Reflection high-energy electron-diffraction analysis of the Si(111)-(7×7) reconstruction

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(Received 18 March 1994)

Most of the techniques used to determine the structure of reconstructed surfaces are relatively insensitive to displacements perpendicular to the surface, especially those of subsurface atoms. Reflection high-energy electron diffraction (RHEED) is sensitive to these displacements. We have performed a dynamical simulation of RHEED intensities and show that for the Si(111)-7×7 reconstruction, the dimer-adatom stacking-fault model optimized by *ab initio* parallel computation has given more accurate atomic positions than previous determinations by other approaches. This indicates that the relative intensities of reflections in a RHEED pattern contain important, sensitive surface structural information.

The Si(111)-7×7 surface reconstruction was observed through low-energy electron diffraction (LEED) in 1959 (Ref. 1) and has been perhaps the most extensively studied surface structure since then. It took about a quarter of a century to determine the basic model or key ingredients of this reconstruction before the atomic topography of the surface was observed[2] by scanning tunneling microscopy (STM) and the dimer-adatom stacking-fault (DAS) model was proposed by Takayanagi *et al.*,[3] through studies using transmission high-energy electron diffraction (THEED). During that period of time, a large number of models were proposed based upon studies of the surface with virtually every surface analytical technique available for surface structure determination.[4–14] As well as experimental investigations, various theoretical methods of surface energy minimization were also applied to study the model structures.[10,15–17] The DAS model has now been widely accepted because it is supported by three major techniques in this consistent collective investigation, namely, STM[2], THEED,[3] and ion scattering (IS).[10] The efforts have turned to refinement of the structure because detailed structural information is always a basis for understanding a wide range of chemical and physical properties of surfaces. In terms of structural refinement, some techniques which played key roles in determining the DAS model may suffer from some inherent shortcomings. For example, what is observed in STM,[2] in fact, is the topography of the valence-electron cloud of the top atomic layer and the quantitative information about individual coordinates of nuclei in deeper layers seems beyond the reach of the technique. There is almost no information about vertical displacements in a THEED pattern.[3] The number of atoms per row measured in IS versus scattering angle[10] is also not yet sensitive enough to resolve individual atomic positions. But we still have some available techniques on the scene of this further investigation, namely, LEED-I/V curve analysis,[18] x-ray surface diffraction,[19] and reflection high-energy electron diffraction (RHEED) rocking-curve analysis.[20] Nevertheless, the discrepancies among the results generated by these techniques are still significant,[19] especially for the vertical displacements. In theoretical investigation, the semiempirical tight-binding method[21] and, more recently, an *ab initio* parallel computation method[22] have been carried out for this structural analysis. The discrepancies between these two calculations are less than ±0.027 and ±0.112 Å for lateral and vertical displacements, respectively. However, the worrying problem is that significant discrepancies between theoretical calculations and experiments still remain.[19]

In this paper, we report the results of intensity analysis of the RHEED pattern recorded from the Si(111)-7×7 surface by Ino [Ref. 7, Fig. 4(a)]. The RHEED patterns calculated with several sets of data for the structure, obtained with different approaches, were compared to the observed pattern. Based upon simple comparison of visually estimated characteristic intensity ordering between the observed and calculated patterns, the relative closeness of these data sets to the real structure can be assessed. The multislice formalism of Cowley and Moodie with a recently developed edge-patching method[23,24] was applied to the dynamical calculations of the RHEED patterns. The details of this approach can be found in previous publications.[25,26]

The observed RHEED pattern used in the analysis was taken along the $[\bar{1}\,\bar{1}2]$ azimuth [Ref. 7, Fig. 4(a)]. The DAS model has the symmetry of the two-dimensional (2D) space group $P3m1$. The smallest 2D unit cell representing the periodicity along $[\bar{1}\,\bar{1}2]$ is $7/\sqrt{2}a_0 \times 21/\sqrt{6}a_0$, twice as large as its primitive unit cell, where $a_0 = 5.43$ Å is the magnitude of the *bulk* primitive unit-cell vector of Si. In the calculation, the selvedge includes 4 reconstructed atomic layers, as in the *ab initio* calculation,[22] and the bulk includes 15 atomic

layers. The optimized coordinates of the atoms in the fifth layer given by LEED and Keating's relaxation[18] are nearly the same as their bulk positions, and applying the bulk position to the fifth layer will not have significant effects on RHEED intensities. The size of the supercell is

$$31/\sqrt{3a_0}[111]\times 7/\sqrt{2a_0}[\bar{1}10]\times 21/\sqrt{6a_0}[\bar{1}\,\bar{1}2]\ .$$

