relation which links the drift term and the diffusion term. The field values in parentheses correspond to the experimental situation ($T = 355°K$, $d = 1.2$ mm, and $a = 3.5$ Å). The most interesting aspect of the calculated values for the critical field is the fact that they differ by six orders of magnitude depending on the dimensionality of the problem. The calculated critical fields are very large for the three- and two-dimensional cases; they are extremely low for the one-dimensional case because of the inefficient trapping probability which has been pointed out above. The measured value $E_c = 5 \times 10^3$ V/cm shows that the system phenanthrene-PMDA is not an ideal one-dimensional system. In order to determine the deviation from one-dimensionality more accurate measurements of the mobility tensor have to be performed together with model calculations taking into account the real lattice geometry.[12] The presented experimental data, however, show that it is challenging to search for photoconductive systems with a higher degree of one-dimensionality. Furthermore, the experiments themselves provide a novel method for ascertaining the one-dimensionality of the conduction process.

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[11] For times large in comparison with the CC-hopping time one gets a one-dimensional CC-trapping rate of $k_{diff} = (F_1/2)(v_{th}/a)^{1/2}/\sqrt{t}$. Experimentally the square-root dependence cannot be verified because it would occur at electric field strengths on the order of 1 V/cm and at photocurrents of less than 10^{-11} A. In the "real experiment" the trapping rate is time independent because of a "residual three-dimensionality" up to fields where the field-induced trapping takes over with a rate which is also time independent and which is $k_{diff} = \mu E/a$.

[12] As far as the experiments perpendicular to the stack axis are concerned one expects a two-dimensional diffusion process with lower mobility values. For this case a field effect would be expected at much higher electric fields.

Energy Bands of Reconstructed Surface States of Cleaved Si

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Coordinates of atoms in the first and second layers of Si(111) 2×1 have been determined which yield surface energy bands in good agreement with experiment. Two surface resonances in angular photoemission data previously assigned to dangling-bond surface states are identified as arising from the maximum in the lower dangling-bond band and from a saddle point in the upper back-bonding band.

Semiconductor surfaces exhibit superlattice structures which have previously been discussed by many authors. *In principle,* these superlattice configurations can be deduced from sufficiently accurate analysis of low-energy electron-diffraction (LEED) data. *In practice,* however, multiple scattering effects make theoretical calculations extremely sensitive to small errors. Recent difficulties with the structures for chalcogens on Ni(100) surfaces and with the Si(100) superlattice indicate that further theoretical refinements are necessary before this approach can yield structural information.[1] We believe that much more direct and precise determination of atomic coor-

dinates is possible through spectroscopic information obtained at energies near 25 eV (compared to the 50–200-eV range in which LEED data can be obtained reproducibly and subjected to reliable theoretical analysis).

Dramatic resonances in the angular photoemission spectrum $N(E, \theta, \varphi)$ have been observed[2] for atomically clean Si(111) 2×1 (cleaved) surfaces. In this Letter we propose a theoretical interpretation of these resonances in terms of the energy levels of dangling-bond and back-bonding states of a specific model of the reconstructed surface. While the observed resonance energies disagree strongly[2] with the energies associated with a relaxed 1×1 model[3] of the (111) surface, they are in good agreement with the energies we obtain for the reconstructed 2×1 surface. We show that the positions of the observed resonances are a sensitive measure of the magnitude and type of displacements associated with surface reconstruction.

In our model the four atoms comprising the surface unit cell in the first two atomic layers are displaced, while the remaining atoms occupy the sites of a semi-infinite lattice. The displacements are vertical and they are -0.29 Å (into the crystal) and 0.35 Å for the atoms in the first layer, and 0.24 Å for both atoms in the second layer. With this atomic configuration, the dangling- and back-bond surface energy bands can be determined accurately using bulk and surface tight-binding parameters as described previously.[3] Our results are shown for the entire valence region in Fig. 1. The region of greatest interest is the upper left quadrant.

