

## Electronic structure of Si(111)-Cl by angle-resolved secondary emission and electron energy loss

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Angle-resolved secondary emission from the Si(111)-Cl( $7 \times 7$ ) system shows strong evidence for a series of resonances near  $k_{\parallel} = 0$  at  $4.6 \pm 0.1$  eV above the vacuum level, with evidence for other resonances at  $k_{\parallel} = 0$  at  $2.6 \pm 0.1$  eV and about 7 eV. Using the ionization potential of this surface determined from photoemission measurements of other workers, these data are found to be in excellent agreement with predictions of calculations by Schlüter and Cohen. Angle-resolved energy-loss spectra, taken with the effective primary beam emerging at an angle of  $77^\circ$  with respect to the surface normal, show no angle-dependent structure, indicating that the transitions observed are from flat occupied bands, i.e., localized states. The peak in the loss spectra at  $8.7 \pm 0.1$  eV, apparently mainly due to transitions involving  $p_z$  orbitals, is compared with predictions of both the tight-binding calculation reported by Pandey, Sakurai, and Hagstrum, and the pseudopotential calculation of Schlüter and Cohen.

### I. INTRODUCTION

A number of studies have recently been made of the electronic structure of a monolayer of chlorine chemisorbed onto Si(111) surfaces. By comparing polarized-photoemission data with predictions from the calculated valence-band structure, Schlüter *et al.*<sup>1</sup> deduced that chlorine chemisorbs onto a Si(111)  $2 \times 1$  surface in a onefold covalent configuration. A similar configuration was found for chlorine chemisorbed onto Si(111)  $7 \times 7$  and  $1 \times 1$  surfaces, by Pandey, Sakurai, and Hagstrum,<sup>2</sup> (referred to as PSH), again by comparison between predicted and observed uv-photoemission spectra. These workers found no significant differences between the photoemission data for Si(111)-Cl( $7 \times 7$ ) and Si(111)-Cl( $1 \times 1$ ) surfaces, respectively, an observation used here to justify the comparison of experimental data from the  $7 \times 7$  system with calculations for the  $1 \times 1$ . One of the predictions of the model of PSH was the existence of an unoccupied  $\sigma$ -antibonding orbital ( $\sigma^*$ ) that should be observed in energy-loss spectra.<sup>2</sup> In the onefold configuration the axis of the  $\sigma$  bond between a chlorine and its underlying silicon is parallel to the surface normal, and to the  $z$  axis in the system of coordinates used here.<sup>2</sup>

In more recent work, Schlüter and Cohen<sup>3</sup> (SC) report band-structure calculations of surface states and resonances for the silicon-chlorine system.<sup>4</sup> In these calculations a self-consistent pseudopotential was employed to predict dispersion curves for occupied states, and for unoccupied states and resonances up to 16 eV above the top of the valence band. From these results were calculated constant-initial-state photoemission spectra, which were compared with experimental re-

sults.<sup>5</sup> The electron-energy-loss spectra of Sakurai *et al.*<sup>6</sup> were compared with the band-structure results in a more qualitative way.<sup>3</sup>

From the above studies it can be said that the occupied states of this system have been probed in a detailed manner by uv-photoemission experiments. The experimental probing of the unoccupied states and resonances has been much less detailed, and the interpretation of the available spectra is less straightforward. This is partly because the methods used so far to probe the unoccupied levels have involved measurement of a joint density of states between occupied and unoccupied levels. Less than ideal agreement was reached for the calculated and experimental constant-initial-state photoemission spectra,<sup>3</sup> and the significance of the agreement between the energy-loss spectrum and predicted interband transitions was in doubt, somewhat, due to uncertainty in the magnitude of the correction to be made for the effect of the dielectric constant on the energy losses.<sup>3</sup>

In the first of the experimental methods described here, that of angle-resolved secondary electron emission, electrons are excited into resonances from which they are diffracted into the vacuum.<sup>7,8</sup> Dispersion curves of resonances have been deduced from such data for a metal,<sup>9</sup> and for a semiconductor with a reconstructed surface.<sup>8</sup> The present results, the first to be reported for a chemisorbed layer, are compared with the band structure calculation of Schlüter and Cohen in Sec. II. The information deduced from these measurements, similar to that found in various electron reflection measurements,<sup>10</sup> is just of the resonance. So far as is known there is no memory of the initial state; no joint-density-

of-states effects.

