

the core region show a behavior marked mainly by unusual  $\langle \mu^4 \rangle$ , reflections involving the valence electrons exhibit a temperature dependence wholly unexpected and unaccountable in terms of the above discussion. It thus appears that the origin of this is a temperature-dependent valence-electron density in real space. While the absolute accuracy of electron density maps<sup>3</sup> is subject to some uncertainties (form factor, extinction, etc.), Fig. 1, and others not presented here, clearly indicate that there appear to be significant changes in the real-space electron density with temperature. This result supports differences seen between electron density maps<sup>3</sup> at 300 K and at 13.5 K. Furthermore, any model based on thermal excitation over  $\sim 100$ -K fine structure in the density of states should also produce the significant change in real-space electron density indicated by the x-ray results. Density-difference maps to facilitate such a comparison are in progress.

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## Atomic and Electronic Structures of Reconstructed Si(100) Surfaces

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New structural models for  $2 \times 1$  and  $4 \times 2$  reconstructed (100) surfaces of Si determined from energy-minimization calculations are presented. The optimal  $2 \times 1$  and  $4 \times 2$  structures are found to correspond to asymmetric dimer geometries with partially ionic bonds between surface atoms, resulting in semiconducting surface electronic bands. The atomic and electronic structures for the  $2 \times 1$  and  $4 \times 2$  reconstructed surfaces are discussed.

The (100) surface of Si has been the subject of a large number of experimental<sup>1-10</sup> and theoretical<sup>11-18</sup> studies. Low-energy-electron diffraction<sup>1-7</sup> (LEED) and He diffraction<sup>8</sup> measurements show the surface to be either  $2 \times 1$  or  $4 \times 2$  reconstructed. Many models<sup>1-6, 11-16</sup> for the surface structure have been proposed. Most of these can

be grouped into dimer,<sup>11,12,14</sup> vacancy,<sup>6,13,14</sup> or conjugated-chain-type models.<sup>2,15</sup> Comparisons of the calculated surface electronic structures<sup>17,18</sup> for the various  $2 \times 1$  models show that the dimer results are generally in better agreement with photoemission data<sup>9,10</sup> than the other two models, but all three models give a metallic surface elec-

tronic structure which is in disagreement with recent angle-resolved photoemission spectra.<sup>10</sup> A recently suggested  $2 \times 1$  dimer model, with atomic relaxations extending over the first five layers at the surface, has a calculated<sup>4</sup> LEED spectra in much better agreement with experiment than other structural models; our calculations indicate, however, that its surface electronic remains metallic. Despite this, LEED studies indicate<sup>2,4</sup> that such deep relaxations are needed to explain the experiment spectra.

In this paper, the results of surface structure calculations based on an energy-minimization procedure are discussed. The method used here is similar to that used in previous calculations<sup>19</sup> on the  $2 \times 1$  reconstructed (111) surfaces of Si and the (110) surfaces of several tetrahedrally coordinated semiconductors. Many different structural models were tested to determine the optimal surface geometry of Si(100). The calculations support the idea that the driving force for both the  $2 \times 1$  and  $4 \times 1$  reconstructions arises from dimerization. The most important result of these calculations is that the symmetric dimer model<sup>1</sup> (for which the in-plane displacements of surface atoms forming a dimer are equal in magnitude but in opposite directions) is unstable. When only surface atoms are allowed to relax, the total energy is lowered by nearly 0.16 eV/atom by the formation of "asymmetric" and partially ionic dimers.<sup>20</sup> This value increases substantially to 0.23 eV/atom (0.46 eV/dimer or equivalently 240 ergs/cm<sup>2</sup>) when subsurface relaxation effects are also included. In the calculations, relaxations of the first five atomic layers at the surface were considered. With the exception of the surface layer the atomic relaxations, as shown schematically in Fig. 1, are nearly the same as those obtained by Appelbaum and Hamann.<sup>12</sup> The calculated atomic displacements from their *ideal and unrelaxed positions* (Fig. 1) are found to be (in angstroms):  $\Delta x_1 = 0.46$ ,  $\Delta x_{1'} = -1.08$ ,  $\Delta z_1 = 0.04$ ,  $\Delta z_{1'} = -0.435$ ,  $\Delta x_2 = -\Delta x_{2'} = 0.115$ ,  $\Delta z_2 = \Delta z_{2'} = 0.014$ ,  $\Delta z_3 = -0.12$ ,  $\Delta z_{3'} = 0.11$ ,  $\Delta z_4 = -\Delta z_{4'} = -0.07$ ,  $\Delta x_5 - \Delta x_{5'} = 0.034$ . For these displacements all bond lengths at the surface remain within 2% of their bulk values.

