Atomic structure of the Si(001)$c(4\times2)$ surface

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We have studied the atomic structure of the Si(001)$c(4\times2)$ surface with kinematic low-energy electron diffraction calculations compared with the constant-momentum-transfer-averaged low-energy electron diffraction intensity curves collected by Webb *et al.* The results show that the reconstruction mechanism of the surface is unbuckled dimerization, that the $c(4\times2)$ reconstruction extends to about the sixth atomic layer, and that there is an oscillatory multilayer relaxation in the surface. We present a model for the atomic structure of the surface which gives a reasonably good agreement with the experimental curves.

I. INTRODUCTION

The long process of studying the Si(001) surface was started after Schlier and Farnsworth[1] first reported the (2×1) reconstruction of the surface in 1959. Shortly after that, in 1962, Lander and Morrison[2] reported the reconstructed Si(001)$c(4\times2)$ surface. The existence of the $c(4\times2)$ reconstruction was confirmed by Weber *et al.*[3] in 1967. Now, after a relatively inactive period of about a decade, we are obtaining a new understanding of the mysterious silicon surface.

Despite the roughly one hundred papers that have been published on the structures of the Si(001) surface, two primary questions remain:[4–14] What is the reconstruction mechanism of the surface? What is the relation between the $c(4\times2)$ and (2×1) reconstructions? We answer these questions in this paper.

Our own experience in studying the Si(001)2×1 surface with a full dynamical low-energy electron diffraction (LEED) analysis[14] tells us that the investigation of the $c(4\times2)$ reconstruction with a full dynamical LEED analysis is, at least in the present situation, almost impossible. In other words, the method is not powerful enough to solve a complicated structure like this. On the other hand, we recently compared kinematic LEED (KLEED) calculations with the constant-momentum-transfer-averaged LEED (CMTA-LEED) intensity curves in studying the Si(111)7×7 (Ref. 15) and Si(001)2×1 (Ref. 16) surfaces. The results showed that the method has great potential for solving complicated silicon surfaces. Since Ref. 16 is in Chinese and, therefore, is not of easy access for some people, we reproduce some of its curves here in Fig. 1. It is clear that the YJM2 model (where YJM denotes Yang, Jona, and Marcus) is the best compared to the other models in Fig. 1. That is exactly what we have concluded from our full dynamical LEED calculations.[14] Therefore, in the present work, we investigate the atomic structure of the Si(001)$c(4\times2)$ surface with this method.

In view of the fact that the CMTA-LEED experimental curves collected by Poppendick, Ngoc, and Webb[5] from the Si(001)$c(4\times2)$ surface are the only such curves available to us and that our work on Si(111)7×7 (Ref. 15) has shown the reliability of the CMTA-LEED curves of Webb's group, we compare, in this work, our KLEED intensity curves with their experimental curves.

II. METHODS

In this work, we use the same KLEED intensity calculation method as that described in Ref. 15. However, comparison of the calculated curves with the experimental curves has indicated that the electron mean free path Λ of the surface from which the experimental curves were col-

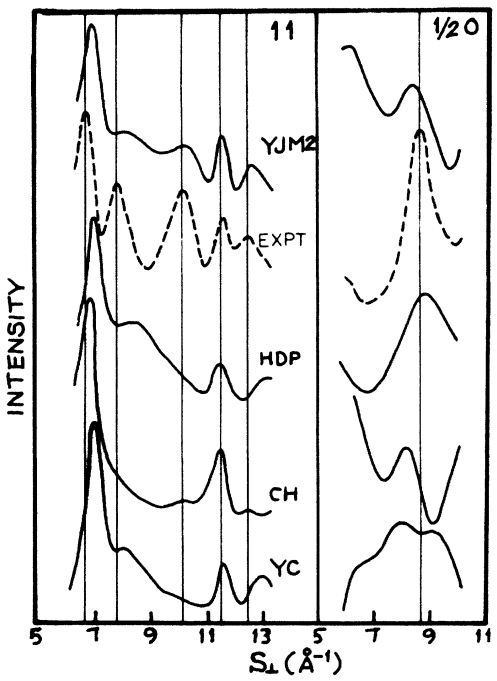

FIG. 1. Low-energy electron diffraction intensity vs momentum transfer curves of (1 1) and $(\frac{1}{2}\ 0)$ beams of the Si(001)2×1 surface. Dashed curves: Constant-momentum-transfer-averaged experimental curves (Ref. 21). Solid curves: Kinematically calculated curves for the YJM2 model (Ref. 17), Holland-Duke-Paton (HDP) model (Ref. 18), Chadi (CH) model (Ref. 19), and Yin-Cohen (YC) model (Ref. 20).