The angle-resolved energy-loss measurement, reported in Sec. III, is also a relatively new type of measurement. This technique, inelastic low-energy electron diffraction (ILEED), was used by Porteus and co-workers<sup>11</sup> to investigate the dispersion of plasmons, particularly surface plasmons, in aluminum. Its use to elucidate surface electronic structure has so far been limited to measurements on the clean Si(111)  $7 \times 7$  surface.<sup>12</sup> Many energy-loss spectra without angular resolution have been reported.<sup>13</sup> Some of the advantages of the measurement with angular resolution are discussed in this paper. Section IV consists of a brief summary

## II. ANGLE-RESOLVED SECONDARY-ELECTRON EMISSION

All measurements reported here were made using the equipment described previously.<sup>14</sup> The silicon-chlorine system investigated was prepared by exposing a (111)  $7 \times 7$  surface at 400 °C to approximately 100 L (1 Langmuir =  $10^{-6}$  Torr sec) of the chlorine gas, as suggested by Weekes.<sup>15</sup> This procedure is believed to produce a monolayer of chlorine covalently bonded to the underlying silicon. The resulting LEED pattern has the same angular distribution as that from the clean  $7 \times 7$  surface, but with greatly reduced intensity in the nonintegral order spots. Both the secondary emission spectra and the energy-loss spectra are different from those of the clean surface.

The secondary spectra recorded from this surface are for electrons emerging into the  $[2\bar{1}1]$  azimuth, and were excited by a 36-eV beam incident at about  $10^\circ$  from the normal in the  $[\bar{2}11]$  azimuth (Fig. 1). The low-energy peak, which moves from about 0 eV at  $0^\circ$  emergence angle out to a kinetic energy of about 2 eV at  $85^\circ$ , is believed to consist of electrons originally excited into bulk states.<sup>16</sup> The reconstructed surface layer scatters electrons emerging from the bulk, so that information about bulk states normally contained in the secondary spectra is obliterated.<sup>16</sup> All other features in the spectra of Fig. 1 are not observed in spectra from the clean silicon surface,<sup>8</sup> and are believed to be due to electrons being excited into surface resonances before being diffracted into the vacuum.<sup>7,17</sup> These are the peak at 2.6 eV at  $77\frac{1}{2}^\circ$ , the series of peaks at about 4.6 eV at angles of emergence between  $77^\circ$  and  $87^\circ$ , and the broad feature at about 7 eV appearing near grazing emergence.

There are two conservation laws for electrons coherently crossing ordered plane surfaces; energy is conserved, and

