Reexamination of the structure of a laser-stabilized Si{111}1×1 surface

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The graphitelike model recently proposed by Jones and Holland for the structure of a laser-stabilized Si{111}1×1 surface is subjected to a new low-energy electron-diffraction (LEED) intensity analysis and compared to the relaxed-bulk model produced by earlier LEED analyses. Three different reliability factors applied to the normal-incidence data, and visual evaluation of non-normal-incidence data, discriminate unambiguously in favor of the relaxed-bulk model against the graphitelike model.

In a recent article, Jones and Holland[1] (JH) propose a new model for the atomic structure of a laser-stabilized Si{111}1×1 surface. The new model consists of a graphitelike double layer of atoms, obtained from bulklike Si{111} by contraction of the first interlayer spacing by 89.7% and expansion of the second interlayer spacing by 25.5% with respect to the corresponding bulk values. Thus, the bonds between atoms in the first and atoms in the second layer are shortened from 2.35 to 2.22 Å, while the bonds between atoms in the second and atoms in the third layer are lengthened from 2.35 to 2.95 Å. The model was chosen on the basis of a low-energy electron diffraction (LEED) intensity analysis of the six-beam normal-incidence experimental data published by Zehner *et al.*[2] JH suggest that their model may settle the ongoing controversy over the structure of a laser-stabilized Si{111}1×1 surface. We briefly recall below the nature of this controversy.

The structure of laser-stabilized Si{111}1×1 was first studied by Zehner *et al.*[2] with LEED, with the conclusion that it consists of a relaxed-bulk termination, the first interlayer spacing being contracted by a 25.5% and the second expanded by 3.2%. A very similar conclusion had been reached by Shih *et al.*[3] in an earlier study of a Te-stabilized Si{111}1×1 surface. This relaxed-bulk (RB) model also found support in the self-consistent total-energy calculations of Northrup *et al.*[4] The same model, however, was found to be inconsistent with both the photoemission study of Eastman *et al.*[5] and with the ion-scattering studies of Culbertson *et al.*[6] and of Tromp *et al.*[7] of laser-stabilized Si{111}1×1. The latter studies, in particular, led to the suggestion that large displacements (0.4 Å, corresponding to 51.3% contraction of the first interlayer spacing) of the top-layer atoms perpendicular to the surface would be required to explain the ion-scattering results. These large displacements would lead to changes in bond length which were considered "chemically unreasonable".[8] To avoid this difficulty Bennett *et al.*[8] proposed a stacking-fault model for Si{111}7×7 which they claimed to be valid for a laser-stabilized Si{111}1×1 surface as well. This model is allegedly consistent with the ion-scattering results, and it was suggested that it reproduces the LEED intensity data as well.[8] However, the latter statement is found to be incorrect when dynamical calculations of this stacking-fault model are compared with experimental data from Si{111}1×1, i.e., this model does not pass the LEED test.[9]

It is in the context of this controversy that JH proposed the graphitelike (GL) model in order to reconcile the ion-scattering results requiring large atomic displacements with a new interpretation of the LEED intensity data. Quite apart from the "reasonableness" of the bond lengths required by the GL model,[10] it is important to try and check JH's conclusion that two such different structural models as the RB and the GL models produce an almost equally good description of LEED intensity data. JH carried out full-dynamical intensity calculations with a constant damping length λ_{ee} of 8 Å and including eight layers of atoms, the scattering properties of the Si core being described by six phase shifts. The quality of the fit between theoretical and experimental LEED spectra was evaluated with the R factor of Pendry,[11] the RB model producing $R_P=0.40$ and the GL model, $R_P=0.38$. We have independently examined the GL model and compared it with the RB model using the experimental data of Zehner *et al.*[2] We confirm JH's finding that both models produce remarkably similar LEED spectra but, in contrast to JH's conclusions, we find that the RB model gives a better description of the LEED intensity data than the GL model. In addition, consideration of non-normal incidence data clearly supports the RB over the GL model. We present below the evidence for all these conclusions.