The significance of the surface energy bands shown in Fig. 1 is that they depict $E_n(\vec{k}_s)$ for surface states as well as surface resonances. The states are identified by studying the paired surface wave functions of a slab containing enough layers to reduce the splitting of the even and odd members of a pair to less than 0.01 eV. Previous work has shown that[3] on a relaxed 1×1 surface the local density of states $N_s(E)$ of the relaxed surface layer is two-dimensional in character, and that the analytic singularities of $N_s(E)$ coincide with the critical points $\vec{k}_{sc}$ at which $\partial E_n(\vec{k}_s)/\partial \vec{k}_s = 0$. It is evident that the relaxation of the surface layers must be sufficiently large to produce distinct back-bonding as well as dangling-bond bands in order for $N_s(E)$ to behave in this manner. However, the reconstructed bands shown in Fig. 1, which we have derived in order to explain the data described below, differ from the bulk energy
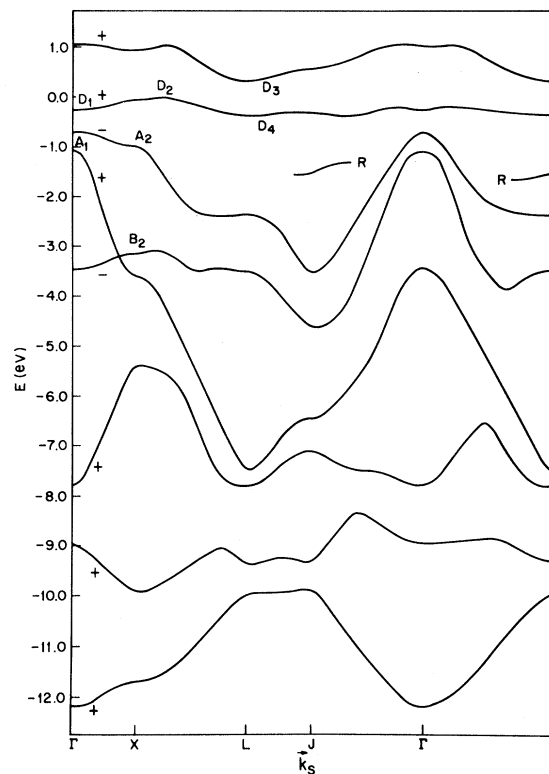

FIG. 1. Surface energy bands of Si(111) 2×1 for surface wave vectors $\vec{k}_s$ along various directions in the surface Brillouin zone. The energies are measured from the valence band edge. No distinction between true surface states and resonances has been made. The bands denoted by R are strong resonances only in a very limited region of the surface Brillouin zone. Because of the reflection symmetry about the normal plane containing Γ-X, the energy bands along Γ-X are designated by $+$ and $-$ showing their parity. The point L is the corner of the rectangular reconstructed Brillouin zone, and X and J denote the centers of its long and short sides.

bands by more than the relaxed bands, ensuring two-dimensional character for $N_s(E)$.

Evidence for a superlattice energy gap in the dangling-bond band has been obtained in infrared transmission experiments[4] on cleaved Si. A strong, asymmetric absorption peak centered near 0.45 eV was found. According to Fig. 1, this peak may be associated with direct transitions (e.g., $D_4 \to D_3$) or with indirect ones (e.g., $D_2 \to D_3$) or possibly even with bulk $\to$ surface transitions. It seems likely to us that the large cleaved surface used in the multiple internal reflection experiment[4] had a high density of steps. Moreover, the observed peak is probably excitonic in origin, with the hole wave packet contain-

ing significant contributions from the neighborhoods of both D_2 and D_4. In our model the peak energy of 0.45 eV lies between the direct-transition threshold, $E(D_4 \to D_3) = 0.65$ eV, and the indirect threshold, $E(D_2 \to D_3) = 0.30$ eV.

We now turn to an analysis of the resonances which are observed in angular photoemission spectra.[2] Interference patterns between plane waves composing the final state as well as the symmetry of the initial state determine the angle (θ_r, φ_r) at which resonant peaks reach their maximum amplitude. Energy bands in the final-state region (about 10 eV above the valence band edge) are broad and nearly-free-electron in character, while we find narrow surface valence bands. Thus we expect that the resonance structure of $N(E, \theta_r, \varphi_r)$ over and above that of $N(E)$ reflects primarily structure in $N_s(E)$, the density of surface states. Note that the limitations on resolution imply that $N(E, \theta_r, \varphi_r)$ as observed is in reality the integral of $N(E, \theta, \varphi)$ for θ and φ ranging over intervals of several degrees centered around θ_r and φ_r. As a result one expects two-dimensional critical-point singularities in $N_s(E)$ to be imaged in the experimental profile $N(E, \theta_r, \varphi_r)$. We identify the strong peak[2] near -1.2 eV (below E_F) in $N(E, 25°, 0)$ as the result of a logarithmic singularity in $N_s(E)$ associated with a two-dimensional saddle point (probably A_2 in Fig. 1), while the edge near -0.4 eV in $N(E, \pi/4, 0)$ is attributed to a step-function singularity in $N_s(E)$ resulting from a two-dimensional maximum (probably D_2 in Fig. 1).