$$k_{\parallel \text{out}} = k_{\parallel \text{in}} + b_{\parallel},$$

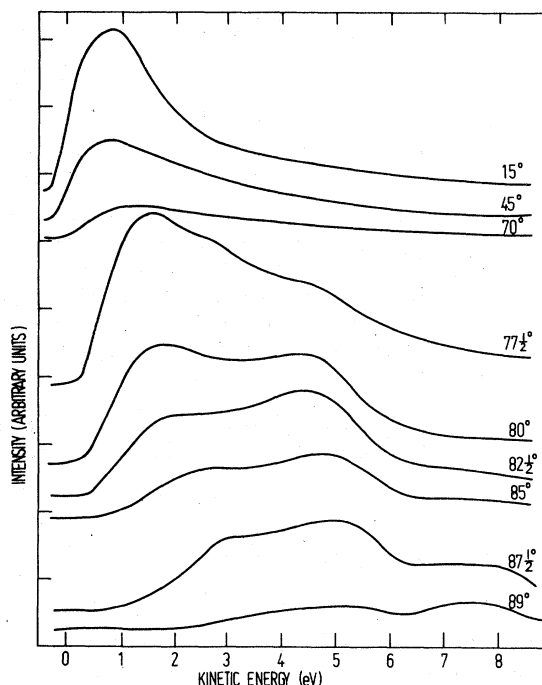


FIG. 1. Secondary emission spectra from the Si(111)-Cl( $7 \times 7$ ) system in the  $[2\bar{1}1]$  azimuth. Take-off angles relative to the surface normal are indicated. The intensity of the spectra at angles greater than  $70^\circ$  has been amplified by a factor of 10.

where  $k_{\parallel}$  is the component of wave vector parallel to the surface, and  $b_{\parallel}$  is one of the surface reciprocal lattice vectors.<sup>18</sup> Using these conservation laws the dispersion curves of the resonances corresponding to the peaks of Fig. 1 can be plotted out, as shown by the plots of Fig. 2(a). The observed states appear at values of  $k_{\parallel}$  close to zero in the reduced zone of the reciprocal lattice of the  $7 \times 7$  structure.

It has been shown by ultraviolet-photoemission spectra that the structure of occupied electronic states for the chlorine-covered  $7 \times 7$  surface is almost identical to that for the chlorine-covered  $1 \times 1$  surface.<sup>2</sup> Here we compare the experimental dispersion curve for resonances in the  $7 \times 7$  surface with the calculated curves for the  $1 \times 1$  surface.<sup>3</sup> There are no adjustable parameters in this comparison, as the ionization potential of the Si(111)-Cl( $7 \times 7$ ) surface is known to be  $5.9 \pm 0.2$  eV.<sup>19</sup>

Comparing the two sets of data as they stand [Figs. 2(a) and 2(b)], the strongest agreement is the very clear experimental evidence for resonances at 4.6 eV near  $k_{\parallel} = 0$ , just as predicted by Schlüter and Cohen<sup>3</sup> (Fig. 2(b)). There are two kinds of disagreement between experiment and theory, however; first, the observed resonances

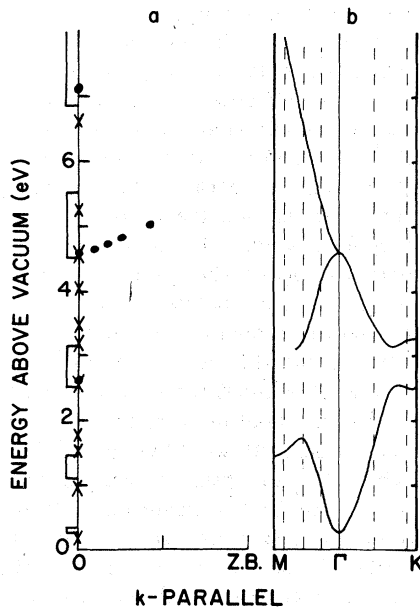


FIG. 2. (a) Dispersion curves of resonances from secondary emission in the  $[2\bar{1}\bar{1}]$  azimuth (dots). In this case the zone boundary is appropriate to the Si(111)-Cl( $7 \times 7$ ) structure. The boxed regions of the ordinate represent the values of  $E$ , at  $k_{\parallel} = 0$ , which can be observed in these experiments. The crosses represent the positions of  $k_{\parallel} = 0$  resonances predicted by theory. See text. (b) Dispersion curves calculated by Schlüter and Cohen (Ref. 3). In this case the zone boundary is appropriate to the Si(111)-Cl( $1 \times 1$ ) structure. The vertical dashed lines represent the values of  $k_{\parallel}$  from which electrons can be diffracted into angles appropriate to  $k_{\parallel} = 0$  states in the  $7 \times 7$  structure.

at 2.6 and about 7 eV are not predicted by the calculation, and second, the predicted resonance at 0.25 eV [Fig. 2(b)] at  $\Gamma$  is not observed. The lack of observation of predicted resonances is easily accounted for; only electrons emerging from resonances at large angles relative to the surface normal are observed in secondary emission from reconstructed surfaces.<sup>8</sup> For  $k_{\parallel} = 0$ , these states are at energies in the boxed regions of the ordinate in Fig. 2(a).