The formation of an asymmetric dimer results in a charge transfer of  $0.36 \pm 0.02$  electrons from the "down" to the "up" atom of the dimer [i.e., from atom 1' to atom 1 in Fig. 1(b)]. When screening effects are ignored, this should result in an increase of 0.51 eV in the work function of the ionic surface relative to that of the covalently

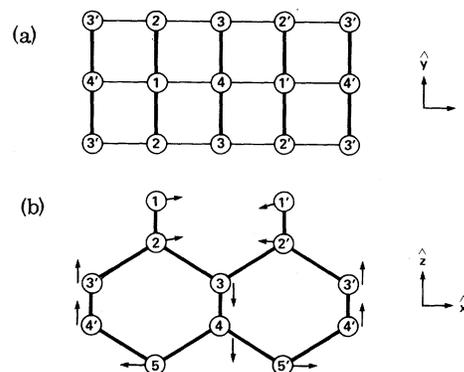


FIG. 1. Top and side views of an ideal Si(100) surface. The atoms denoted by 1 and 1' are surface-layer atoms, 2 and 2' are second-layer atoms, etc. The dimerization of the surface leads to the formation of strong bonds between atoms 1 and 1'. Directions of atomic displacements from ideal positions are shown in (b).

bonded (symmetric dimer) surface. The actual increase should be appreciably smaller because of substrate polarization effects. The relatively large value of the charge transfer makes it necessary to examine the magnitude of Coulombic contributions to the total energy since only band-structure and lattice-strain energies (and no electrostatic terms) were included<sup>19</sup> during the energy-minimization process. This can be done in the following approximate manner. The first ionization energy and the electron affinity of an isolated Si atom are 8.15 eV and approximately 1.39 eV, respectively.<sup>21</sup> The removal of one electron from a Si atom and its addition to a second one, therefore, costs 6.76 eV. For two such atoms (or a dimer pair) 2.35 Å apart the Coulombic interaction lowers the energy by 6.12 eV. The electrostatic interaction energy of such a dimer pair with all other dimers on a  $2 \times 1$  reconstructed surface of Si is calculated to increase the energy by<sup>22</sup> 0.04 eV/dimer. The total of these terms (6.76-6.12+0.04) amounts to nearly 0.68 eV/dimer for one unit of charge transfer between the atoms of the dimer. For a charge transfer of 0.36 electrons, as calculated above, the total Coulombic energy is, therefore, 0.09 eV/dimer. Since all screening effects have been ignored, this represents an upper limit to the value of the Coulombic energy at the surface; the actual value of this term is expected to be substantially (~factor of 2) lower. At its full value of 0.09 eV/dimer this term is nonnegligible and is about 20% of the 0.46 eV/dimer reduction in

band-structure and lattice-strain energies resulting in going from the symmetric to the asymmetric configuration. The inclusion of Coulomb effects in the total-energy model should tend to reduce, in the process of a self-consistent calculation, the asymmetry of the dimer and the magnitude of the charge transfer for both the  $2 \times 1$  and  $4 \times 2$  structures.

The occupied and empty surface states near the valence-band maximum (VBM) for symmetric (covalent) and asymmetric (ionic)  $2 \times 1$  dimer models involving only surface-layer reconstructions are shown in Fig. 2. The results for the covalent dimer calculated from the tight-binding model as a test of the model are in good agreement with the more accurate results from self-consistent pseudopotential calculations.<sup>17</sup> Both calculations show a metallic surface electronic structure for the symmetric dimer. For the ionic dimer, however, semiconducting surface bands are obtained. The highest filled surface state for the five-layer relaxed ionic dimer model is at 0.18 eV below the bulk VBM and the lowest empty state is 0.6 eV above it. The predominant orbital symmetry of both states is  $p_z$  like with some  $s$ -like symmetry also mixed in. With respect to the valence-band maximum, the energy of the filled state at  $\Gamma$  is about 0.2 eV higher and the band dispersion appreciably larger than the

