Diffraction of He at the reconstructed Si(100) surface

M. J. Cardillo and G. E. Becker Bell Laboratories, Murray Hill, New Jersey 07974 (Received 2 July 1979)

We present a study of the Si(100) surface using thermal-energy-He diffraction. We find that the clean surface reconstructs with a primary (2×1) two-domain periodicity and with substantial additional intensity indicating a secondary reconstruction. We are unable to order the latter using several annealing procedures and consistently obtain diffuse streaks extending across the reciprocal net at the half-order positions. We interpret this reciprocal net in terms of a disordered $c(2 \times 4)$ structure which in addition contains $p(2 \times 2)$ and possible $c(2 \times 2)$ regions. The half- and integer-order intensities vary with incident angle and wavelength in a manner qualitatively describable by semiclassical rainbow scattering. The differential cross section for incoherent scattering has structure similar in angle to the coherent intensities suggesting weak energy losses or surface disorder. Specular intensity scans indicate that the surface is extremely rough on the scale of the He wavelength, with large phase shifts, significant shadowing, and a breakdown of the uniform-attractive-well approximation. The extreme roughness makes a simple global fitting procedure unlikely and the lack of an ordered surface suggests that it will be difficult to fit calculations with a model structure.

INTRODUCTION

The outermost layers of atoms in all the common semiconductors undergo reconstruction. The resulting periodicities of these surfaces have been known from low-energy-electron diffraction (LEED) for some time.¹ Despite numerous experimental investigations and theoretical studies. the geometrical configurations of most of these surfaces remain essentially unsolved. One of the basic problems in LEED structural analyses is the penetration of the electron beam to a depth of ≈ 10 Å with strong multiple scattering occurring at and between each layer. In addition the crystals may not become periodic in the direction perpendicular to the surface until five layers deep. This would require that a calculation of the scattering intensities of a reconstructed material includes not only the complicating effects of multilayer scattering but a structural model with perhaps different geometries for each of the 3-5 layers of atoms probed by the beam.

The analysis of the diffraction of thermal energy atoms from these surfaces appears to be an attractive complement. At the low energies employed (10-100 meV) the atoms do not penetrate with the result that the diffraction observed is due to the two-dimensional periodic potential of the outermost *exposed* layer. Although there may be significant multiple-scattering effects with atom scattering, only a single geometry is in question. It is now clear that useful atom diffraction data can be obtained from any periodic surface with reasonable experimental effort. Presently the most commonly studied aspect of atom diffraction is a determination of the atom-surface potential. However, we are primarily interested in geometric structures and have studied the diffraction of He from silicon single crystals with the intent of deriving model structures for the outermost layer. A determination of the outer layer geometry would then provide a more penetrating structural probe (LEED) with a basis for resolving the structure of the entire reconstructed selvedge. We have reported our initial observations from the Si (100) and Si (111) surfaces previously^{2,3} and in this paper we discuss the diffraction of He from the reconstructed Si (100) surface in detail.

The reconstruction of the silicon (100) surface was observed more than twenty years ago by Farnsworth and Schlier (FS) using low-energy electron diffraction.⁴ Since then there have been a large number of experimental and theoretical studies of the geometry and electronic structure.⁵ To date the configuration of the outermost layers of atoms remains unsolved. No model vet proposed has resulted in acceptable agreement with LEED data. The dimerization of adjacent rows of doubly bonded surface atoms [referred to as the Farnsworth, Schlier, Levine (FSL) $model^{6}$ with a subsurface relaxation of strain extending several layers deep [Appelbaum and Hamann $(AH)^7$] is in the best (but not acceptable) agreement with LEED data.8

In addition to the geometrical arrangement of surface atoms, there remains a question as to the equilibrium periodicity of the clean reconstructed surface. FS originally observed a 2×1 periodicity. Subsequently, Lander and Morrison (LM)⁹ observed a $c(2 \times 4)$ surface structure and to account

1497

for this proposed a variation of the dimer model with alternate vacancies. The $c(2 \times 4)$ had not been seen subsequent to the LM work and in most studies was simply ignored. Recently, Poppendieck, Ngoc, and Webb (PNW)¹⁰ have reported a sharp $c(2 \times 4)$ reciprocal net for the (100) surface in which the quarter-order beams are weak in intensity but sharp.

In this paper we present diffraction data which may be sufficient to determine the appropriate model for the outermost exposed atoms of the (100) reconstructed surface. In addition we present and discuss results pertinent to the equilibrium periodicity of the surface, coherent versus incoherent scattlering, interference in the specular beam, and qualitative observations on the prospects for a scattering calculation appropriate to this surface.

EXPERIMENTAL

The apparatus has been described in detail previously¹¹ and we mention here only the essential components. It consists of three stainless chambers in tandem, each pumped by oil diffusion pumps. In the beam formation chamber a free jet expansion of helium through a 30 μ m nozzle aperture produces a nearly monoenergetic beam. The source may be heated to ≈ 1800 K or cooled to 95 K with liquid nitrogen to vary the He beam velocity. Alternatively, He can be mixed on line with heavier gases and decelerated. Most of the data we present are obtained for a pure He jet formed at either 300 or 95 K. These beams have the following properties. At 300 K, $\overline{E} = 0.063$ eV, $v_{mp} = 1.76 \times 10^5$ cm/sec, $\overline{\lambda} = 0.565$ Å, full width at half maximum (FWHM) $\approx 10\%$. At 95 K, $\overline{E} = 0.020 \text{ eV}$, $v_{mb} = 1.0 \times 10^5 \text{ cm/sec}, \overline{\lambda} = 0.98 \text{ Å}, \text{FWHM} \approx 3.5\%,$ where \overline{E} is the energy and $\overline{\lambda}$ the wavelength corresponding to the most probable velocity v_{mp} of the distribution. In the middle chamber the beam is square-wave modulated, typically at 200 Hz, for ac detection of the total He scattering. A filament light source and photodiode provide the reference. A gate valve is situated between the modulation and scattering chambers with apertures collimating the beam to 0.06° , 0.3° , or 1° , as well as a window seal. All the data presented are for beams collimated to 0.06°. This collimation corresponds approximately to a maximum coherence width of the incident He beam of ≈ 600 Å for normal incidence.