Figure 1 allows visual comparison of LEED spectra calculated for the RB and the GL models with the corresponding experimental normal-incidence data of Zehner *et al.*[2] Note that the energy range extends from 60 to

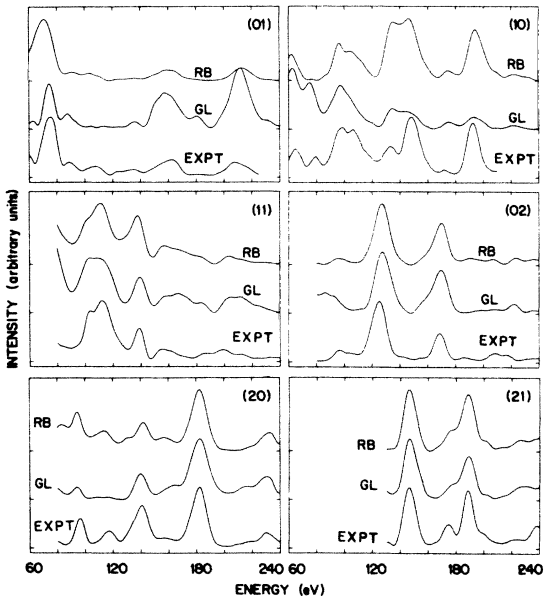

FIG. 1. Normal-incidence LEED intensity spectra for laser-stabilized Si{111}1×1. RB and GL denote curves calculated for the relaxed-bulk and the graphitelike model, respectively.

about 240 eV. Both models give an acceptable, indeed mostly good, description of the experimental data, and it is obvious that a decision between the two models can in this case only be made with objective measures of the fit such as reliability factors. Table I lists the values of three reliability factors for all six experimental spectra and for three calculation modes. In the first and the second mode, eight phase shifts were used to describe the wave function and ten layers were taken into account, the energy range being 60–240 eV in the first and 90–200 eV in the second mode. In the third mode, the calculations were made with six phase shifts and for eight layers, as done by JH,[1] the energy range extending from 90 to 200 eV. The electron absorption was taken into account with an imaginary part of the potential $V_{0i}=-4.25$ eV in all but two cases (designated RB2 and GL2 in Table I) in which the electron damping length was chosen to be $\lambda_{ee}=8$ Å, as done by JH. Three reliability factors were used: the Zanazzi-Jona r factor,[12] the Pendry R factor,[11] and the mean-square R factor.[13] The results in Table I show that in all three modes of calculations all three reliability factors discriminate in favor of the RB against the GL model.

This result is confirmed by examination of non-normal-incidence data. For a laser-stabilized Si{111}1×1 surface such data are not available but for a Te-stabilized Si{111}1×1 surface LEED intensity data at $\theta=8°$, $\phi=0°$ have been published by Jepsen *et al.*[3] There is no confirmed proof that laser-stabilized and Te-stabilized Si{111}1×1 surfaces have the same structure, but Yang and Jona[14] have shown that the available normal-incidence LEED data from the two surfaces are essentially the same, indicating that the two structures are at least very similar to one another. We have calculated LEED intensity spectra at $\theta=8°$, $\phi=0°$ for both the RB and the GL model, and compared them to the corresponding experimental spectra for Te-stabilized Si{111}1×1. For three of the available spectra visual evaluation is sufficient to disqualify the GL model, as shown in the upper three panels of Fig. 2.

The overall conclusion of this study is therefore in contrast with JH's conclusion that the GL model "describes the LEED data as well as" the RB model.[1] We find that the RB model fits the available data substantially better than the GL model, so that the latter must be discarded.