Angle-averaged photoemission spectra[5-7] show a peak in the density of states at about -0.4 eV relative to the top of the valence band which can be interpreted as arising from the occupied dangling-bond band. The position and dispersion of this band are also consistent with those derived from angular photoemission experiments.[8] Some of the other interesting features in photoemission (111) 2×1 spectra[5] are the presence of a peak in the photoemission density of states at about -3.0 eV and a very broad peak in the energy range -5.5 to -10.0 eV below the top of the valence band. These features are absent from other surfaces and are presumably associated with the surface states shown in Fig. 1. The peak at -3.0 eV can be associated with a saddle point near B_2. The large broad peak may arise as a result of the presence of a number of saddle points distributed in this energy region. It should be noted that because of lowering of symmetry on reconstruction, the true surface states that were present in this

energy region on the relaxed 1×1 surface become resonances and are split giving rise to a broad peak in the density of states.

Qualitative understanding of the energy bands for the 2×1 surface can be obtained by considering the (folded-back) energy bands for the 1×1 surface[3] in the reconstructed Brillouin zone. Corresponding to each band in the 1×1 Brillouin zone, there are two bands in the 2×1 zone which are split apart and can be associated with the two nonequivalent atoms. Thus the upper (unoccupied) dangling-bond band state is associated predominantly with the surface atoms which move into the crystal strengthening the corresponding back bonds; as a result its wave function is predominantly p_{111} in character. In contrast, the lower (occupied) dangling-bond band is associated with the raised atoms and has a significantly large s character. A large part of the energy gap arises because of the difference in the s-p orbital contents of the two bands. Similar interpretations can be given for other bands, e.g., the bands A_2 and B_2 are associated with the weakened and strengthened back bonds on the raised and lowered atoms, respectively. The net charge on the raised surface atom is $-0.76|e|$ and on the lowered surface atom $+0.36|e|$; the remaining $-0.4|e|$ is localized mainly on atoms in the second layer.

The most striking feature of Fig. 1 is that the back-bonding superlattice energy gaps (e.g., between A_2 and B_2) are about 3 times as large as similar dangling-bond gaps (e.g., between D_3 and D_4). The former arise primarily from σ interactions in the potential well between the first and second layers, while the latter depend primarily on π interactions in the region outside the first layer. As a result of σ-well interactions, the back-bond band is quite flat near A_2 and the saddle point there gives rise to a strong logarithmic peak in $N_s(E)$.

We have settled on the present model after studying surface energy levels at Γ, X, L, and J for 26 distinct atomic configurations. We have also analyzed the effect of three kinds of small displacements (~ 0.1 Å) to describe possible Jahn-Teller distortions: (a) raising and lowering of alternate rows of atoms in the first (surface) layer (present model), (b) lateral displacement of surface atoms toward or away from the nearest surface neighbors, and (c) lateral displacement of surface rows toward or away from the nearest rows. With small displacements one can discard (b) because it does not create a significant energy gap between the upper and lower surface bands

(dangling bond) in the reduced surface Brillouin zone. Both (a) and (c) create such a gap, but (c) can be discarded as it broadens the two bands, causing overlap between them, which is energetically unfavorable (cf. the effect of band overlap in the Hg chalcogenides compared to their Cd counterparts[9]). An unsatisfactory feature of both lateral displacement models is that in order to produce a significant gap, at least one of the bonds between the surface and the second-layer atoms is appreciably shortened. This strengthening of the bond gives rise to a surface state about 1.0 eV below the bottom of the valence band. Such surface states can be observed only in the presence of a high step density obtained from a poor cleave.[10]

In conclusion, we have examined many qualitatively different models and have shown that only one of these gives dangling-bond and back-bond surface states that are in semiquantitative agreement with angular photoemission and other data. Four atoms have been displaced from their bulk positions by substantially greater amounts than were previously thought necessary.[1] While our proposed atomic coordinates are not unique, they are severely constrained by the need for a large splitting of the back-bond bands,[3] by the absence of a surface state split off from the bottom of the valence band,[10] and by the necessity for a proper energy gap between the dangling-bond bands.[4] We believe that these very-low-energy constraints provide much more significant measures of atomic displacements than have so far been achieved by, e.g., kinematical analyses of LEED data in the 50–200-eV range.[1]

Because of the complexity of this problem, the research reported here was carried out independently of, but essentially concurrently with, work on the same problem by Appelbaum and Hamann.[11] From self-consistent calculations of the effect of back-bond stretching on the energy levels of Si(111) 1×1 they have ingeniously arrived at a qualitative model which agrees with our 2×1 model in all essential features. In particular, they have ascribed the two resonances seen in angular photoemission to two occupied surface-energy-band critical points associated chiefly with dangling and stretched back bonds. They have also recognized the essential role played by reconstruction in lowering the occupied dangling-bond band from its calculated position above the bulk valence band maximum (relaxed 1×1) to below it (reconstructed 2×1).

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