The scattering chamber has a base pressure 1 $\times 10^{-10}$ Torr and contains a differentially pumped quadrupole mass spectrometer (base pressure 1 $\times 10^{-10}$ Torr) collimated to either 1.46° or 0.55°

and capable of rotating up to 200° about the crystal axis at a distance of ≈ 10 cm. In addition, there are LEED optics, an Auger electron (AES) spectrometer, each on bellows allowing 10 cm of travel to the crystal, and a differentially fed ion sputter gun. The silicon crystal is at the center of the chamber on a manipulator shaft capable of two independent angle variations, θ —the polar angle (in the plane of the beam and surface normal) and ϕ —the azimuthal angle. The crystal is heated from the back side by radiation (up to 1000 °C) and/or electron bombardment (1350 °C). Data from three crystals are presented here, each a 1.1 cm square held against a 1 cm diameter Ta cylinder by two Ta wires across opposite corners. The region of apparent constant temperature when heating to >900 °C is a circle of ≈ 6 mm diameter. Within this circle the AES spectra, LEED, and atom diffraction patterns are uniform.

The silicon crystals were cut to within $\frac{1}{2}^{\circ}$ of the (100) plane, polished, and oxidized to a depth of approximately 20 Å. They were inserted into the UHV chamber where two separate cleaning procedures were used. The first crystal studied was cleaned by 1 KV Ar⁺ ion bombardment at room temperature with subsequent annealing at ≈ 850 °C for 5-10 min. This procedure was continued until it yielded a sharp 2×1 two-domain LEED pattern and an AES spectrum with a trace of carbon as the sole impurity. The C(272 eV)/Si(92 eV) peak-topeak ratio was typically reduced to ≈ 0.005 before atom diffraction patterns were recorded. This same procedure was used for the data reported earlier.² The second surface preparation procedure consisted of simply heating the crystal (center region) to ≈ 1350 °C and then lowering the temperature slowly (2-5 K/sec). This procedure is similar to that used by Poppendieck *et al.*¹⁰ and is considerably simpler than ion bombardment. The typical AES C/Si ratio for these surfaces is ≈0.001.

The crystal was generally aligned in plane using the sharp specular beam and in azimuth by one or more of the diffracted beams. The accuracy of the angles of incidence and scattering (measured from the surface normal) is estimated to be $\Delta \theta_i \approx 0.2^\circ$ and $\Delta \theta_r \approx 0.1^\circ$, respectively. The relative azimuth angle ϕ could be set to $\approx 0.5^{\circ}$ but its absolute position could be uncertain by 2° . The crystal was cleaned at the beginning of a run and then flashed to ≈ 900 °C approximately every 15-20 min. For each crystal prepared by the high temperature treatment, about every third heating it was brought to > 1250 °C and reduced in temperature slowly. The alignment of the crystal and peak heights for the various diffraction beams were spot checked during and after each run.

EXPERIMENTAL RESULTS

A. Surface preparation

Despite the numerous careful UHV studies of the Si(100) surface¹² there remains doubt as to the clean equilibrium surface periodicity. In most LEED studies the two-domain 2×1 pattern is reported whereas LM⁹ reported two-domain $c(2\times 4)$ in which there is noticeable streaking. Recently PNW¹⁰ reported a sharp $c(2 \times 4)$ in which the quarter order beams were found to be $\approx 2\%$ of the intensity of the integer peaks although sharp. In the latter study the apparent surface contamination was reported to be to less than 2/1000 of the Si AES peak height. For reference in Fig. 1 we have drawn the real space and reciprocal space unit mesh for the two-domain (2×1) and $c(2 \times 4)$ periodicities with the beams indexed so as to simplify discussion of the atom diffraction spectra.

Two UHV preparation procedures have been generally employed in other laboratories for the Si(100) surfaces: ion bombardment followed by annealing at ≈ 850 °C for a period of ≈ 15 min, or high temperature heating (≈ 1300 °C) followed by a slow reduction (≈ 2 ° per sec) to room temperature (PNW used the latter.)¹⁰ We have tried both procedures and find essentially no difference in the atom diffraction intensities. In Fig.2 we plot the results of two scans in the [10] direction for θ_i



FIG. 1. (a)-(d) Real-space unit nets for several periodicities discussed in the text for the Si(100) surface. The top three atom layers are shown with the largest circle representing the outermost layer. (e)-(f) Reciprocal unit nets for the (2×1) and $c(2\times4)$ periodicities with two orthogonal domains. The beam indexing and definition of ϕ used in this paper are indicated.



FIG. 2. Reduced intensities $(I_0 = \text{incident beam intensity})$ for differently prepared surfaces versus scattering angle θ_r for $\theta_i = 70^\circ$, $\lambda = 0.57$ Å. The scattering plane projects onto the [T0] direction. Curve (a) is for a surface Ar⁺ bombarded and annealed at 850 °C for 15 min. The AES C/Si ratio is 0.005. Curve (b) is for a surface heated to ~1300 °C and then cooled at ~2° per sec. The AES C/Si ratio is ~0.001. For curve (a) the detector acceptance angle $\Delta \theta_r$ is 1.45°, whereas for curve (b) it is 0.55°.

= 70° and λ = 0.57 Å. Curve (a) is for a sputtered and annealed surface whereas curve (b) is for a high temperature treated surface. For curve (a) the acceptance angle $(\Delta \theta_r)$ of the mass spectrometer for a point source on the crystal is 1.45° whereas for curve (b) $\Delta \theta_r \approx 0.55^\circ$. The proportionate reduction in background in (b) is nearly the change in solid angle into the detector as expected, yet the reduced intensities of the diffracted beams are essentially the same. The width of the diffracted beams are consistent with $\Delta \theta_r$ and the wavelength dispersion of the incident He beam $[\Delta\lambda (FWHM)/\lambda] \approx 12\%$ for curve (a), 10% for curve (b). Since the diffraction intensities versus angle are directly related to the scattering potential of the unit mesh and thereby the geometrical structure, we believe that the local surface geometries for the two preparations are essentially equivalent. In addition the AES C/Si ratios are ≈ 0.005 for (a) and ≈ 0.001 for (b), suggesting that small amounts of carbon contamination do not affect the local structure vis-á-vis diffraction intensities.

We note that we have observed extreme sensitivity of the specular He peak to contamination, particularly at grazing incidence. Contamination effects occurring in times of the order of a few seconds and estimated to be $\approx 10^{-3}$ monolayers (from a background pressure $P = 2 \times 10^{-10}$ Torr) are readily observed via the falloff of the specular beam and its subsequent restoration upon flashing to 850 °C. We infer that the specular peak is equally sensitive to surface roughness and in particular to lack of long-range order. In Fig. 2 the specular beam for (b) is measureably higher than



FIG. 3. He diffraction scans over θ_r for four different azimuthal settings labeled A through D. The reduced intensities are plotted against ΔK_{\parallel} , the reciprocal space coordinate, and the abscissa is rotated by the azimuthal angle ϕ . This allows a vertical correspondence between the reciprocal net (or LEED pattern) drawn above and the atom diffraction scan. The experimental parameters for these runs are $\theta_i = 70^\circ$, $\lambda = 0.57$ Å ($\overline{E} = 63$ meV), and $\Delta \theta_r = 1.45^\circ$.



