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Structural studies of Si(111)2×1 surfaces using low-energy electron diffraction

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The structure of the Si(111)2×1 surface is studied using dynamic low-energy electron diffraction analysis at three different off-normal electron incidence angles, with emphasis on the π-bond chain model. The optimum π-bond chain geometry has a buckling of 0.35 Å between the two chain atoms and a large distortion in the subsurface layer. The bond length of surface chains is determined to be 2.25 ± 0.02 Å by detailed analysis. We compare our results with those of other authors.

Among the many reconstructed semiconductor surfaces, the cleaved Si(111) surface exhibits a simple reconstructed structure whose two-dimensional surface unit cell is only twice as large as that of the bulk configuration. A number of investigations have been performed concerning this 2×1 structure[1-5] and the π-bond chain model originally proposed by Pandey[6] has gained support from several experimental and theoretical results.[7,8] The main features of the chain model are a large displacement of surface atoms from bulk positions and a resultant π-bond formation between two surface atoms which leads to a zigzag chain. It has been shown, however, that Pandey's original geometry is not compatible with the results of low-energy electron diffraction (LEED) studies,[9,10] and modified forms, which contain buckling of chain atoms, have been proposed by several authors. Northrup and Cohen have reported a new geometry on the basis of total energy calculations.[11] Himpsel *et al.* have studied the geometry of the π-bond chain model by LEED analysis.[12] Tromp, Smit, and van der Veen have also determined optimum positions by medium-energy ion scattering.[13] All these results include a large buckling (0.2–0.4 Å) in the topmost layer and subsurface relaxation.

As for Himpsel's LEED analysis results[12] at normal electron incidence, fairly good coincidence between experimental and calculated I-V curves has been obtained for their optimum geometry, but some discrepancy between them still exists. Moreover, there does not yet seem to be any final agreement on the magnitudes of these atomic displacements between these different authors.

We have conducted a structural analysis of the π-bond chain model by consistent LEED measurements to eliminate such uncertainty. Experimental intensity-energy (I-V) curves obtained at three different electron incidence angles [(1) $\theta=2°$, $\phi=270°$, (2) $\theta=10°$, $\phi=270°$, and (3) $\theta=6°$, $\phi=90°$] have been compared with calculation (here θ is the polar angle measured from the surface normal, and ϕ the azimuthal angle from the [$1\bar{1}0$] direction parallel to the surface). Integral and fractional order beams taken into account are illustrated in Fig. 1(a). The other experimental details are given in Ref. 14.

Seven geometric parameters concerning atomic positions down to the fourth atomic layer were varied over a wide range, including the bond length of the topmost chain

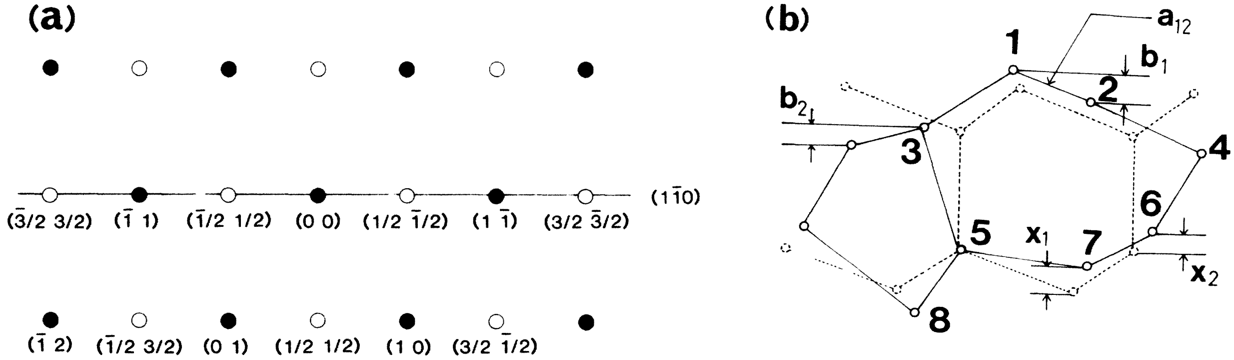

FIG. 1. (a) Diffraction spots from the Si(111)2×1 surface. All beams taken into consideration are indexed. The solid line shows the ($1\bar{1}0$) mirror plane. (b) Side view of modified π-bond chain structure with the structural parameters. Dashed line indicates a bulk configuration.

TABLE I. The values of the structural parameters and the coordinates of eight atoms in the first and the second overlayers for the optimum π-bond chain geometry. The x, y, and z axes are parallel to the $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}0]$, and $[\bar{1}\bar{1}2]$ directions, respectively.

