Inelastic low-energy electron diffraction from a silicon (111) 7×7 surface*

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Inelastic low-energy electron diffraction from a silicon (111) 7×7 surface can be explained in terms of transitions from an occupied state, observed in photoemission, to unoccupied states whose existence is observed or implied from secondary electron emission. The density of states of the surface-state conduction band is reported. This band extends from 2.3 to about 12 eV above the top of the valence level, with a maximum density at 7 eV. A surface exciton is observed at 1.9 eV.

I. INTRODUCTION

Measurements of inelastic low-energy electron diffraction[1] (ILEED) from a Si (111) 7×7 surface are reported and discussed in this paper. The measurements are made at a time when the surface has already been studied by other techniques: photoemission, energy-loss spectra without angular resolution, and energy- and angular-dependent secondary electron emission. The present data are consistently interpreted on a simple band model which is derived from the previous measurements.

The model interpretation of ILEED data has been developed by Porteus and others,[1,2] based on earlier work of Davisson and Germer, and of Turnbull and Farnsworth.[3] In these experiments it is found that an electron must suffer a Bragg-type diffraction event before emerging from the solid. Observed inelastic events are then classified as loss-before-diffraction (LD) or diffraction-before-loss (DL) events. In a series of ILEED spectra each type of scattering has a recognizable character.

Conservation laws for an electron crossing an ordered surface play an important part in the interpretation of ILEED[1,4]: energy is conserved and

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

where $k_{\parallel}$ is the component of wave vector parallel to the surface, and $b_{\parallel}$ is a surface reciprocal-lattice vector. Measurement of ΔE and $\Delta k_{\parallel}$ for a maximum in the loss spectrum, relative to the primary beam, gives information about E and $q_{\parallel}$ for a maximum in the excitation spectrum within the solid. In the simplest cases the excitation spectrum can consist of contributions from single-particle and collective excitations. From the most detailed ILEED work to date, Porteus and Faith have derived the surface-plasmon dispersion curve for aluminum.[2]

A detailed theory of the inelastic scattering of low-energy electrons in surface regions has been made by Mills and others.[5,6] For the $\Delta k_{\parallel}=0$ loss processes reported in this paper, the approximations applied by Mills are appropriate. In this case the energy-loss function is proportional to

$$\mathrm{Im}\{-1/[\epsilon(q_{\parallel},\omega)+1]\} \approx q_{\parallel} d \epsilon_2^s/(\epsilon_1^b+1)^2, \qquad (1)$$

where d is the thickness of a surface layer of complex dielectric constant $\epsilon^s(\omega)$, which is superimposed on the surface of a semi-infinite dielectric with bulk dielectric constant $\epsilon^b(\omega)$. The dielectric-constant approach to the analysis of electron energy losses has a substantial literature.[7] Angle-resolved energy-loss spectra from cleaved silicon and germanium surfaces have been analyzed with the aid of this model.[6] The optical constants of the surface layer were derived from the $\Delta k_{\parallel}\approx 0$ spectra.

In energy regions removed from zeroes of the denominator term in Eq. (1), structure in the loss function depends mainly on ϵ_2^s, which on a microscopic model is made up of contributions due to single-particle excitations.[8] Bauer has considered the theory of single-particle excitations for the case of inelastic scattering of low-energy electrons in bulk crystals.[9] The probability for Coulomb excitation consists of two terms, one dependent on the matrix element involved, the other on structure in the generalized joint density of states, $\Delta k_{\parallel}$ unrestricted. The results of the theory are parallel, in many respects, to the results of calculations of optical absorption, for which $\Delta k = 0$.[8] Bauer's theory is valid for a plane in k space in the bulk of the crystal, and so should apply within the "plane" containing the surface overlayer mentioned above.

In summary, the relative importance of the different factors which contribute to the loss function, Eq. (1), will be stated. Most of the structure in ϵ_2^s is expected to come from structure in the generalized joint density of states. The matrix element term is generally considered to be a slowly varying function of energy for $\Delta k_{\parallel}=0$ processes.[8,9] The bulk dielectric constant $\epsilon_1^b(0,\omega)$ is known for silicon.[10] The denominator in Eq. (1) will not in-

troduce any sharp structure into the loss function in the energy region of interest in this work, although it can shift peak positions. The theory of Mills was not extended to $\Delta k_{\parallel} \neq 0$ processes. Nevertheless, it is expected that the generalized-joint-density-of-states term will be the dominant factor in the energy-loss function for these processes, too: There will only be energy losses with ΔE, $\Delta k_{\parallel}$, if unoccupied states are separated from occupied states by these amounts of energy and k vector. To a first approximation, then, structure in the loss spectra reflects structure in the generalized joint density of states. This is the approximation which has been used in the interpretation of energy-loss spectra without angular resolution.[11–13]

II. RESULTS AND DISCUSSION

A. ILEED

The ILEED data, shown in Fig. 1(a), were recorded for electrons emerging in the $\langle 2\bar{1}\bar{1}\rangle$ azimuth using apparatus described elsewhere.[14] The incident 32-eV beam was at a polar angle of 17° in the $\langle 0\bar{1}\bar{1}\rangle$ azimuth. Spectra were recorded every 1° from 60° to 90° from the surface normal, although only a selection are shown here. The visibility of the loss spectra against the secondary electron cascade background was maximized when a strong elastic diffraction peak (7, 0) was observed emerging at an angle of 79° from the surface normal. The observations are consistent with the hypothesis that the emerging (7, 0) elastic beam was the principal primary beam for the loss spectra reported here, in DL processes. The probable backgrounds due to cascaded secondaries have been drawn for all the spectra, although only one is shown, by the dotted line, in Fig. 1(a). The spectra after subtracting the backgrounds are in Fig. 1(b). The range of energy losses observed in the ILEED is from about 2–12 eV.