FIG. 4. He diffraction scans plotted as in Fig. 3. The experimental parameters are $\theta_i = 50^\circ$, $\lambda = 0.98$ Å ($\overline{E} = 20$ meV), and $\Delta \theta_r = 0.55$ Å. Note the sharpness of the diffracted beams at large ΔK_{\parallel} compared to Fig. 3 as a result of the reduction of the dispersion in wavelength from FWHM =10% at $\lambda = 0.57$ Å to FWHM =3.5% at $\lambda = 0.98$ Å.

for (a). We have observed this for other spectra generated by the two surface preparation procedures. It appears that the high temperature treatment and slow anneal, in addition to being a considerably faster and simpler procedure, produces a more well-ordered surface but not significantly different in local structure.

B. Surface periodicity

In order to determine the periodicity of the surface from He scattering with in-plane detection, we scan the scattered angle θ_r for a sequence of azimuths ϕ at constant angle of incidence θ_i . In Figs. 3 and 4 we plot the results for $\theta_i = 70^\circ$, $\lambda = 0.57$ Å and $\theta_i = 50^\circ$, $\lambda = 0.98$ Å, respectively. The atom diffraction data have been plotted versus ΔK_{\parallel}

= $(2\pi/\lambda)(\sin\theta_i - \sin\theta_r)$, i.e., the parallel momentum transfer, on an abscissa which is rotated by the appropriate value of ϕ . In this manner the atom diffraction spectra can be directly compared by vertical lines to the reciprocal net or diffraction pattern displayed by LEED which is drawn above to the appropriate scale. For Fig. 3 $\Delta\theta_r = 1.45^\circ$ and for Fig. 4 $\Delta\theta_r = 0.55^\circ$.

The reciprocal net we have drawn in both figures has integer- and half-order circles representing diffraction beams as in the two-domain (2×1) surface. Rather than the quarter-order beams expected for the $c(2 \times 4)$ surface we have drawn in a diffuse streaking of intensity which extends completely across each unit mesh. This shaded pattern schematically depicts what we observe for *both* incident conditions (and *both* surface preparations) with He atom scattering. It is the proper description of the apparent [(2n+1/2), (2n+1/2)] peaks we reported previously for the parameters appro-

priate to Fig. $3.^2$ This surface (and in Ref. 2) was prepared by sputtering and annealing at 850 °C. No hint of the "extra" diffuse intensity was observed in LEED. The data in Fig. 4 were obtained for the surface prepared with the high temperature anneal. The reciprocal net drawn, including the additional diffuse intensity, was also observed for this preparation on the LEED screen at low incident electron energies ($\approx 25-30$ eV). This additional intensity is extremely weak in LEED, but is the basis for the detail of the schematic reciprocal net drawing. Despite numerous attempts with gradual temperature reductions (as in Ref. 10) and long anneals (>10 hours) at temperatures between 650-900 °C we were unable to sharpen the diffuse intensity into quarter-order beams. We also note that we have occasionally observed streaking along the $[0\overline{1}]$ and $[\overline{1}0]$ directions which extend out from the sharp integral and half-order beams.



FIG. 5. Diffraction scans taken in the [$\overline{10}$] direction for a series of incident angles θ_i . For $20^\circ \le \theta_i \le 60^\circ$, the data extend from $\theta_r = 90^\circ$ to the instrument cutoff resulting from the detector blocking the incident beam. For these plots $\lambda = 0.98^\circ$ and $\Delta \theta_r = 0.55^\circ$.

C. Scattered intensities

We have recorded a set of diffraction spectra for the [10] direction taken over a wide range of incident angle for two wavelengths, $\lambda = 0.98$ Å and $\lambda = 0.57$ Å. They are presented in Figs. 5 and 6, respectively. The results plotted in Fig. 5 are for $\Delta \theta_r = 0.55^{\circ}$ and the He source at 95 K which yields $\Delta \lambda / \lambda = 3.5\%$. In this figure the diffraction peaks are considerably sharper than in Fig. 6 for which $\Delta \theta_r = 1.45^{\circ}$ and $\Delta \lambda / \lambda = 12\%$ at $\lambda = 0.57$ Å. The background is higher in Fig. 6 reflecting the increase in solid angle at the detector.

Several features of these spectra may be noted. Over some angular regions there is a distinct alternation of intensities in the diffracted beams whereas in other angular regions their variation in intensity appears smoother. This is a consequence of the two orthogonal domains at the surface which independently contribute to in-plane scattering. Both domains contribute to the integer-order beams whereas only one domain contributes to the half-order beams. The envelopes of intensity maxima and minima are often described as rainbow scattering.¹³ Within a specific region of scattering angle, the half- and integerorder beams from one domain may be at a rain-



FIG. 6. Reduced intensities versus scattering angle with $\lambda = 0.57$ Å, $\Delta \theta_r = 1.45^\circ$ for three angles of incidence as indicated.

bow minimum whereas the scattering from the "integer domains" to that angular region comes from a rainbow maximum. This will result in an alternation in intensity between half- and integer-order beams. If the situation is reversed then the intensity will be smooth over some angular region as the integer-order beam intensities are dominated by the "half-order domain" contribution. Increasing the diffracted beam density would allow independent analysis for each domain. This could be obtained with low-energy neon diffraction.

The diffraction intensity scattered in the plane of the incident beam and surface normal amounts to less than 1% of the incident beam intensity for any of the spectra we have obtained. This is of the same order as the total in-plane diffracted intensity for the Si(111)7 \times 7 surface.³ However, the density of diffracted beams in the region of reciprocal space corresponding to in-plane scattering is considerably higher for the $Si(111)7 \times 7$ surface (approximately a factor of 10). We would thus expect the Si(100) intensities to be a factor of 3 higher if the surfaces are of comparable smoothness and had similar Debye-Waller factors. The lower in-plane intensity than expected is consistent with the (100) surface being somewhat disordered and/or more open that the $(111)7 \times 7$.