lected was about 3.5–4.5 Å. Thus throughout the work, the value of Λ is taken to be within this range. In such a case, the scattering amplitude of the atoms of the 16th layer is less than 1% of that of the first layer. Therefore, the models we have tested are all of 16-layer slabs.

With our KLEED method, the calculation of all six intensity curves of a model takes only 5 s of CPU time of a DPS8/52 computer. However, the surface structure is so complicated that its unit cell has tens of unknown geometric parameters and it is almost impossible to solve the structure with a trial and error method; therefore we employ the orthogonal experimental design (OED)[22,23] which is an optimization scheme proven to be a very powerful tool in LEED crystallography.[22,14] We call the method that combines the KLEED calculations with the OED scheme the KLEED-OED method.

As mentioned above, the $c(4\times2)$-reconstructed surface has tens of unknown parameters. Consequently, we employ the orthogonal table $L_{64}(4^{21})$, which means that in each round of the OED method, one has only to do calculations for 64 models. After doing that, one can find out the best model (parameter combinations) among a total of 4^{21} models.[23] Here the number 21 is the number of parameters the table can handle each time, and the number 4 is the number of values each parameter may have. Clearly, the gain of using the $L_{64}(4^{21})$ table is $4^{21}/64=6.87\times10^{10}$.

III. MODELS AND CALCULATIONS

To date, most of the published papers on the reconstructions of the Si(001) surface favor the buckled-dimer reconstruction mechanism.[6–9] Our Si(001)2×1 model of this type has agreed well with experiment.[14] Therefore, we test the $c(4\times2)$ reconstruction models of this mechanism first.

It should be pointed out that in the work of Jona *et al.*,[6] Chadi,[7] and Ihm *et al.*,[8,9] the $c(4\times2)$ reconstruction was limited to the first atomic layer. Clearly, for any model that has only one layer with a $c(4\times2)$ reconstruction, even if that layer has a buckling of a few tenths of 1 Å, the KLEED intensity of its quarter-order beams should not vary significantly with the electron energies. In fact, we see from the CMTA-LEED curves of Poppendick *et al.* that the intensity of the two quarter-order beams does vary significantly with the electron energies (see Fig. 4). That implies that the $c(4\times2)$ reconstruction of the surface extends into the deep layers. Accordingly, our program can handle models with a maximum of six $c(4\times2)$-reconstructed atomic layers. Besides, the program allows the atom layers 7–16 to have different layer-spacing relaxations.

If the surface does not have any symmetry except the $c(4\times2)$ translational symmetry, to specify a model of the surface, which has six $c(4\times2)$-reconstructed layers and ten relaxed (1×1) layers, one needs a total of 82 geometric parameters. Moreover, in this case, there may be eight equivalent domains[14] and we have to calculate the single-domain curve for 17 beams in order to get the six domain-averaged curves corresponding to the six experimental curves. This is really a big job even with the KLEED-OED method, and we do not think it must be done at this preliminary stage of studying the structure.

In this work we keep some of the twofold rotation axes of the truncated surface in our models. Figure 2 shows schematically a model of this kind, which still has 44 geometric parameters. As mentioned above, the orthogonal table $L_{64}(4^{21})$ can handle 21 parameters in each round of OED. We adjust first the parameters of atoms in the top few layers and the z parameter of some atoms in the deeper layers; then fixing some or all of the parameters at values optimized by the preceding rounds of OED, adjust other parameters, and so on, until all the parameters are optimized as possible.