The total number of atoms in the supercell is 1772. The sampling array is set as $990[111]\times 280[\bar{1}10]$ and the number of slices along $[\bar{1}\,\bar{1}2]$ is 40, i.e., the potential sampling rates are 10.2, 10.4, and 0.86 points/Å in [111], $[\bar{1}10]$, and $[\bar{1}\,\bar{1}2]$, respectively (10–15 points/Å is conventional for multislice simulation[27,28]). The energy of the incident beam is 20 keV and the incident beam is along the $[\bar{1}\,\bar{1}2]$ azimuth, the same as the experimental pattern [Ref. 7, Fig. 4(a)]. The angle of incidence in the experiment was not quantitatively measured in Ref. 7. It is estimated as $\sim 2.58°$, just above the threshold angle of the (0,1) reflection, according to the position of this reflection shown in the observed pattern. The justification of this estimation will be discussed later. The Debye-Waller factor for all atoms is set at 0.35 Å^2 to reduce the scale of the problem at this initial stage. The crystal absorption is taken into account by taking the imaginary part of the potential as 0.1 of its real part as is conventional in THEED calculations.

Figure 1 shows the observed RHEED pattern [Ref. 7, Fig. 4(a)] (a) and the patterns calculated with the data of the DAS model optimized by *ab initio* parallel computation[22] (b) and (c), LEED (Ref. 18) (d), Keating relaxation[18] (e), and unrelaxed DAS model (f). For Fig. 1(c), the vertical coordinate of each adatom was set 0.23 Å (30% of the bulk interplanar distance of 0.78 Å in [111]) lower than the position given by *ab initio* parallel computation,[22] as an example of testing the sensitivity of RHEED to the vertical displacement. The spacing between the higher-order Laue zones as shown in Fig. 1(a) is slightly larger than that shown in the calculated patterns (b)–(f). This is because the calculated patterns display the radii of the Laue zones (on the Ewald sphere), whereas in the experimental pattern the zones are projected onto a plane (the plane of the fluorescent screen).