The data for $\theta_i = 50^\circ$ in Figs. 5 and 6 provide an interesting comparison. The background in Fig. 5 has been suppressed by reducing $\Delta \theta_r$, and the diffraction is enhanced at large ΔK_{\parallel} using a longer wavelength. However, we note that the envelopes of scattered intensity with angle show remarkable similarity. This similarity extends to the apparent incoherent scattering in Fig. 6 which dominates for $\theta_r < 20^\circ$. A similar angular dependence of diffraction intensities was noted for the Si(111)7×7 surface at different wavelengths.³ However, the high angular resolution of the detector (suppression of diffuse scattering) for that report did not permit a comparison with incoherent scattering.

D. Specular intensity

The specular beam represents a unique probe of surface structure that is sensitive to vertical displacements because only normal momentum (k_{\perp}) is transferred. We have examined the variation of specular intensity with incident polar angle for a sequence of azimuths starting from the [11] and [10] directions. We have found it difficult to extract the detailed fine structure from these curves with sufficient accuracy to determine a consistent set of bound-state energy levels.¹⁴ The structure due to resonances appears weak and broad in angle. In addition there is extreme sensitivity to contamination near grazing incidence even at 2×10^{-10} Torr. However, the principal difficulty results from the intense interference oscillations of the specular intensity in its variation with θ_i , which are of structural interest independent of the analysis of the attractive well. For an illustration of the general reproducibility of these data, in Fig. 7 we have plotted the results of specular intensity scans taken on four different days for two different crystals for the same nominal incident conditions. The vertical dashed lines on Aand B indicate the change in intensity upon flashing the crystal to 900 °C. The integration time is of the order of 30 sec per point. The entire curve C was obtained in a single more rapid sweep in or-



FIG. 7. Specular intensity versus incident angle along the [II] direction for four separate runs several days apart on two different crystals. The arrows show the direction with time and the dashed lines indicate points where the crystal was flashed. Curves A and B were taken on one crystal. Curves C and D are from a second crystal with a more accurate alignment. Note the general agreement of features for $\theta_i < 70^\circ$ for A and C. Curve D was taken with a high density of points for accuracy. Note the magnitude agreement between C and D after flashing for $\theta_i > 70^\circ$.



FIG. 8. Specular intensity variation with $\cos\theta/\lambda$ for two incident wavelengths (energies). For the upper (a) curves $\lambda(63 \text{ meV}) = 0.57 \text{ Å}$ and $\lambda(21 \text{ meV}) = 0.98 \text{ Å}$. In the bottom curves (b) the abscissa has been adjusted for a uniform shift of λ due to an assumed attractive well depth of 11 meV.

der to reduce serious contamination, whereas for D the data are intended to be closely spaced in angle for accuracy. This sequence illustrates the difficulty in obtaining an accurate reproducible result for this surface. However, a careful inspection of curve C reveals it to have most of the general and specific features of the other curves. In particular it reproduces the region $\theta_i < 70^\circ$ for A in detail and the absolute height of D for $\theta_i > 75^\circ$. We may therefore qualitatively use C at $\lambda = 0.98$ Å for comparison to a similar run for a different crystal taken for $\lambda = 0.57$ Å at the same azimuth. This is done in Fig. 8 where we have anticipated the structural significance of this data by plotting versus $(\cos\theta)/\lambda$ which is proportional to Δk_{\perp} . The data from which Fig. 8(a) is obtained have similar features which occur over quite different angular regions. It is not obvious which if any of the features are due to bound state (surface) resonances. Oscillations which arise from structural interference are expected to vary nearly as $q' = (2\pi/\lambda')$ × $\cos\theta'$, where λ' and θ' are the "effective" wavelength and incident (scattered) angle within the range of the attractive potential. In Fig. 8(a), in which the vacuum wavelength and angle are used, the data are similar in contour but shifted, i.e., scaled differently along the abscissa. This shift is apparent when we replot the data in Fig. 8(b) where we have adjusted λ for each curve to the effective λ' appropriate to an attractive well depth of 11 meV. The following equations are applicable to the angle $(\theta_i - \theta_i')$ and wavelength $(\lambda - \lambda')$ in the presence of a uniform attractive well of depth D:

 $\lambda \sim (20/E)^{1/2}$ where λ is in Å and E in meV, (1)

$$\lambda' = \lambda \left[E/(E+D) \right]^{1/2}, \tag{2}$$

$$\theta_i = \arcsin\left[(1 + D/E)^{1/2}\sin\theta_i'\right]. \tag{3}$$

For specular scattering

$$q_{\perp} = \Delta k_{\perp} = \left(8\frac{mE}{h^2}\right)^{1/2} \cos\theta_i = 4\frac{\pi}{\lambda} \cos\theta_i \text{ where } k = 2\frac{\pi}{\lambda}$$
(4)

and in the presence of a uniform well of depth D

$$q'_{\perp} = \Delta k'_{\perp} = \left(8\frac{mE}{h^2}\right)^{1/2} \left(\cos^2\theta_i + \frac{D}{E}\right)^{1/2}.$$
 (5)

Note that only λ' and not q' has been used in the abscissa of Fig. 8(b). The similarity in these curves is now striking in its detail. However, adjusting the wavelength for a uniform attractive potential without a corresponding inclusion of its refractive effect $(\theta - \theta')$ cannot be justified on simple physical grounds. This correlation would be appropriate if the effective attractive potential acted radially on the incident He from the individual atomic scattering centers. The long-range nature of the attractive part of rare-gas atom potentials is well documented and rules out this possibility. A more likely explanation of the correlation in Fig. 8(b) is that the well depth varies significantly across the surface, and in particular is deepest in the troughs. If the structure in Fig. 8 arises from the interference between primarily a flat region within a trough where the attractive well is ~11 meV deeper than a flat region higher in the unit mesh, then a correlation of the type in Fig. 8(b) may be expected to hold. This result suggests a breakdown in the simple uniform attractive well approximation often used in atomsurface scattering calculations. A more complex parametrization of the He-surface potential, perhaps an additive potential, will be required for a structural calculation.

