of optimized chain structure in Å.

	X		Y	Z	
	This work	LEED (Ref. 13)		This work	LEED (Ref. 13)
1	1.11	1.09	1.92	-3.91	-3.90
2	4.43	4.45	0	-3.91	-3.93
3	2.21	2.21	0	-3.20	-3.21
4	5.54	5.54	1.92	-3.06	-3.08
5	2.21	2.22	0	-0.92	-0.89
6	5.54	5.54	1.92	-0.65	-0.69
7	0.08	0.09	0	0.05	-0.02
8	3.24	3.24	1.92	-0.05	-0.09
9	0.91	0.95	0	2.28	2.18
10	2.34	2.34	1.92	2.13	2.11
11	4.30	4.34	1.92	3.56	3.37
12	5.42	5.46	0	3.26	2.99

Several remarks can be made with respect to the optimum structure at which we arrive. Firstly, the tilt of the top chain is in fair agreement with theoretical results: 0.09 (Ref. 11) to 0.19 Å (Ref. 9). Secondly, the tilt of the second-layer chain is in the same direction as the top chain. (If the elastic energy is minimized in a Keating-type calculation a tilt in the opposite direction is found.) Again, this result agrees with theory.<sup>11</sup> Finally, the vibration enhancements are reminiscent of our results obtained on the very similar GaSb(110) surface.<sup>12</sup> There, the surface vibration amplitudes are enhanced by a factor of 1.6. These enhancements occur because of the small restoring forces occurring when the top and bottom chains are tilted, or sheared along the  $[\bar{1}10]$  direction. These motions require only bond bending and no bond stretching. Since the top chain is flatter than the chains in the GaSb(110) surface, one may expect that it is even softer and vibration amplitudes still larger. The enhancements we find may partly be due to surface disorder associated with steps. However, the high quality of the single domain cleaves used in this study [average misorientation of the surface normal from the  $[111]$  direction was less than  $1^\circ$ ], and the excellent reproducibility on three different samples suggest that the contribution of disorder to the surface peak is not more than a few

percent. In a LEED study performed simultaneously with this ion scattering study, using the ion scattering results as a guidance, a structure very similar to the one reported here was found to give reasonable agreement between measured and calculated  $IV$  curves.<sup>13</sup> The coordinates resulting from the LEED study are also given in Table I. The major difference is that the LEED study finds an inward relaxation of the top chain of  $\sim 0.23$  Å, not inconsistent with our present results. In conclusion, this ion scattering study has resulted in a structure model for the Si(111)-(2×1) surface that fully explains the experimental results and gives strong support to the  $\pi$ -bonded chain model. The model is modified by introducing a moderate tilt in the top chain and a small tilt in the second-layer chain. We find clear evidence for a strong enhancement of surface thermal vibration amplitudes.

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