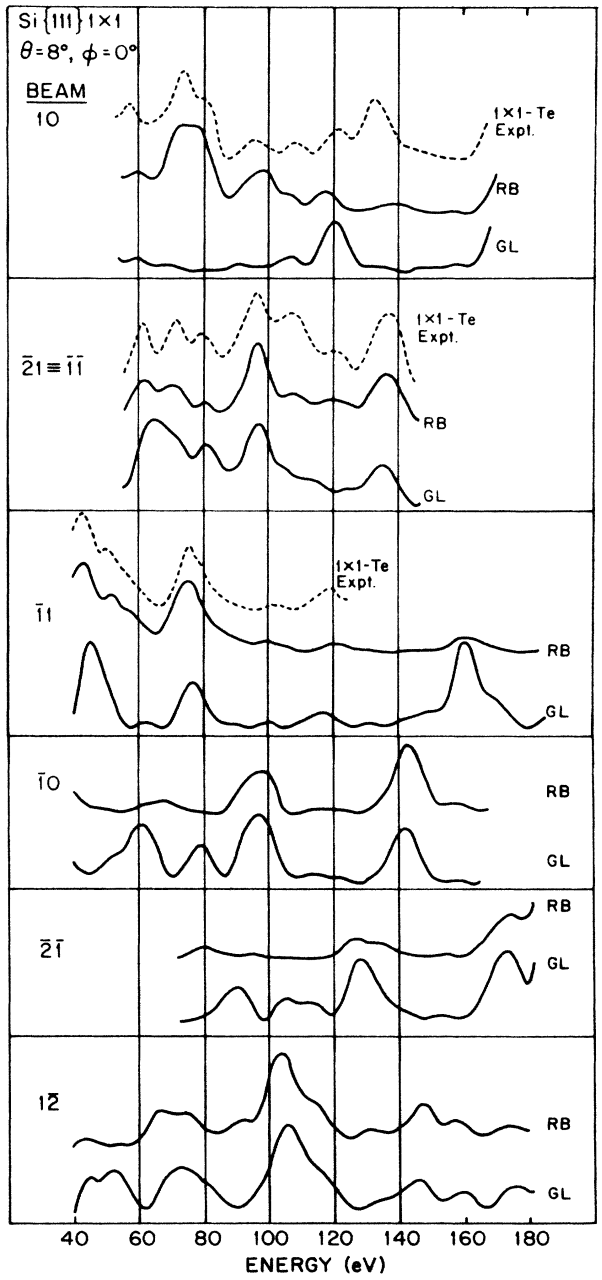

FIG. 2. Calculated LEED intensity spectra for the relaxed-bulk (RB) and the graphitelike (GL) model compared with experimental curves from a Te-stabilized Si{111}1×1 surface at $\theta=8°$, $\phi=0°$.

TABLE I. Reliability factors for the relaxed bulk (RB) model and the graphitelike (GL) model of Si{111}1×1. The models are defined as RB: $\Delta d_{12}=-25.5\%$; $\Delta d_{23}=+3.2\%$, $\Delta d_{34}=+5.0\%$; GL: $\Delta d_{12}=-89.7\%$; $\Delta d_{23}=+25.5\%$; $\Delta d_{34}=0\%$, with Δd_{ik} denoting the change in spacing between layers i and k. r_{ZJ} denotes the Zanazzi-Jona r factor (see Ref. 12), R_2 denotes the mean-square r factor (see Ref. 13), and R_P denotes the Pendry r factor (see Ref. 11). All intensity calculations used for this table were done with an imaginary part $V_{0i}=-4.25$ eV, except for RB2 and GL2 in which the imaginary part was adjusted to correspond to a damping length $\lambda_{ee}=8$ Å, as done by JH (Ref. 1). The phase shifts were calculated with procedures given by Lee and Beni (Ref. 17) and Si atomic wave functions given by Clementi and Roetti (Ref. 18). (a) Intensity calculations with eight phase shifts for ten-layer slab with energy range 60–240 eV, (b) eight phase shifts for ten-layer slab with energy range 90–200 eV, and (c) six phase shifts for eight-layer slab with energy range 90–200 eV.