One may conclude from Fig. 8 that an assignment of a selected set of the features in the spec-



FIG. 9. Specular intensity scans versus incident angle θ_i at $\lambda = 0.98$ Å for a series of azimuthal settings ϕ [see Fig. 1(e)]. Note the sharply varying amplitudes at $\theta_i > 65^\circ$ and the gradual shifting of the maxima near $\theta_i = 60^\circ$.

ular data to surface resonances will be difficult at best due to the large amplitude oscillations arising from structural interference. Resonance features are often identified by taking advantage of the fact that they occur at a constant distance in reciprocal space from reciprocal lattice rods.¹⁴ Thus they may be straightforwardly assigned to a particular reciprocal lattice rod by noting their center of rotation as the azimuth is varied. In contrast, structural interference is approximately independent of azimuth for surfaces which are not "too rough." In Fig. 9 we present the specular intensity versus θ_i for a series of azimuths ϕ away from the [11] direction in small steps as indicated. Although the coarse intensity envelopes are similar, each curve is notably different in both amplitudes and detailed contour of the principle features. In addition, only some of the weaker features are persistent and appear to move continuously in θ , as ϕ is varied. Along the [10] direction (Fig. 10) the specular intensity shows similar consistency in gross shape but with large amplitude variations as the azimuth is varied. There



FIG. 10. Specular intensity scans versus incident angle at $\lambda = 0.57^{\circ}$ for azimuths near the [10] direction.

are not continuous series of sharp features easily ascribable to surface resonances which can be tracked with sufficient accuracy in angle.

DISCUSSION

A. Surface periodicity

Although the two-domain (2×1) LEED pattern has been reported most frequently, the results of He diffraction clearly indicate that the equilibrium Si(100) surface has a more complex unit mesh as reported by both LM⁹ and PNW.¹⁰ However, in contrast to the latter authors we are unable to anneal these crystal surfaces to a well-ordered single periodicity despite a range of different preparation procedures. The surfaces we have studied are essentially uncontaminated and show evidence of similar local atomic structure as demonstrated in Fig. 2. We interpret the reciprocal net drawn in Figs. 3 and 4 as arising from a principal second-order reconstruction in one direction with a minor second-order reconstruction in the perpendicular direction. It is the phasing of the minor reconstruction from row to row along the direction of the principal reconstruction which results in the streaks. The various sequences of phase will yield at least $p(2 \times 2)$ and $c(2 \times 4)$ periodicities

and perhaps larger periods. Making use of a buckled dimer as an illustration of the principal reconstruction,¹⁵ examples of these phasings and their associated unit mesh are drawn with alternating dimer types serving as the minor reconstruction in Fig. 11. If there were no coupling (random phase) of the minor second-order reconstruction between vertical dimer rows, then the two degenerate domains rotated by 90° would produce a narrow-lined cross extending through the half-order spots. However, a random phasing between rows implies that the rows are uncoupled with only onedimensional ordering of the minor reconstruction. It can be shown that one-dimensional ordering must be of restricted length depending on the strength of the coupling. This would broaden the line cross into diffuse bands as drawn in Figs. 2 and 3.

If the $c(2 \times 4)$ surface is indeed the lowest free energy configuration for Si(100), as suggested by LM⁹ and PNW,¹⁰ then it appears to be nearly degenerate with at least one other periodicity, i.e., the $p(2 \times 2)$ and perhaps the $c(2 \times 2)$ as well. For a given model structure this conclusion has interesting implications. For example, Chadi¹⁵ has recently carried out semiempirical total energy minimizations for a large number of model reconstructions of the Si(100) surface. He finds the SFL⁶ symmetric dimer model the lowest in energy of those which have been previously suggested (subsurface strain not included). It is well documented that this surface would have a metallic surface state band and perturbations to the symmetric dimer have been suggested¹⁶ to remove it con-



FIG. 11. Illustration of the various periodicities discussed in the text based on the tilted dimer proposed by Chadi (Ref. 15). The shaded atom is elevated with respect to its dimer partner. The alternation of the tilting will yield $p(2\times 2)$ or $c(2\times 2)$ depending on the phasing of adjacent rows. Note that the motion anticipated in the second layer to relieve strain is equivalent for the $p(2\times 2)$, $c(2\times 4)$, and $c(2\times 2)$ but not for the (2×1) .

sistent with the $c(2 \times 4)$ periodicity. Chadi finds tilting of the dimer by forcing one atom up and the other down removes the metallic state and lowers the total energy by 0.16 eV/atom. Simply tilting the dimer leaves the surface in a 2×1 periodicity (Fig. 11). If the tilting is alternated along the dimer row, which seems clearly favorable if strain in the second and third layer is considered, a . $p(2 \times 2)$ or $c(2 \times 4)$ periodicity results depending on whether adjacent rows are in phase or of alternate phase, respectively. Chadi finds each of these configurations similar in total energy with the $c(2 \times 4)$ and $p(2 \times 2)$ somewhat lower than 2×1 (by ≈ 0.05 eV/atom). He further notes that the $c(2 \times 2)$ structure is essentially equivalent to the $c(2 \times 4)$. We have illustrated each of these structures in Fig. 11. The results of Chadi's calculations are in accord with our interpretation of the reciprocal net observed with atom diffraction and LEED. It is possible, however, that other structural models of the principal or minor second-order reconstruction may have similar relative energies when they are additionally perturbed so as to form $c(2 \times 4)$, $p(2 \times 2)$, or $c(2 \times 2)$ periodicities.

An observation specific to a model of a slightly distorted dimer is of interest. Note that although the $c(2\times 2)$, $c(2\times 4)$, and $p(2\times 2)$ are calculated to be of similar total energy, only the latter two are readily interconverted as the difference is simply in the phases of the buckling of adjacent rows. On the other hand the conversion of $c(2\times 2)$ to $c(2\times 4)$ requires the breaking of (a row of) the dimer bonds, estimated to be 2 eV in bond strength. The activation energy for this process must be comparably high with the consequence that annealing out domains or rows of $c(2 \times 2)$ dimers would require very high temperatures. Since the $c(2 \times 2)$ and $c(2 \times 4)$ are very similar in energy, the fluctuations between them at temperatures at which there would be a reasonable interconversion rate would be large. Thus it might not be possible to obtain a surface of pure $c(2\times 4)$, or perhaps the rate of temperature reduction in this high temperature anneal would have to be extremely slow, specifically at some critical region where the interconversion rate goes through ≈ 1 . It is of interest that previously PNW¹⁰ have prepared surfaces by heating their crystals to very high temperatures (≈ 1300 C) with extremely slow annealing. PNW anneal at half the temperature reduction rate as reported here and observe a sharp $c(2 \times 4)$ whereas we observe streaks through the $c(2 \times 4)$ positions. No other observations of the $c(2 \times 4)$ except the original study of LM (streaked) have reported it. Furthermore, if the $c(2 \times 4)$ is the primary periodicity and there are residual rows of $c(2 \times 2)$ dimers, they may be bordered by an extended boundary of

another periodicity such as $p(2 \times 2)$. On the other hand, note that no $c(2 \times 2)$ regions are required to fit the reciprocal net we observe. Small domains of $c(2 \times 4)$ and $p(2 \times 2)$ are sufficient. These domains should be easily interconverted. If one is slightly lower in energy then it should appear sharpened at lower temperatures provided that the barrier to interconversion is not too high. We have not attempted diffraction runs at temperatures below 300 K.