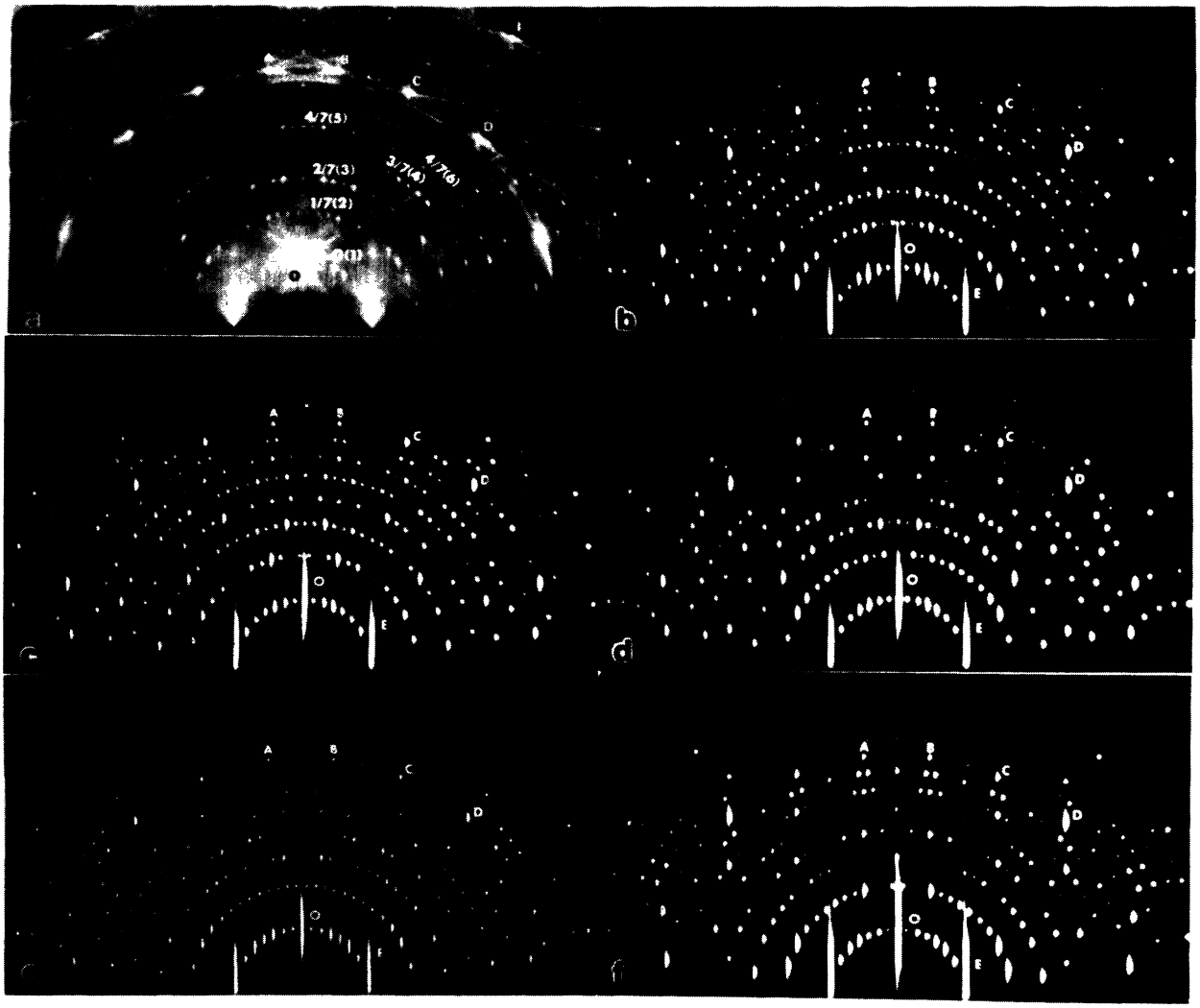

FIG. 1. Observed RHEED pattern from the Si(111)-7×7 reconstructed surface (a) and the patterns calculated with the data of the DAS model optimized by *ab initio* parallel computation (b), (c), LEED (d), Keating relaxation, (e), and unrelaxed DAS model (f).

The strong streaky effect of the reflections (0,0) and $(0,\pm1)$ shown in the calculated patterns (b)–(f) is an artifact. The Fourier transform is performed within a limited window imposed upon the vacuum wave field in the dimension normal to the surface. This produces a streaking of the spots, which is much exaggerated in the figure because these spots are oversaturated in order to show weak spots. The true angular spread of the momentums of the reflected electrons is much smaller than it appears on the picture ($\Delta\theta \approx 1.18$ mrad).

In Fig. 1(a), six characteristic groups of reflections in five zones are marked for comparison. Their indices are listed in Table I. The indexing used by one of us is adopted.[7] For (group number) GN 1 (zero-order Laue zone), both (a) and (b) show the same intensity ordering and weak intensity for the (0,5/7) reflection. The intensity of (0,5/7) is much stronger in (c)–(f). Figures 1(e) and 1(f) completely lose the correlation with (a) in terms of intensity ordering. Similarly, for GN 3 [second (Laue zone) LZ], (c)–(f) all present (2/7,10/7) and/or (2/7,11/7) as strong reflections unlike (a) and (b), where these two reflections are extremely weak. For GN 4 (third LZ), both (c) and (d) show (3/7, 12/7) with extreme low intensity and (e) has been (3/7,11/7) and (3/7,12/7) missing, while both (a) and (b) have these two reflections with relatively strong intensities. For GN 5 and 6, (b) also matches (a) better than (c)–(f) in terms of intensity ordering.

By the above comparison of visually estimated intensity features, we can conclude that (b) has the best match to (a) while the matches between (c)–(f) and (a) get regressively worse. In other words, compared to the data generated by LEED and Keating's relaxation method, the result of the *ab initio* parallel computation is closer to the true structure as judged by the RHEED experiment. There is almost no match between (a) and (f) as expected: the unrelaxed DAS model contains high strain energy and cannot be a stable structure. It should be pointed out that as the data given by Refs. 18 and 22 and the unrelaxed DAS model show, the major discrepancies between these different approaches occur in the vertical coordinates to which RHEED is most sensitive. This explains why the RHEED pattern can distinguish their differences in results in such a simple way.