More difficult is the fact that resonances are observed where none are predicted, i.e., at 2.6 and 7 eV in Fig. 2(a). It is probable that these observations are related to the presence of very weak nonintegral order diffraction spots in the LEED pattern from this surface: Electrons in resonances can be diffracted, so that electrons at the values of  $k_{\parallel}$  shown by the vertical dashed lines in Fig. 2(b) can be diffracted to appear at angles appropriate for  $k_{\parallel} = 0$  states. When such diffraction processes are considered, resonances at an effective value of  $k_{\parallel} = 0$  are pre-

dicted by the band structure of Fig. 2(b) at those energies marked by crosses in Fig. 2(a). Within the limits of accuracy of the data (up to  $\pm 1$  eV for the calculated high-energy resonances,  $\pm 0.1$  for the observed values) there is now very good agreement between theory and experiment for resonances at  $k_{\parallel} = 0$  at 2.6, 4.6, and 7.1 eV above the vacuum level.<sup>20</sup>

The comparison will be taken further. For resonances along the  $\Gamma$ - $K$  direction of Fig. 2(b) it is only from those at the values of  $k_{\parallel}$  shown by the dashed vertical lines that electrons can be diffracted into the  $[2\bar{1}\bar{1}]$  azimuth. Observation of the lone peak at 2.6 eV in the spectra of Fig. 1, here attributed to resonances along  $\Gamma$ - $K$ , is consistent with this statement. From resonances along  $\Gamma$ - $M$ , however, which direction in reciprocal space lies in the  $[2\bar{1}\bar{1}]$  azimuth in real space, electrons can be diffracted into the  $[2\bar{1}\bar{1}]$  azimuth at angles corresponding to  $k_{\parallel} \neq 0$ . Apart from the peaks around 4.6 eV, structure corresponding to electrons with  $k_{\parallel} \neq 0$  is not apparent in Fig. 1. The makeshift comparison between the experimental data from the  $7 \times 7$  surface and the calculated curves for the  $1 \times 1$  surface is satisfactory in that it explains the data, but is lacking in that  $k_{\parallel} \neq 0$  resonances predicted by theory are not observed. Overall, we take an optimistic view, and emphasize the agreement.

### III. ANGLE-RESOLVED ENERGY-LOSS SPECTRA

#### A. Data

The energy-loss spectrum shown in Fig. 3 was measured with a nominal beam input energy of 29 eV at an angle of incidence of  $20^\circ$  in the  $[2\bar{1}\bar{1}]$  azimuth. From the observed LEED intensity distribution it is probable that the primary beam for the loss spectrum was the emerging  $(7, 0)$  beam, diffracted at an angle of  $77^\circ$  in the  $[2\bar{1}\bar{1}]$  azimuth, i.e., at close to grazing emergence. The loss peak at  $8.7 \pm 0.1$  eV (Fig. 3) was not present in spectra recorded when no intense diffraction peak was observed at grazing emergence, no matter what other diffracted beams were observed.

Loss spectra were recorded every  $5^\circ$  in the  $[2\bar{1}\bar{1}]$  azimuth. Only one spectrum is shown, as the peak at 8.7 eV loss did not change significantly with change of take-off angle. No fine structure could be seen on the peak, even when an overall energy resolution of 0.2 eV was used.