In view of the fact that our buckled dimer model for the Si(001)2×1 surface gives good agreement with our experiment either with full dynamical calculations[14] or with KLEED calculations,[16] naturally, we start the KLEED-OED optimization process from the parameter values of that model. As expected, the calculations show that these values need some adjustments. After 85 rounds of OED, which are equivalent to 3.7×10^{14} models, and some single-model calculations, which are inserted between rounds of OED when the eye indicates that it is necessary, we have the optimized model of this work. The parameters of all its 24 atoms in the six topmost layers which have the $c(4\times2)$ reconstruction are shown in Table I. Its overall layer spacings are shown graphically in Fig. 3. Its calculated intensity curves and their corresponding experimental curves are shown in Fig. 4. Its mean x-ray r factor is 0.21.

Very recently, Northrup[11] proposed a new model for the Si(001)$c(4\times2)$ surface, in which the second-layer atoms are dimerized and the surface atoms form π-bonded chains. The model gives an r factor of 0.40 and, therefore, is unacceptable. To improve the agreement, starting from this model, after 18 rounds of OED, we have reached a model which gives an acceptably small r factor of 0.22. However, looking at the calculated curves

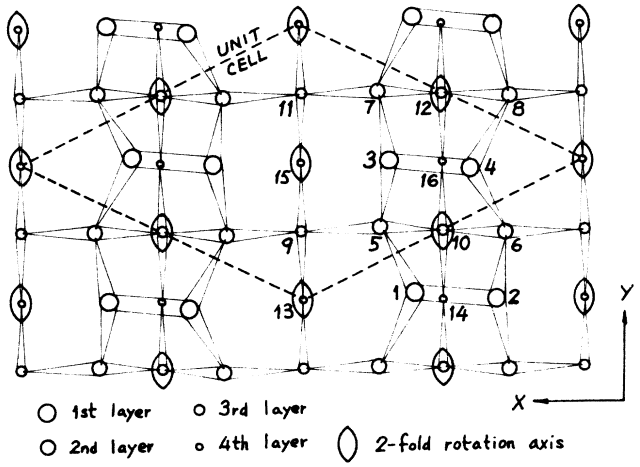

FIG. 2. Schematic top view of a dimer model of the Si(001)$c(4\times2)$ surface with perspective view of bonds. The x, y, and z axes form a right-handed coordinate system. The numbers are the sequence number of the atoms in the top 4 layers.

TABLE I. Geometry of the optimized model (see text). Δx, Δy, and Δz are shifts of the atoms from bulk positions along respectively the x, y, and z axes shown in Fig. 1 (in Å).

Shift	Layer / Atom no.	1	2	3	4	5	6	7	8	9	10	11	12
				1			2				3		
Δx		−1.140	0.490	−0.490	1.140	−0.200	0.200	−0.060	0.060	0.020	0.000	−0.020	0.000
Δy		0.200	0.020	−0.020	−0.200	0.072	−0.072	0.080	−0.080	0.310	0.000	−0.310	0.000
Δz		−0.017	−0.022	−0.022	−0.017	−0.047	−0.047	−0.249	−0.249	−0.022	0.012	−0.022	0.007
				4			5				6		
Shift	Layer / Atom no.	13	14	15	16	17	18	19	20	21	22	23	24
Δx		0.000	0.030	0.000	−0.030	0.016	−0.038	0.038	−0.016	0.015	−0.015	0.015	−0.015
Δy		0.000	0.222	0.000	−0.222	−0.059	−0.002	0.002	0.059	0.014	−0.014	−0.014	0.014
Δz		−0.015	0.043	0.018	0.043	−0.008	−0.019	−0.019	−0.008	−0.128	−0.128	−0.134	−0.134

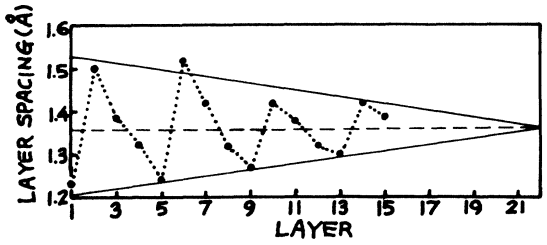

FIG. 3. Overall layer spacings of the optimized model. The dashed line shows the bulk layer spacing. The dotted line is a guide to the eye. The solid lines are the envelopes.

of the model, we must conclude that the model could not be right.