Model	R factor	Beams 01	10	11	20	02	21	Mean
				(a)				
RB	r_{ZJ}	0.1866	0.1777	0.0845	0.0968	0.1006	0.0845	0.1134
GL	r_{ZJ}	0.1869	0.2935	0.1175	0.1179	0.1415	0.1265	0.1514
RB	R_2	0.3082	0.2136	0.0803	0.1257	0.1257	0.0363	0.1418
GL	R_2	0.5364	0.5968	0.1152	0.2018	0.1710	0.0558	0.2661
RB	R_P	0.4238	0.3884	0.5080	0.3597	0.4781	0.3647	0.4187
GL	R_P	0.4496	0.4678	0.4919	0.3479	0.7135	0.4672	0.4959
				(b)				
Rb	r_{ZJ}	0.0845	0.1446	0.0939	0.0998	0.0836	0.0769	0.0903
GL	r_{ZJ}	0.2315	0.2374	0.0995	0.1308	0.1213	0.1071	0.1445
RB	R_2	0.1069	0.1739	0.0750	0.0759	0.0863	0.0234	0.0867
GL	R_2	0.4015	0.2933	0.0654	0.2276	0.1456	0.0413	0.1886
RB	R_P	0.2724	0.3057	0.5387	0.1786	0.3402	0.2668	0.3123
GL	R_P	0.4018	0.4317	0.4450	0.3888	0.5997	0.3523	0.4436
				(c)				
RB	r_{ZJ}	0.1187	0.2033	0.1326	0.1314	0.0934	0.1344	0.1244
GL	r_{ZJ}	0.2474	0.2589	0.1438	0.1462	0.1053	0.1215	0.1592
RB2	r_{ZJ}	0.0927	0.1949	0.1361	0.1753	0.0988	0.2001	0.1342
GL2	r_{ZJ}	0.1597	0.2508	0.1426	0.1332	0.1322	0.2049	0.1543
RB	R_2	0.1130	0.2089	0.0945	0.1257	0.0869	0.0357	0.1060
GL	R_2	0.4309	0.3159	0.1001	0.2450	0.1252	0.0388	0.2020
RB2	R_2	0.1524	0.1985	0.1019	0.3976	0.0797	0.0588	0.1573
GL2	R_2	0.2588	0.3508	0.1012	0.1833	0.1115	0.0586	0.1696
RB	R_P	0.3148	0.4740	0.5711	0.3197	0.3589	0.3281	0.3917
GL	R_P	0.4355	0.5037	0.5235	0.3597	0.6268	0.3640	0.4751
RB2	R_P	0.3707	0.4190	0.6220	0.5458	0.3740	0.4714	0.4640
GL2	R_P	0.3388	0.4747	0.5359	0.4068	0.6401	0.4382	0.4792

Three questions arise: First, why did JH find almost the same value of the Pendry R factor for the RB and the GL model (0.40 and 0.38, respectively)? A complete answer to this question is difficult to get but a probable explanation is related to the fact that JH used six phase shifts and eight layers with a damping length of 8 Å. Table I shows that under these conditions the differences between R factors are indeed small, but if one uses eight phase shifts the differences are large.

The second question concerns the more general problem raised here by the fact that two different structure models (RB and GL) produce markedly similar LEED spectra. That a (secondary) minimum of the reliability factor occurs at or in the vicinity of the parameter values of the GL model is a fact. What remains to be established is whether it is a unique or a common event in LEED crystallography, and what can be done to avoid ambiguous solutions of structural problems when such an event occurs. Approximate repetition of the shape of LEED spectra for different values of interlayer distances is a common event in LEED crystallography that was pointed out first by Andersson and Pendry[15] in 1975. In the present case there are two interlayer distances (the first and the second) changed between the RB and the GL model, but while the first interlayer spacing decreases from 0.58 Å in the RB model to 0.08 Å in the GL model, the second interlayer spacing increases from 2.425 Å in the RB model to 2.95 Å in the GL model, so that the distance between first and third layer (3.01 Å in RB, 3.03 Å in GL) remains almost unchanged. The recipe for discrimination between two different models that produce similar LEED spectra was given before[16] and consists in using large experimental data sets, including, in particular, non-normal-incidence data. For example, the lower three panels in Fig. 2 show that clear differences between the RB and the GL model are expected in the 10, 21, and 12 spectra at $\theta=8°$, $\phi=0°$ (but the corresponding experimental spectra are not available at this time). Differences are also expected at $\theta=15°$, $\phi=0°$ (not shown).

The third question concerns the discrepancy between

the LEED results and the ion-scattering results for the structure of the laser-stabilized Si{111}1×1 surface. The present work reiterates the fact that the RB model passes the LEED test adequately and is therefore the only candidate acceptable to LEED for the structure of Si{111}1×1 at the present time. One can never be sure, of course, that another model does not exist that can reproduce the experimental intensity data better, but such a model has not been proposed at the time of writing. *It is more probable that the RB model represents correctly at least the average structure of the ordered part of the surface.* A possible explanation of the discrepancy is the presence of both ordered and disordered regions on the surface. However, no unusual amount of diffuse background has been reported. Another possible explanation may lie in the existence of a disordered layer of Si atoms on top of the bulk termination (LEED is mostly insensitive to disorder, ion scattering is very much affected by it), although it would be difficult to understand why, in such a case, the first interlayer spacing should be contracted as much as 25.5%.

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