Another consideration when discussing the disordered intensity from the buckled dimer model is the step density on a surface. If a crystal is cut to within $\frac{1}{2}^{\circ}$ accuracy then there will be typically 20 dimers in the [10] direction between step edges at least on alternate terraces. If the step edge is not parallel to the [01] direction then there will be particular locations along the edges where the dimerizing pairs will have to shift to accommodate the angle of the step. This can be accomplished with jogs in the step edge of 7.68 Å while maintaining $c(2 \times 4)$ or $p(2 \times 2)$ periodicity on the surface. A lower energy jog of 3.84 Å can be obtained by shifting the dimers by one atom, i.e., having a local $c(2 \times 2)$ row. The difference in energies between these jogs can easily be of the order of 2 eV which at 20 dimers/terrace row is to be compared with energy differences of < 0.1eV/dimer that Chadi finds between $c(2 \times 2)$ and $c(2 \times 4)$. The extent of $c(2 \times 2)$ regions formed by this mechanism would depend on the direction as well as *angle* of miscut of the crystal and could vary between samples.

A close inspection of the diffuse streaks in the atom diffraction patterns of Figs. 3 and 4 shows repeated indication of structure in the form of a poorly defined splitting of the streak along its axis. For example, in Fig. 4 projection B cuts through the streak at the $(\frac{1}{24})$ position. The intensity is actually a minimum at the center of the streak axis. The same behavior may be clearly noted in other places in this figure and weakly in Fig. 3 as well for projections B and C. There the structure is not as pronounced due to the angular spread accepted by the detector. In Fig. 4 projection C shows sharp structure at the $\left[\frac{1}{2}\right]$ positions. If our interpretation of these streaks is correct, including the suggestion of a nearly one-dimensional ordering of limited coherence, then this "splitting" may be characteristic of some most probable coherence length along that dimension. One may roughly estimate the distance to be 25 Å, i.e., 6 or 7 coupled dimers. We note that for there to be some most probable coherence length in one dimension requires more than one-dimensional ordering forces. Subsurface strain and dipole interactions of the postulated charge shifts

will both extend across the rows and perhaps provide sufficient two-dimensional ordering forces.

B. Coherence and the in-plane cross section

A substantial amount of in-place scattering appears as incoherent scattering. In particular for $\Delta \theta_r = 1.45^{\circ}$ and $\lambda = 0.57$ the background in Figs. 3 and 5 is quite evident and we estimate that it dominates the integrated diffracted intensities by more than an order of magnitude. It is apparent in Fig. 6 that the incoherent background has structure. For $\theta_i = 70^\circ$ there is an obvious scattering cutoff near $\theta_r = 0^\circ$ and at $\theta_i = 50^\circ$ there appears to be a prominent rainbow at $\theta_r = -10^\circ$. One expects that incoherent scattering at these energies is the result of either lack of surface order or excitation of bulk and surface phonons. We previously estimated the density of diffraction intensities for the Si(100) as low compared to the Si(111)7 \times 7 surface, since we do not expect their Debye-Waller factors to be substantially different. If the background contains a large contribution arising from surface disorder, then much of the scattering may be (quasi-) elastic but phase randomized. The differential cross section for this scattering should be equivalent to classical scattering from the unit mesh. Indeed, if the inelastic contribution is dominated by small $|\Delta k|$ transfer (low-energy phonons) then we may expect the inelastic differential cross section to be only slightly broadened compared to the classical elastic cross section, and therefore the angular distribution of background intensity to contain the essential structural information of the unit mesh.

A detailed comparison of Figs. 5 and 6 illustrates this correspondence. For $\lambda = 0.57$ Å, $\theta_i = 50^\circ$ there is a prominent background peak at $\theta_r = -10^\circ$ (Fig. 6). Using simple classical rainbow scattering (specular reflection from a hard wall) we may assign this maximum to a point of inflection in the unit mesh potential. If we assume a uniform attractive well with a depth of 10 meV extending out from a structural hard wall we may derive the angle α of the appropriate point of inflection within the unit mesh. For this well depth $\alpha = 27.3^{\circ}$. For $\lambda = 0.98$ Å a similar maximum should then appear at $\theta_r = -19.8^\circ$. At $\theta_i = 50^\circ$ this angle is just at the instrument cutoff (Fig. 5). However, there is clearly an increase in the integer beam $(\overline{4}0)$ intensity and in the background near cutoff. The same rainbow peak will shift predictably with incidence angle and at $\theta_i = 60^\circ$ it may be calculated to appear at $\theta_r = -12^\circ$. In Fig. 5 there is a clear maximum in *diffracted* intensity occurring at this angle. Similarly at $\theta_i = 70^\circ$, $\lambda = 0.98$ this rainbow maximum is calculated to shift to $\theta_r = -6^\circ$ and again there is

an obvious maximum in diffracted and background intensity at this angle. Note that the half-order beams fit smoothly into the intensity contour for these maxima. This *identifies the domain* for which the angle of the inflection point has been determined.

Several other correspondences can be traced from background structure to diffraction intensities for the two wavelengths. Another example is the small maximum in the background at $\lambda = 0.57$, $\theta_i = 30^\circ$ occurring at $\theta_r = 67^\circ$ [between the $(\frac{5}{2}0)$ and $(\overline{3}0)$ beams]. This yields a point of inflection at -15.5°. From this one calculates a maximum at $\theta_r \approx 90^\circ$ for $\theta_i = 30^\circ$ and one at $\theta_r = 63^\circ$ for $\theta_i = 20^\circ$, $\lambda = 0.98$ Å. These simple exercises serve to illustrate the applicability of semiclassical theory to structural analysis using atom scattering. Higher-order interference phenomena occurring between trajectories scattered to the same angle within the unit mesh, i.e., supernumerary rainbow oscillations, are apparently damped by instrumental broadening.