Recently, Pandey[12] has presented a new reconstruction mechanism for the Si(001) surfaces. Since the mechanism does not allow a $c(4\times2)$ reconstruction, while the experimental curves are from a $c(4\times2)$-reconstructed surface, we could not test the mechanism.

We did not try to optimize the model proposed by Poppendick *et al.*[5] because the model has too many broken bonds to be believed energetically favorable.

IV. DISCUSSION

(i) Briefly, what we have done is to search among a total of 4.6×10^{16} models which are divided into two different types of reconstruction mechansims and which have wide parameter value ranges. All the models consist of six $c(4\times2)$-reconstructed layers containing 24 atoms and ten relaxed (1×1) layers containing ten atoms, having

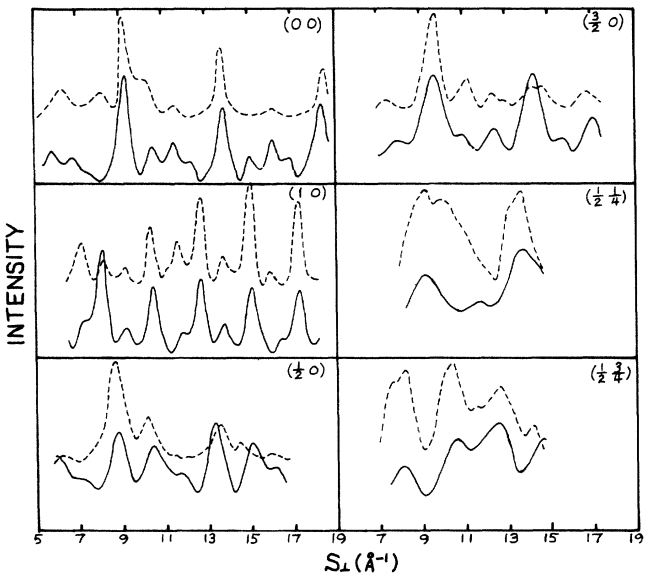

FIG. 4. Experimental intensity curves (dashed curves) of the (0 0), (1 0), $(\frac{1}{2}\ 0)$, $(\frac{3}{2}\ 0)$, $(\frac{1}{2}\ \frac{1}{4})$, $(\frac{1}{2}\ \frac{3}{4})$ beams for low-energy electron diffraction on the Si(001)$c(4\times2)$ surface averaged at constant-momentum transfer S (Ref. 5), and the calculated kinematic intensity curves (solid curves) of the optimized model with the electron mean free path equal to 3.5 Å.

a total of 34 atoms with 44 parameters. After doing that, we searched out the optimized model that can pass the test of the r factor although we cannot say the agreement is perfect. In contrast to what we got is what we used to get it: The whole work took only about 10 h of CPU time of the computer. These could be achieved only with the KLEED-OED technique.

(ii) The work indicates that the reconstruction mechanism of the Si(001) surfaces is dimerization, and that the $c(4\times2)$ reconstruction features an ordering of different dimer orientations forming a zigzag pattern. This is in agreement with the result of a recent scanning tunneling microscopy (STM) work by Tromp *et al.*[13] Also, this is in accordance with the suggestion of Jona *et al.*[6] and the conclusion of Chadi[7] and Ihm *et al.*[9] However, the fundamental assumption of their theoretical calculations that the $c(4\times2)$ reconstruction exists only in the first atomic layer was not correct, since in the optimized model, the reconstruction extends to about the 6th atomic layer.