#### B. Discussion

For incident electron energies sufficiently high for the Born approximation to apply, a dielectric formalism can be used to describe the energy loss

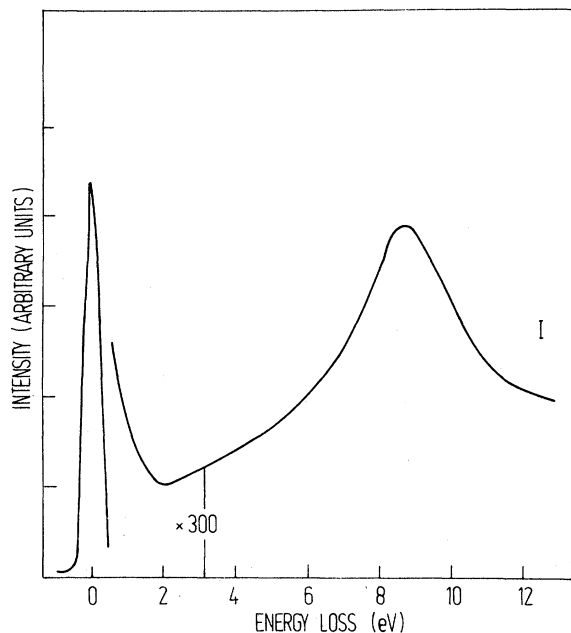


FIG. 3. Energy-loss spectrum from the Si(111)-Cl(7 $\times$ 7) system.

spectra.<sup>21</sup> In this case the energy of a peak in the loss spectrum need not coincide with the peak in the optical absorption spectrum.<sup>22</sup> This approximation does not apply at the low incident beam energy employed here, for which Bauer has described an appropriate model for the loss processes.<sup>23</sup> On a band model, peaks in the loss spectra correspond to maxima in the generalized ( $\Delta k_{\parallel} \neq 0$ ) joint density of states between the occupied and unoccupied levels.<sup>23</sup> On a localized orbital model (i.e., the flat-band limit for occupied and unoccupied levels) the energies of peaks in a loss spectrum correspond to one-electron energy differences between occupied and unoccupied orbitals.

In the absence of a calculation of the energy-loss spectra we offer the following, semiquantitative discussion of the data in Fig. 3. There are two kinds of selectivity in the loss processes observed here. The first is that the matrix element for an excitation will have a significant value only when both occupied and unoccupied orbitals occupy the same region of space. For example, in the loss spectrum of clean silicon, losses due to the excitation of electrons from bulk valence to bulk conduction bands were observed, as were losses due to dangling bond to surface resonance excitations: No transitions from bulk to surface resonances were observed, however.<sup>24</sup> In the present case we do not expect to see strong Cl  $p_{x,y} \rightarrow$  Cl  $p_z^*$  transitions, nor bulk to surface orbital transitions.

The other cause of selectivity in the present en-

ergy loss experiment is the almost grazing emergence of the effective primary beam. Again referring to the loss spectrum for clean silicon, evidence for the 3.5-eV bulk loss is quite clearly apparent in angle-resolved spectra associated with normally emergent primary peaks,<sup>25</sup> and with angle-integrated loss spectra.<sup>24</sup> No such loss peak is observed in the spectra recorded for nearly grazing emergent beams.<sup>12</sup> In these cases the primary electrons apparently spend most time in the selvedge region, i.e., between the topmost atomic layer and the vacuum. Such will be the case for the spectra reported here. Therefore, before knowing anything else about the spectra, the above considerations would lead us to expect that the most prominent loss peak would be due to transitions involving Cl  $p_z$  orbitals, or resonances: i.e., Cl  $p_z \rightarrow$  Cl  $p_z^*$  or Cl  $p_z \rightarrow$  resonance. With this background the experimental loss spectra will be compared first with the localized orbital calculation of PSH, and then with the band structure calculations of SC.