On the other hand, obvious discrepancies between (a) and (b) still remain, for example, for reflections in the third Laue zone, (3/7,n/7), where $1 \le n \le 8$. At this stage, we cannot carry out further structure refinement based upon the multislice formalism because currently it is slow in handling such a large unit cell and the quantitatively acquired RHEED pattern is not available yet. The reasons for the residual discrepancies between (a) and (b) remain to be established. Nevertheless, a study of possible reasons for the discrepancies will certainly be useful for experimental refinement in the future. We always have three contributions to the error in this kind of problem: (1) experimental errors in data acquisition, dependent upon conditions of both samples and instrumentation; (2) errors in simulating experimental data; (3) approximations made in theoretical computations. Here we mainly address the errors in the simulations.

In the simulation of (b), a universal Debye-Waller factor was applied to all atoms to reduce the size of the problem. This is a bold approximation. Surface atoms are expected to have thermal vibration different from bulk atoms. They also tend to vibrate more anisotropically. Error may also be involved in the way crystal absorption is introduced, although 0.1 is considered as a conventional value in THEED calculations.

The angle of incidence θ and mean inner potential V_0 are two correlated and sensitive parameters in quantitative RHEED analysis. An error in V_0 can be approximately translated into a correction in the effective θ, and vice versa. For an open structure like the Si(111)-7×7 reconstruction, the V_0 defined for bulk loses its physical meaning in the selvedge. Significant discrepancies in V_0 among the experimental values for bulk Si and between the experimental values and the Doyle-Turner potential[29] further complicate the situation. In this case, it becomes even more difficult because θ was not measured with sufficient accuracy. To understand the effect of these uncertainties, we calculated the RHEED patterns with the data of Brommer *et al.* at five angles of incidence, $\theta = 2.48°$, 2.53°, 2.58°, 2.63°, and 2.68°, without varying V_0. The patterns calculated for $\theta = 2.48°$, 2.53° lost the correlation with (a): the intensities of $(0,\pm1)$ reflections were reduced nearly to zero. Note that the threshold angle for the reflection is 2.56°. The pattern calculated for $\theta = 2.68°$ lost the correlation with (a): the (0,0) became a low intensity reflection. The two remaining calculated patterns correlated well with each other and with (a) in terms of intensity ordering. These results mean that the angle of incidence outside the crystal θ_o for (a) is in the range of $2.61° \pm 0.05°$, if the V_0 of the Doyle-Turner potential is right ($|V_0|_{DT} = 13.9$ V). The approximate value of the angle of incidence inside the crystal then can be

TABLE I. Indices of six characteristic groups of reflections on the RHEED patterns observed and calculated from the Si(111)-7×7 reconstruction. The h indexes the order of different Laue zones in the RHEED patterns of the reconstructed surface and k the order of reflections in each Laue zone (see Ref. 18).

Group No.	h	k
1	0	2/7, 3/7, 4/7, 5/7
2	1/7	1/7, 2/7, 3/7, 4/7, 5/7, 6/7, 7/7, 8/7
3	2/7	1/7, 2/7, 3/7, 4/7, 5/7, 6/7, 7/7, 8/7, 9/7, 10/7, 11/7
4	3/7	8/7, 9/7, 10/7, 11/7, 12/7, 13/7, 14/7, 15/7
5	4/7	1/7, 2/7, 3/7, 4/7, 5/7, 6/7, 7/7, 8/7
6	4/7	10/7, 11/7, 12/7, 13/7, 14/7, 15/7, 16/7

calculated by considering the refraction effect caused by V_0: $\theta_i = 3.02° \pm 0.05°$. If the V_0 of the Doyle-Turner potential is incorrect, the range of θ_o will be different from the estimated value, but the estimated range of θ_i will stay the same and the correlation in terms of intensity ordering presented between (a) and (b) will not be lost. More detailed discussion of this point will be given elsewhere.[30] Further investigation of this issue should be pursued based upon digitally acquired and quantitatively calculated intensities of RHEED patterns.

Through the above investigation, we have evaluated several sets of atomic coordinates, optimized by different approaches, for the Si(111)-7×7 reconstruction. The results show that the data set optimized by *ab initio* parallel computation, so far as RHEED can judge, is the closest to the true structure of the surface. The evaluation is based upon visually estimated intensity ordering of reflections in a single observed RHEED pattern. The reason that this works is that the relative intensities of reflections in a RHEED pattern contain important, sensitive surface structural information. This approach apparently has a lot of room for improvement, but the results have already shown that further investigation using this approach on the Si(111)-7×7 reconstruction, or surface structures in general, is very promising. On the other hand, the speed of the multislice approach still needs to be increased in the future, by improvements in both the software itself and computing power.