It is interesting to consider the advantages of diffraction of a light element such as He to the scattering of a heavier element such as Ar, which at low incident energies may be dominated by quasielastic collisions with a cross section equivalent to that of classical elastic scattering. In the case of classical scattering there is a high density of information, namely intensity at all angles, the distribution of which can be simulated from a structural model and the use of simple classical mechanics. However, assumptions about the nature of the scattering must be made, and in particular, the energy dependence of the quasielastic cross section is required. In addition structural details will be washed out. Complications due to coherent interactions which are not related to the local structure are avoided. Examples of these complications are lack of long-range crystal order, slight contamination, and coherent interference from terraces or domains at different heights.

On the other hand, although the diffraction intensities for an in-plane scan at a specific incident condition are limited in information (6-12 amplitudes per scan in Fig. 5), the scattering process appropriate to the peak intensities is explicit, i.e., it is elastic and coherent. The periodicity of the surface effectively spatially resolves the elastic coherent scattering without the need for experimental energy discrimination. The density of information can be increased by varying θ_i , ϕ , and λ continuously. In the specific case of Si(100) with two contributing domains, their relative contributions can be in principle be separated with the assignment of the diffracted beam orders. Thus, we see that diffractive and classical scattering are in some sense complementary. For a structure as complex and open as the reconstructed Si(100) both sources of data may be required. The diffraction of Ne, with a shorter wavelength and higher density of beams, might be an interesting compromise.

C. Specular intensities and approximate scattering theories

It appears from Figs. 7-10 that the specular intensity scans we have obtained are not amenable to an accurate analysis for bound state (surface) resonances. For Si(100) the required periodic heating to \approx 1300 °C with an accurate return in angular alignment added to the possibility that each recleaned surface might be slightly different in overall periodicity make the study of surface resonances a more difficult experiment than we were prepared to carry out. In addition, we have scanned through features we believe are associated with surface resonances and we do not find them nearly as sharp or deep as has been observed for other surfaces.¹⁴ If their angular width is assumed to be lifetime broadened, we may roughly estimate a characteristic surface resonance distance of 20-30 Å. This is consistent with our interpretation of the limited coherence in the surface periodicity or alternatively may simply be a result of the large Fourier coefficients of an open rough surface. Large Fourier components (rough surface) would yield a high probability for rescattering the He atom to the vacuum thereby reducing its surface residence time.

Our principal interest is in the geometric structure of the (100) surface and the data of Figs. 8-10 appear appropriate for this consideration. The specular beam is unique and simpler than the diffracted beams in its structural information content as it results solely from perpendicular momentum transfer Δk_{\perp} . It is some measure of the height distribution of the flat regions within the unit mesh. For weakly corrugated surfaces the phase shifts between the (minimally three) specular scattering regions are small compared to the He wavelength and a scan over polar angle results in a smooth envelope of diffracted intensity which is azimuth independent. This has been demonstrated in He scattering from NiO where one Fourier coefficient of the potential of amplitude 0.14 Å suffices to describe the surface.¹⁷ The Bragg condition for diffraction normal to the surface is $2d\cos\theta = n\lambda$. Within the experimental range of θ_i on NiO less than $\pi/4$ phase shift evolves for $\lambda \approx 0.57$. For this surface a simple global scattering theory, namely the eikonal approximation, is

valid and provides a reasonably good description of all the diffracted beams.

The results in Figs. 8-10 indicate very large phase shifts—more than an order of magnitude larger than for NiO- as would be expected for any of the models yet proposed for the Si(100) surface. The extremely strong variation in the amplitudes of the specular intensity scans with azimuth are not within the eikonal scattering model. The data in Figs. 9 and 10 indicate large shadowing effects again characteristic of a very rough surface. The large variations in contour of the scans for only a few degrees change in azimuth are a result of the complexity and depth of the outer layer geometry. In addition, the results presented in Fig. 8, as well as the shifting of the maxima in Figs. 9 and 10, illustrate that the uniform well depth is not a good approximation for this surface. Semiclassical scattering calculations¹⁸ for this system confirm the open rough nature of the Si(100) surface and yield estimates for in-plane multiple scattering from 10-30% as well.

Despite the large phase shifts, an elementary analysis of Fig. 8(b) can be made as an illustration of the potential utilization of specular scattering. The Bragg equation for constructive interference normal to the surface is

 $2d_{\perp}\cos\theta' = n\lambda'$

where d_{\perp} is a planar spacing in the normal direction or simply the heights of flat (specularly scattering) regions within the unit mesh. From Fig. 8(b) we may assume that the principal maxima which occur at $\cos\theta/\lambda' = 0.64$ and 0.28 arise from constructive interference from which $\Delta n = 1$. We therefore derive $d_{\perp} = \Delta n \lambda'/2 \cos \theta = 1.39$ Å. This value is remarkably close to the interlayer spacing for the Si(100) surface of 1.36 Å. Considering the large coherence width of the incident He beam, this interference might be associated with terraces separated by monatomic steps. However, if the constructive interference results from separate terraces, the interference is due to phase evolution over equal effective attractive potentials and the abscissa of Fig. 8(b) is not appropriate for this interpretation. Alternatively one may consider interference within the unit mesh. The Si(100) surface is sufficiently open that even in the absence of a reconstruction one may expect specular scattering contributions from at least two exposed layers. These layers are also displaced by 1.36 Å and would generate maxima separated as shown in Fig. 8(b).

The scattering from the deeper layer may be affected by a more attractive interaction than that from the top layer and can lead to the correlation shown in Fig. 8(b). Dimerization of the top layer

21

would open the surface further and enhance the contribution from the second and third layers where the well depth is postulated to be deeper. Semiclassical scattering calculations¹⁸ show the scattering from the dimer model to be dominated by the peripheral regions of the unit mesh. Furthermore, the tilting of the dimer, as proposed by Chadi,¹⁵ would split the heights between these layers thereby adding secondary oscillations to Fig. 8(b) roughly of the spacing shown. For example, there are several oscillations about each principla maxima displaced by ~0.06 Å⁻¹ which at $d_{\perp} = 1.36$ Å would arise from vertical structure displacements of $\sim 0.2-0.3$ Å about the average layer spacing. A more accurate analysis would require the data in Fig. 8(b) to be corrected for the refraction and wavelength shift of the average interaction potential in addition to the phase evolution due to the well depth difference implied by using $\cos\theta/\lambda'$. This refinement would enable the absolute positions of these features to be predicted in addition to their relative positions.