0.3 eV width indicated by angle-resolved measurements.<sup>10</sup> The experimental data seem to be intermediate between the calculated results for the  $2 \times 1$  and  $4 \times 2$  structures. For the  $4 \times 2$  surface, the atomic structure of which is described below the highest surface state is about 0.7 eV below the VBM and the band associated with it have a narrow ( $\approx 0.3$  eV) bandwidth. Another disagreement between the calculated and experimental results for the  $2 \times 1$  structure is the observation<sup>10</sup> of two sets of surface states at the  $J'$  point of the Brillouin zone in the angle-resolved measurements. The states are approximately 0.4 and 0.9 eV below the VBM with the interesting feature that the 0.4 eV states have the same energy as the topmost surface states at  $\Gamma$ . Calculations for a variety of  $2 \times 1$  structural models nearly always reveal<sup>23</sup> only one state at  $J'$  in this energy range. The discrepancy between the theoretical and experimental results can be resolved if the underlying unit cell is larger than  $2 \times 1$  such that the states at  $\Gamma$  and  $J'$  are related by an umklapp process. The *centered*  $4 \times 2$  unit cell does *not* provide a reciprocal-lattice vector to connect the  $J'$  and  $\Gamma$  points of the  $2 \times 1$  structure, however, it does connect  $J'$  to states near  $\Gamma$  which the calculations show to have nearly the same energy as  $\Gamma$ . Another intriguing but very speculative possibility is the existence of  $2 \times 2$  domains at the surface for which the  $\Gamma$  and  $J'$  points of the  $2 \times 1$  cell become equivalent. If one assumes the dimer model to be correct, the open nature of the Si(100) surface leads to diverse possibilities for arranging the dimers. Calculations for rectangular and centered  $2 \times 2$  structures show them to be energetically as favorable as the  $2 \times 1$  and  $4 \times 2$  structures. Treating the ionic dimer as a dipole, the primary difference in the total energy between the various structures is in subsurface relaxations and dipole-dipole interaction energies. The  $2 \times 2$  structures could provide another explanation for the forbidden  $(\frac{1}{2} \frac{1}{2})$  and  $(\frac{3}{2} \frac{3}{2})$  diffraction spots seen in He backscattering measurements.<sup>8</sup> Recently broad streaked diffraction patterns running across the reciprocal unit mesh through the  $(\frac{1}{2} \frac{1}{2})$  spots have also been observed<sup>24</sup> in LEED measurements leading to the suggestion<sup>24</sup> of a partially disordered surface with  $2 \times 2$  like transition regions. Similarly streaked LEED patterns have been observed by Jona *et al.*<sup>25</sup> for the Ge(100) surface.

The energy-minimization approach was also used to determine a possible structure for the  $4 \times 2$  reconstructed surface of Si(100). The rec-

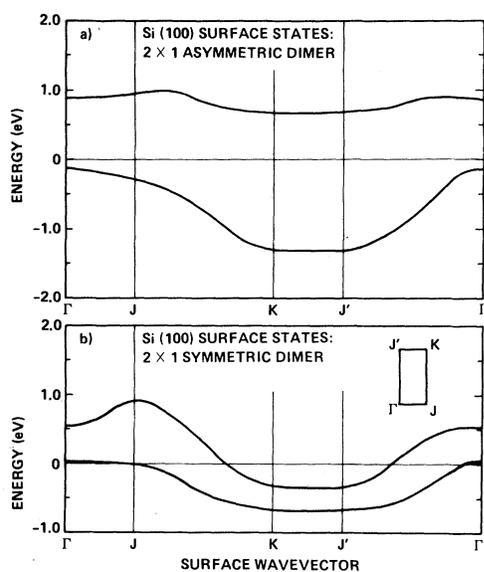


FIG. 2. Filled and empty surface-state bands near the valence-band maxima (at  $E = 0$ ) for two different  $2 \times 1$  dimer models, in which only the surface-layer atoms are displaced.

tangular  $4 \times 2$  reconstructed surface of Si(100). The rectangular  $4 \times 2$  unit cell, the rhombohedral primitive cell, and the directions of atomic displacements of first-layer atoms from their ideal, unrelaxed positions are shown in Fig. 3. The surface atoms labeled 1 and 2 (similarly the ones labeled by 3 and 4) form asymmetric dimers similar to those in the  $2 \times 1$  structure. The primary difference between the two structures is in the arrangement of the dimers. Whereas, along the  $x$  direction the  $2 \times 1$  surface exhibits a repetitive up-down, up-down geometry, the  $4 \times 2$  cell shows an up-down, down-up pattern which leads to a more electrostatically stable structure. A charge transfer of 0.36 electrons between type-1 and -2 atoms in Fig. 3 the same as for the  $2 \times 1$  structure is calculated. The dimer arrangements in the  $4 \times 2$  structure lead to a gain of 0.12 eV/dimer in surface Madelung energy over the  $2 \times 1$  structure when substrate polarization effects are ignored. Subsurface relaxations similar to those for the  $2 \times 1$  case are found to lead to a significant reduction ( $\approx 0.16$  eV/dimer) in the total energy of the  $4 \times 2$  structure also. Except for the difference in the arrangement of dimers at the surface, the atomic displacements of the  $4 \times 2$  structure were taken to be similar to those in the  $2 \times 1$  structure. The change in total energy in going from the symmetric dimer model (with only surface reconstruction) to the five-layer asymmetric model is calculated to be 0.48 eV/dimer. As mentioned previously the highest occupied surface state for the  $4 \times 2$  structure is found to be 0.7 eV below the VBM. A generally flat empty surface state 0.35 eV above the VBM is also obtained. The overall shapes of the local density