(iii) The most significant difference between the (2×1) and the $c(4\times2)$ reconstructions is that the former consists of buckled dimers[14] with an overall buckling of 0.4 Å, while the latter consists of unbuckled dimers. Recently, Pandey[12] has concluded that the unbuckled dimer is energetically more favorable than the buckled dimer. Comparing our (2×1) and $c(4\times2)$ models with Pandey's conclusion, one may conclude that the $c(4\times2)$ structure is the stable reconstruction of the Si(001) surface and if there is no disturbance, for example, from thermal motion, the surface has to be $c(4\times2)$ reconstructed. In fact, Kevan and Stoffel[24] recently did see the transition from a (2×1) to a $c(4\times2)$ reconstruction in Ge(001) surface at low temperature. The (001) surfaces of germanium and silicon are generally thought to reconstruct in a similar way, and a preliminary work on the Ge(001)2×1 structure[26] has already shown this directly.

In contrast to our conclusion, Tromp *et al.* have concluded that the (2×1) reconstruction consists of unbuckled dimers, while the $c(4\times2)$ reconstruction consists of buckled ones.[13] However, in view of the fact that the STM corrugations are determined not only by the atomic positions but also by the electronic structure of the surfaces,[26–28] their STM topographs may also be interpreted as evidence of our conclusion here.

(iv) Figure 3 clearly shows the deep extended oscillatory multilayer relaxation in the $c(4\times2)$ reconstruction. It is interesting to note that a similar deep extended oscillatory relaxation in the Si(111)7×7 surface has been reported[15] not long ago. Moreover, another work[30] of ours on a type of Si(111)1×1 surface[29] has revealed the existence of an oscillatory multilayer relaxation, too. It seems to us that the existence of a deep extended oscillatory multilayer relaxation is a characteristic of the silicon surfaces or even of homopolar semiconductor surfaces. At the moment, we just could guess that charge density waves might be responsible for this kind of relaxations. We also note that the first layer spacing of 1.2 Å is in agreement with that of Ref. 13.

(v) As mentioned before, the agreement of the optimized model with experiment is not perfect. The possible reasons are as follows: (i) The model parameters need further optimization. (ii) The real surface may not have twofold rotation axes, while the model does. As mentioned earlier, the computing time of the models without any rotation axes will be increased tremendously. Therefore, at this stage, there is no intention to go further. (iii) There might still be some, but not very many,[15,16] errors in the CMTA-LEED experimental curves in the sense that the CMTA gives the kinematic LEED intensity curves. (iv) The surface from which the experimental curves were collected might not be pure $c(4\times2)$ reconstructed.[4,13]

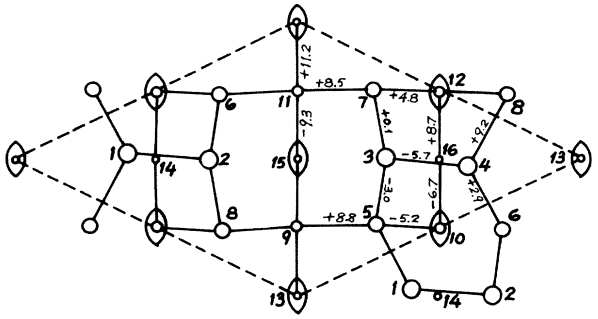

FIG. 5. Bond length strains (%) of the optimized model. The numbers are the same sequence number of the atoms as those in Fig. 1.

(vi) The bond length strains of the top four atomic layers of the optimized model are shown in Fig. 5. Some of the strain percentages look too large. The reason might be twofold: (i) Clearly, these values are very sensitive to the x and y coordinates of the atoms, while the LEED intensities are relatively not. (ii) If the twofold rotation axes should not be there, then, naturally, the existence of them would cause some errors including bond length strains.

V. CONCLUSIONS

(i) The reconstruction mechanism of the Si(001) surface is dimerization. The $c(4\times2)$ reconstruction consists of unbuckled dimers, while the (2×1) reconstruction consists of buckled dimers.

(ii) The $c(4\times2)$ reconstruction extends to about the sixth atomic layer.

(iii) The $c(4\times2)$-reconstructed surface has a deep extended oscillatory multilayer relaxation as does the Si(111)7×7 surface.

(iv) The KLEED-OED technique combined with CMTA-LEED experimental curves has great potential in solving complicated surface structures.

ACKNOWLEDGMENT

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