CONCLUSION

We have presented a detailed set of He atom diffraction patterns for the Si(100) surface. It is clear from these results that He scattering is extremely sensitive to the order and the structure of the outermost exposed layer. This sensitivity and the lack of penetration of the atoms give rise to high expectations for atom diffraction as a structural probe complementary to LEED and other newly developing techniques [e.g., ion scattering and surface extended x-ray absorption fine-structure (EXAFS)]. The He diffraction scans clearly show that the reciprocal net for all our surface preparations is consistent with a secondary reconstruction as reported in two other investigations^{9,10} in addition to the commonly observed (2×1) . However, we are unable to order the surface. The interpretation of the details of the disorder revealed by the atom diffraction patterns suggests a near degeneracy for the different configurations of a secondary reconstruction in accord with recent results of semiempirical total energy calculations for the tilted dimer model of the surface.¹⁵

From a rather elementary analysis of the diffraction intensities, we have illustrated that scattering calculations in the spirit of semiclassical theory should be appropriate for a model structure determination. This is particularly important for large unit mesh surfaces, such as reconstructed materials and some ordered adsorbates, where the number of diffracted beams becomes too large for a full quantum calculation. This study clearly illustrates that specular scattering can be exploited as a structural probe. It is phase sensitive to vertical displacements within the unit mesh and necessarily over the coherence area of the beam as well. A simple analysis of the specular intensity at $\phi = 45^{\circ}$ suggests interlayer vertical distortions also consistent with the buckled dimer model. For a complex unit mesh such as the reconstructed Si(100) or Si(111), specular scattering does not contain nearly sufficient information for a direct structural determination. The illustration we have given is appropriate only for $\phi = 45^{\circ}$. As the azimuth is varied the specular intensity scans change dramatically. For $\phi = 0^{\circ}$, [T0], they are quite different from $\phi = 45^{\circ}$ indicating strong shadowing effects. For a complex open surface such as the Si(100), an optimal analysis may be treating the specular scans in a similar spirit to ion scattering calculations with blocking patterns as a function of angle and energy, except in this case there is the addition of phase interference. Such an analysis may be sufficient to choose between proposed models or for structural problems in which simpler questions are asked as in step height analysis or a choice between adatom binding sites on smooth characterized surfaces (metals).

On the other hand, the primary emphasis of this study is the structure of the Si(100) surface. The experimental results and preliminary calculations¹⁸ indicate that this will be quite a difficult problem to solve were the surface ordered into a single periodicity. The Si(100) surface is extremely rough (open) even to 20 meV He atoms. The path length differences as a function of impact parameter are very large on the scale of the He wavelength. There are strong shadowing effects as seen in the specular intensity scans and the simplifying assumption of a uniform attractive well and hard wall interaction potential is not appropriate (Figs. 8-10). Neither a one-dimensional nor simple scattering theory such as the eikonal approximation is reasonable for this surface. It is likely that a detailed search with semiclassical scattering theory will be required to demonstrate the correct model structure. Due to the open structure the model may have to be quite close before any substantial agreement is realized. Furthermore, it is not clear that a successful structural calculation can be carried out if the surface does not order into a single periodicity. If the disorder in the secondary reconstruction (streaked cross) represents a substantial structural variation from the primary (2×1) reconstruction, the diffraction spectra may be expected to be an incalculable superposition from more than one configuration constituting undetermined fractions of the surface. We note that it may be possible

to order the surface into a single periodicity below room temperature. Alternatively an intentional cutting of the crystal off the (100) plane or doping the surface with a trace of active impurity may serve the same purpose.

The surface sensitivity of thermal energy He scattering from single crystals is well demonstrated in the appearance of "extra" intensity which details the disorder of the secondary reconstruction. An accurate examination of the diffuse streaks and their apparent splitting as a function of temperature would be an interesting study as it might provide the energetics and statistical ther-

- ¹Cf. F. Jona, IBM J. Res. Dev. <u>9</u>, 375 (1965).
- ²M. J. Cardillo and G. E. Becker, Phys. Rev. Lett. <u>40</u>, 1148 (1978).
- ³M. J. Cardillo and G. E. Becker, Phys. Rev. Lett. <u>42</u>, 808 (1979).
- ⁴R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. <u>30</u>, 4 (1959).
- ⁵For a review of experimental work see T. D. Poppendieck, Ph.D. thesis, University of Wisconsin, 1978 (unpublished).
- ⁶J. P. Levine, Surf. Sci. <u>34</u>, 90 (1973).
- ⁷J. A. Appelbaum and D. R. Hamann, Surf. Sci. <u>74</u>, 21 (1978).
- ⁸K. A. R. Mitchell and M. A. VanHove, Surf. Sci. <u>75</u>, (1978) 147L.
- ⁹J. J. Lander and J. Morrison, J. Chem. Phys. <u>37</u>, 729 (1962).
- ¹⁰T. D. Poppendieck, T. C. Ngoc, and M. B. Webb, Surf. Sci. <u>75</u>, 287 (1978).
- ¹¹M. J. Cardillo, C. S. Y. Ching, E. F. Greene, and

modynamics for the different couplings of the secondary reconstruction. A more quantitative analysis of the disorder on the Si(100) surface may thus be of great interest.

ACKNOWLEDGMENTS

The authors acknowledge extensive conversations with E. I. Grimmelmann and J. C. Tully including results of semiclassical scattering calculations presently being performed. We also thank T. M. Rice and J. E. Rowe for several helpful discussions and comments and E. E. Chaban for technical assistance.

G. E. Becker, J. Vac. Sci. Tech. 15, 423 (1978).

- ¹²In addition to the above references, see A. Ignatiev, F. Jona, M. Debe, D. E. Johnson, S. J. White, and D. P. Woodruff, J. Phys. C 10, 1109 (1977).
- ¹³See (a) J. D. McClure, J. Chem. Phys. <u>52</u>, 2712 (1970); (b) G. Boato *et al.*, J. Phys. C <u>6</u>, L394 (1973); (c) J. D. Doll, Chem. Phys. <u>3</u>, 257 (1974); (d) R. I. Masel, R. P. Merrill, and W. H. Miller, J. Chem. Phys. <u>64</u>, 45 (1976).
- ¹⁴See (a) G. Boato, P. Cantini, R. Tatarek, and G. P. Felcher, Surf. Sci. <u>80</u>, 518 (1979); (b) G. Derry, D. Wesner, W. Carlos, and D. R. Frankl, Surf. Sci. <u>87</u>, 629 (1979).
- ¹⁵D. J. Chadi, Phys. Rev. Lett. <u>43</u>, 43 (1979).
- ¹⁶J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. <u>36</u>, 450 (1976).
- ¹⁷P. Cantini, R. Tatarek, G. P. Felcher, Phys. Rev. B 19, 1161 (1979).
- ¹⁸E. K. Grimmelmann and J. C. Tully (unpublished).