	This work			Himpsel *et al.* (Ref. 12)		
$a_{12}=2.25$ Å				$a_{12}=2.25$ Å		
$b_1=0.35$ Å		$b_2=-0.05$ Å		$b_1=0.38$ Å		$b_2=-0.07$ Å
$x_1=0.25$ Å		$x_2=0.15$ Å		$x_1=0.18$ Å		$x_2=0.07$ Å
		First overlayer			Second overlayer	
Atom	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
1	0.0	0.0	0.0	0.00	0.00	0.00
2	0.35	1.92	1.12	0.38	1.92	1.12
3	1.26	0.0	−1.98	1.26	0.00	−2.00
4	1.21	1.92	3.31	1.19	1.92	3.26
5	3.46	0.0	−1.26	3.46	0.00	−1.10
6	3.31	1.92	2.20	3.39	1.92	2.40
7	3.99	0.0	1.03	4.06	0.00	1.20
8	4.31	1.92	−2.32	4.26	1.92	−2.12

atoms, which is fixed at 2.25 Å in most studies. The number of geometries tested was about 8000. Studies using these three different incidence angles are especially important, since they should clarify whether the configuration proposed here is correct, and will enable verification of the correctness of the presently accepted atomic configuration, for which the reliability factor (R factor) is not low enough. If our studies at these angles lead to results similar to those of other authors, they will in turn confirm their conclusions.

The scheme of theoretical calculations based on the dynamic theory is, in principle, the same as that of van Hove and Tong.[15] We modified the program to be able to treat the substrate composed of double layers at close intervals. Furthermore, special care was taken when using the vector processors (Hitac S-810, Hitachi, Ltd.).

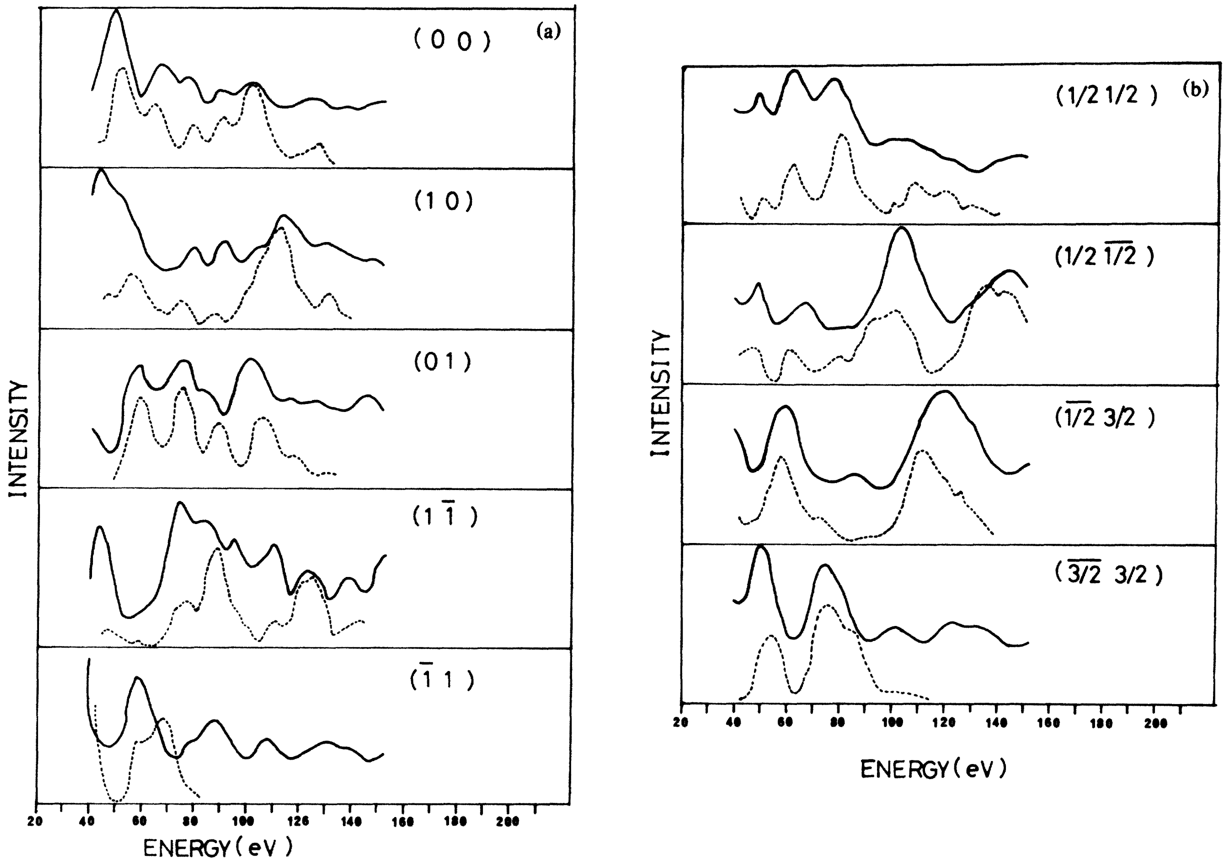

FIG. 2. Comparison of the experimental (dashed curves) and theoretical (solid curves) I-V spectra at $\theta=10°$ and $\phi=270°$.