The results of calculations of PSH indicate three occupied localized states at the surface of the Si(111)-Cl(1 $\times$ 1) system: a  $\sigma$ -bonding orbital at -7.10 eV, and  $\pi$  orbitals at -5.75 and -4.95 eV.<sup>2</sup> The  $\sigma$  orbital and the more tightly bound  $\pi$  orbital have about equal contributions from Cl  $p_z$  wave functions.<sup>2</sup> The vacant  $\sigma^*$  orbitals lie at 1.55 eV, and consist mainly of Cl  $p_z$  wave functions. Assuming equal transition probabilities for all Cl  $p_z \rightarrow$  Cl  $p_z^*$  type excitations, a transition energy of about 8.0 eV is expected for the main peak in the loss spectra; to be compared with the observed 8.7-eV-loss peak.

The results of band-structure calculations of SC are given as dispersion curves along high-symmetry directions.<sup>3</sup> It will be assumed that the  $\sigma$ -bonding states and the more tightly bound  $\pi$  states have equal  $p_z$  contributions, as found by PSH.<sup>2</sup> The  $\sigma$  states form a flat band at about -8 eV, the lower  $\pi$  states show more dispersion, and are centered at about -6 eV, while the  $\sigma^*$  states are spread over about 4 eV, with the maximum density at about 2.5 eV. With the same assumptions as before, a peak in the loss spectrum would be expected at about 9.5 eV, again to be compared with the observed 8.7-eV loss. The agreement between experiment and theory is semiquantitative for both the localized and the plane-wave calculations.

#### IV. SUMMARY AND CONCLUSIONS

The specific conclusions of this work concern the determination of the values of energies and  $k_{\parallel}$  of some of the resonances of the Si(111)-Cl(7 $\times$ 7)

surface, and the demonstration that the energy-loss peak at 8.7 eV represents transitions between flat bands. Evidence was found to show that the calculation of Schlüter and Cohen accurately predicted the higher-energy resonances associated with the surface.

The experimental determination of electronic structure is becoming a well-established area in surface science. The contribution to this area that can be made by the techniques described in this paper will be briefly summarized. Surface resonances observed by angle-resolved secondary emission apparently reflect only final "state" properties. These measurements offer the opportunity to determine the dispersion curves of the resonances directly relative to the vacuum level, and, via photoemission measurements of the ionization potential, indirectly to the top of the valence band. As such, these techniques give results that can be compared directly with calculated resonance dispersion curves.

Angle-resolved energy-loss spectra measure a joint density of states, and are thus more dif-

ficult to interpret than the secondary emission. However, in the two systems studied by this technique so far there are two features which assist in the interpretation. The first is that loss spectra do change as the emergent angle of the effective primary beam is changed. In particular, for an effective primary beam direction which is near grazing emergence, loss peaks due to processes within the selvedge region of the crystal are predominant in the spectra. The other features of angle-resolved spectra are that dispersion in the joint density of states can, in principle, be measured, excitons can be identified, and flat-band conditions can be identified.<sup>12</sup>

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<sup>1</sup>M. Schlüter, J. E. Rowe, G. Margaritondo, K. M. Ho, and M. L. Cohen, *Phys. Rev. Lett.* **37**, 1632 (1976).

<sup>2</sup>K. C. Pandey, T. Sakurai, and H. D. Hagstrum, *Phys. Rev. B* **16**, 3648 (1977).

<sup>3</sup>M. Schlüter and M. L. Cohen, *Phys. Rev. B* **17**, 716 (1978).

<sup>4</sup>Results were presented for clean silicon (111), Si(111)  $1 \times 1$  with chemisorbed hydrogen, and for Si(111)  $1 \times 1$  with "covalent" and "ionic" chemisorbed chlorine.

<sup>5</sup>J. E. Rowe, G. Margaritondo, and S. B. Christman, quoted in Ref. 3.

<sup>6</sup>T. Sakurai, J. E. Rowe, and H. D. Hagstrum (unpublished), quoted in Ref. 3.