This work was supported by the Department of Energy of the U.S.A. through Materials Research Laboratory, University of Illinois at Urbana-Champaign, Grant No. DEFG02-91ER45439.

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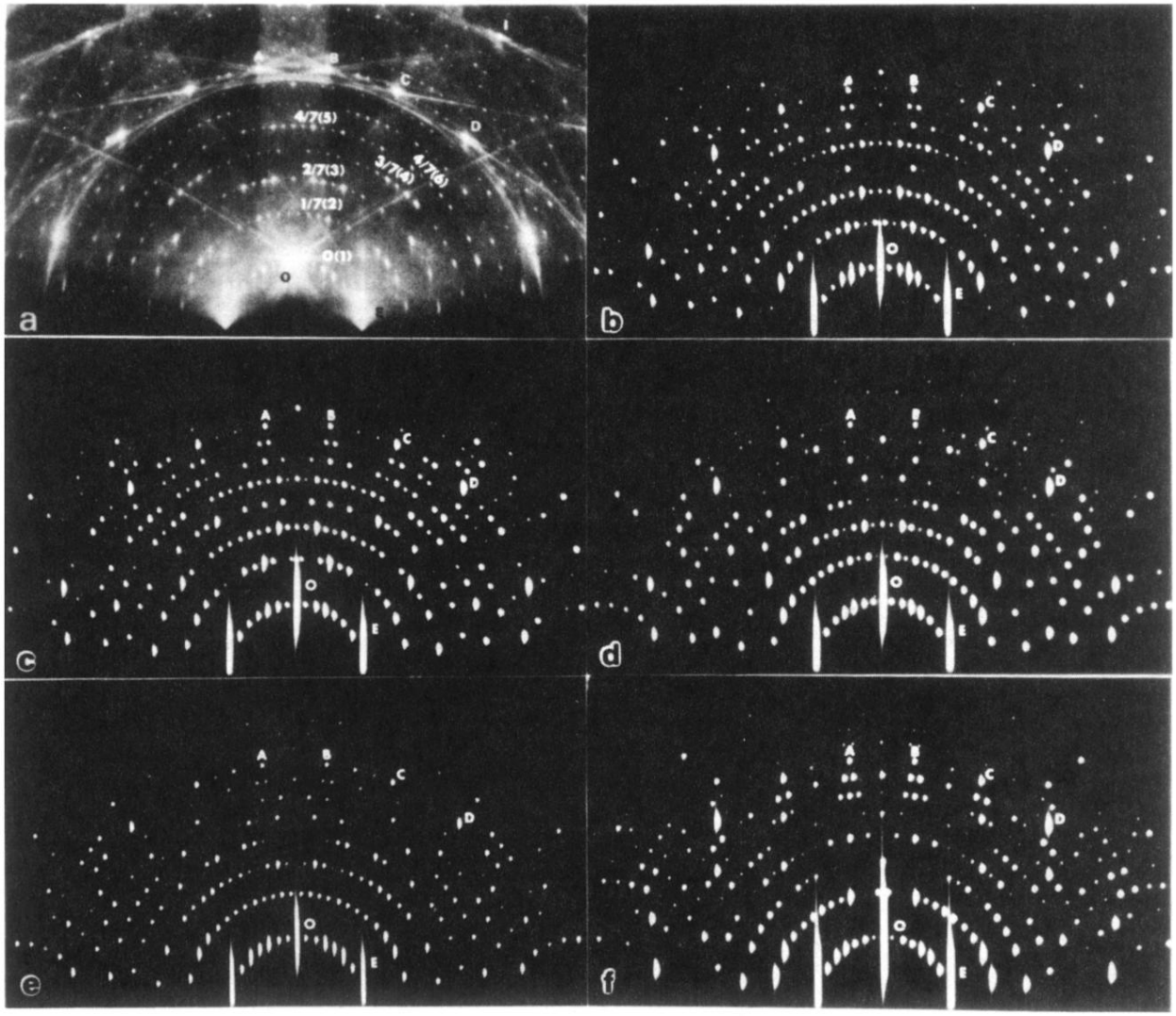

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