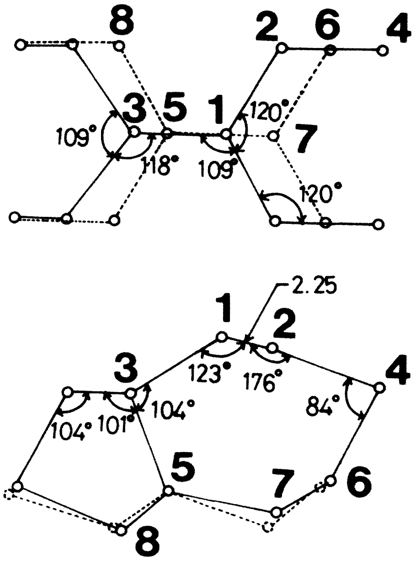

FIG. 3. Top and side views of the optimum π-bond chain structure. Dashed lines denote the bulk configuration of the third and fourth layers.

The fit between the experimental and the theoretical *I*-*V* spectral curves is at first judged mainly by visual inspection. In this procedure, all the structural parameters are roughly adjusted so that the peak voltages and relative heights of corresponding main peaks in the experimental and the theoretical curves are generally coincident with each other. The *R* factor, as defined by Zanazzi and Jona, is then used for further imporvement.[16]

The optimum atomic coordinates as determined in this study are listed in Table I, with the values of some structural parameters shown in Fig. 1(b). We varied a_{12} in small increments from 2.15 to 2.35 Å and found that the most reasonable value was 2.25±0.02 Å as is generally believed. The shape of the *I*-*V* spectra is drastically influenced by b_1 and a_{12}. Our best-fit value of $b_1 = 0.35$ Å is a little smaller than the Himpsel *et al.* result,[12] but larger than those for the Northrup and Cohen[11] and Tromp *et al.*[13] configurations. The most remarkable feature of our result is the large distortions of the third and the fourth layers. The upward displacement of atoms 6 and 7 shown in Fig. 1(b) from their bulk positions amount to 0.15 and 0.25 Å, respectively. All the *I*-*V* spectra for our optimum geometry at an incidence angle of $\theta = 10°$ and $\phi = 270°$ are shown in Fig. 2. As indicated in Fig. 3, for optimum geometry three bonds which belong to atom 2 lie nearly in the same plane, indicating that the electronic states of atom 2 are planar sp^2-like states. It would seem that the π electron assigned to atom 2 tends to be nonlocalized, and so moves about along the top chain, leading to the "one-dimensional" 2×1 structure. In contrast to Pandey's original geometry, such a configuration breaks the symmetry of the two surface layers. This configuration, however, reduces the total energy of the system in accordance with the generation of sp^2-like states in atom 2.[11]

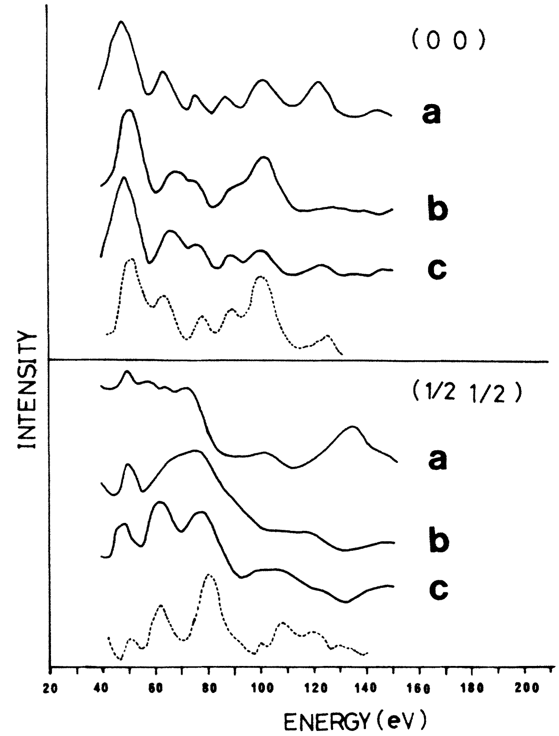

FIG. 4. Comparison of the theoretical *I*-*V* spectra (solid curves) at $\theta = 10°$ and $\phi = 270°$ for different surface geometries, together with experimental data (dashed curves). The solid curves a, b, and c correspond to Tromp's, Jona's, and our results, respectively.

For the configurations proposed on the basis of the π-bond chain model, the agreement between the experimental and the theoretical *I*-*V* curves was not so good, except for Himpsel's result,[12] mentioned above. *I*-*V* curves for Tromp's geometry[13] based on an ion-scattering method also show fairly good agreement for the integral order beams, but not for the fractional beams, at least with respect to our LEED analysis.

In Fig. 4, *I*-*V* spectra are shown for some proposed geometries at $\theta = 10°$ and $\phi = 270°$ for several beams. The *R* factors for Tromp's,[13] Himpsel's,[12] and our geometries at $\theta = 6°$ and $\phi = 90°$ are 0.56, 0.44, and 0.40, respectively.

In summary, the modified π-bond chain model has been optimized by LEED analysis, using experimental data obtained at three different off-normal incidence angles. Detailed research has confirmed that the length of the π-bond chain is shortened by exactly 0.1 Å from the bulk bond length. The optimum geometry includes a large buckling of π-bond chain atoms. On the whole, our result supports Himpsel's conclusion,[12] but shows a rather larger distortion of the two underlying layers than do those of any other authors.

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