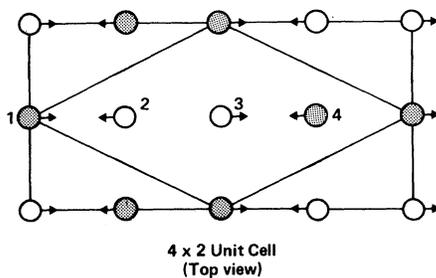


FIG. 3. Directions of atomic displacements from ideal, unrelaxed positions leading to a centered  $4 \times 2$  unit cell are shown. The rhombohedral primitive cell is also shown. Open and dotted circles represent negatively and positively charged surface atoms which are similar to type-1 and type-1' atoms in Fig. 1, respectively.

of states of the first two atomic layers of the  $4 \times 2$  and  $2 \times 1$  surfaces are similar as might be expected from the close resemblance between the two structures.

Many models in addition to the one above for the  $4 \times 2$  surface were considered. In particular a model originally suggested by Lander and Morrison<sup>5</sup> (LM) was also studied. This structure has only two atoms per rhombohedral unit cell in the topmost surface layer. Every atom in the top two layers of the LM model is fourfold coordinated, but this is achieved at a cost of large bond-length increases ( $\approx 11\%$ ) and bond-angle changes ( $\approx 50\%$ ); in addition, half the atoms in the third layer become fivefold coordinated. The LM model is energetically unfavorable. Structures with  $2 \times 1$  or  $4 \times 2$  periodicities can be constructed which achieve fourfold coordination of all atoms with bond-length changes of less than 3.5% and bond-angle distortion energies much smaller than those present in the LM model. These structures were also found to be energetically less favorable than the asymmetric dimer models discussed above. The  $4 \times 2$  multilayer vacancy model of Poppendieck, Ngoc, and Webb<sup>6</sup> obtained from analyses of LEED spectra was not tested.

In conclusion, several different structural models for the  $2 \times 1$  and  $4 \times 2$  reconstructed surfaces of Si(100) were compared through total-energy calculations. The energetically favorable geometries are found to correspond to asymmetric and partially ionic dimers for both structures, leading to semiconducting band structures at the surface. More work on subsurface relaxations for the  $4 \times 2$  structure remains to be done. Hopefully, the energy-minimization method in combination with analyses of LEED and He diffraction spectra will lead to a much better description of the Si(100) surface in the near future.

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<sup>21</sup>C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th Ed., pp. 75 and 89.

<sup>22</sup>The dipole-dipole-like interaction energy has been divided by two to compensate for double counting.

<sup>23</sup>The only exception is a structure with fourfold-coordinated atoms at the surface. This structure is energetically unfavorable and has other features in disagreement with photoemission data [see D. J. Chadi (to be published)].

<sup>24</sup>M. Cardillo *et al.*, to be published.

<sup>25</sup>F. Jona *et al.*, to be published.

## X-Ray Scattering Study of the Commensurate-Incommensurate Transition of Monolayer Krypton on Graphite

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We describe an x-ray scattering study of the commensurate-incommensurate transition in monolayer Kr films physisorbed onto basal planes of  $z$ - $y$ - $x$  exfoliated graphite. At temperatures of 80.0 and 89.3 K there appears to be a single hexagonal-commensurate-to-hexagonal-incommensurate transition which is at least nearly second order with mean exponent  $\beta = 0.30 \pm 0.06$ . In the incommensurate phase we directly observe domain-wall superlattice effects.

The commensurate-incommensurate transition (CIT) of monolayers physisorbed onto simple surfaces is a topic of considerable current theoretical and experimental interest.<sup>1-4</sup> One of the more extensively studied examples of such a transition is Kr adsorbed onto the (0001) basal plane of graphite. At submonolayer densities, Kr forms a commensurate  $(\sqrt{3} \times \sqrt{3})30^\circ$  structure, with one atom per three graphite hexagons.<sup>1,5</sup> At higher surface density, but still in the first layer, the Kr lattice becomes incommensurate with respect to the graphite substrate. Low-energy-electron diffraction (LEED) measurements by Chinn and

Fain<sup>1</sup> have shown that the phase change is apparently a second-order transition from a hexagonal commensurate (HC) structure to a hexagonal incommensurate (HI) structure. The LEED results were interpreted in terms of a one-dimensional dislocation theory<sup>6</sup>; however, more recent theories have emphasized that the two-dimensional nature of the adsorbate modulations is essential.<sup>2</sup> These theories predict either a single first-order transition or two successive transitions, one second order and the other first order. We shall discuss these theories in the context of our experimental results; at this point