<sup>7</sup>Electrons in these surface resonances are generally bound in that their component of wave vector normal to the surface is insufficient for them to escape the surface potential barrier. Electrons enter and leave such resonances by a diffraction process (private communication from E. G. McRae).

<sup>8</sup>P. E. Best, *Phys. Rev. Lett.* **34**, 674 (1975), and *Phys. Rev. B* (to be published).

<sup>9</sup>R. F. Willis, B. Feuerbacher, and N. E. Christensen, *Phys. Rev. Lett.* **38**, 1087 (1977).

<sup>10</sup>E. G. McRae, *Surf. Sci.* **25**, 491 (1971); A. Adnot and J. D. Carette, *Phys. Rev. Lett.* **38**, 1084 (1977); E. G. McRae, J. M. Landwehr and C. W. Caldwell, *ibid.* **38**, 1422 (1977), and references therein.

<sup>11</sup>J. O. Porteus and W. N. Faith, *Phys. Rev. B* **12**, 2097 (1975); C. B. Duke, L. Pietronero, J. O. Porteus, and J. F. Wendelken, *ibid.* **12**, 4059 (1975), and references therein.

<sup>12</sup>P. E. Best, *Phys. Rev. B* **12**, 5790 (1975).

<sup>13</sup>M. Nishijima and K. Fujiwara, *Solid State Commun.* **24**, 101 (1977). See Ref. 12 for earlier references.

<sup>14</sup>P. E. Best, *Rev. Sci. Instrum.* **46**, 1517 (1975); **48**,

696 (1977).

<sup>15</sup>S. Weekes, in a paper presented at the 24th National Symposium of the American Vacuum Society, Boston, 1977 (unpublished); and private communication.

<sup>16</sup>P. E. Best, *Phys. Rev. B* **14**, 606 (1976).

<sup>17</sup>Waves excited into, and subsequently emerging from, a resonance can interfere with waves directly excited into the vacuum. In observations made so far (Refs. 8, 9), the resonances appear as pure Breit-Wigner resonances [J. R. Taylor, *Scattering Theory* (Wiley, New York, 1972), p. 242 and Ref. 10]: i.e., direct excitation of electrons from occupied states to vacuum states occurs with very low probability. Support for this view is seen in the energy-loss spectra of the clean Si(111)  $7 \times 7$  surface (Ref. 12), in which excitations of electrons from occupied dangling bond states into resonances, a process complementary to secondary emission, also appear as pure Breit-Wigner resonances. To this author's knowledge no observation of the direct excitation of electrons from occupied states of a solid to vacuum states has yet been made in experiments of this kind.

<sup>18</sup>C. B. Duke and G. E. Laramore, *Phys. Rev. B* **3**, 3183 (1971), and references therein.

<sup>19</sup>The clean surface ionization potential is  $5.0 \pm 0.1$  eV [M. Erbudak and T. E. Fischer, *Phys. Rev. Lett.* **29**, 732 (1972)]; the change in ionization potential on formation of the chemisorbed chlorine is 0.9 eV (Ref. 2).

<sup>20</sup>The resonance predicted at 5.3 eV was not observed. However, the data of Fig. 1 was taken in angular increments of  $2\frac{1}{2}^\circ$ , as all resonances of this type previously observed had appeared as members of a series (Ref. 8). An isolated peak, similar in nature to that at 2.6 eV in Fig. 1, could have been missed in this study. Subsequent to this realization there has not been an

opportunity to search for a peak at 5.3 eV.

<sup>21</sup>D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1964), p. 182.

<sup>22</sup>H. Ibach and J. E. Rowe, *Phys. Rev. B* **9**, 1951 (1974).

<sup>23</sup>E. Bauer, *Z. Phys.* **224**, 19 (1969).

<sup>24</sup>J. E. Rowe and H. Ibach, *Phys. Rev. Lett.* **31**, 102 (1973).

<sup>25</sup>P. E. Best (unpublished).