The peaks in the spectra are at 1.9 ± 0.1 and 7.0 ± 0.2 eV, with a weak shoulder at 5.0 ± 0.1 eV. Rowe and Ibach have shown that the energy-loss peaks are associated with the (111) 7×7 surface,[13] a conclusion supported by the following observations. For electrons detected at lower take-off angles relative to the surface normal, the energy losses of Fig. 1 were drastically reduced. In conjunction with the theory of Mills this observation also identifies the losses as surface losses: the probability of loss in the surface layer is proportional to the path length in the surface.[5,6] Energy losses occurring in the surface layer could be due to the excitation of various types of transitions between surface, bulk, and vacuum states. As a starting point only transitions from occupied to unoccupied surfaces states will be considered here.

The spectra in Fig. 1 differ from those recorded by Rowe and Ibach[13] in three respects: the weak shoulder at 5.0 eV is reported for the first time in this work, the angular dependence is recorded here, and the shapes of the spectra are shown, indicating that inelastic processes occur at a continum of energies between the two loss peaks.

The intensity of the elastic peak varies by a

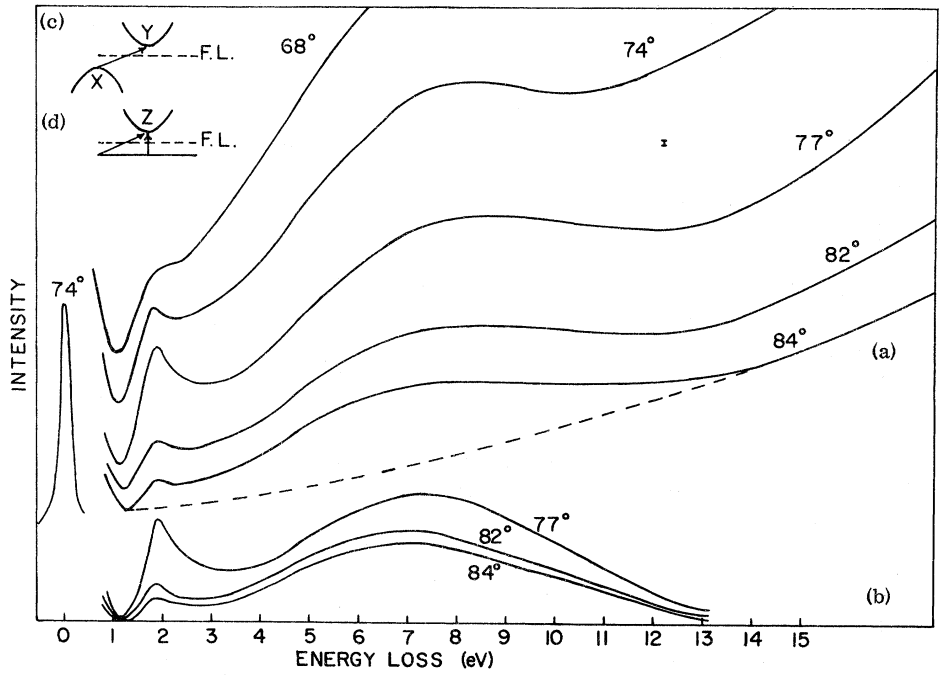

FIG. 1. (a) Energy-loss spectra from Si (111) 7×7 surface as a function of angle from the surface normal in the $\langle 2\bar{1}\bar{1}\rangle$ azimuth. The intensity of the elastic peak shown has been reduced by a factor of 100. The dotted line is the probable cascade secondary background for the 84° spectrum. (b) as in (a), but with the background subtracted. (c) and (d) E-vs-k curves for the hypothetical situations discussed in the text.

factor of 5.0 ± 0.1 over the range of angles for which spectra are reported in Fig. 1. This factor gives an indication of the amount of instrumental, defect, and thermal diffuse scattering, and is the reference against which to compare the other angular dependencies.[15] Over the same angular range the intensity of the broad peak varies by a factor of 2.0 ± 0.4, this factor varying very little with energy loss within the structure. No angular-dependent fine-structure with amplitude larger than the noise bar on Fig. 1 was observed on the broad peak. The intensity of the 1.9-eV loss peak varies by a factor of 4.5 ± 0.2.

Information can be extracted from the observed angular dependencies. Those electrons scattered elastically into angles outside of the diffraction spots can of course be "primary" electrons for inelastic events. In this case the angular dependence of the intensity of a $\Delta k_{\parallel} = 0$ loss process would follow the angular dependence of the intensity of the elastic component. On this argument the 1.9-eV loss peak is associated with a $\Delta k_{\parallel} = 0$ loss process.

The fact that no angular-dependent fine structure is observed in the broad feature is quite remarkable. Remembering that the main structure in ILEED spectra will be due to structure in the generalized joint density of states, consider the two simple band structures shown in Figs. 1(c) and 1(d). Transitions between critical points X and Y would give rise to a peak in the energy-loss spectra at a particular energy and particular Δk. In ILEED measurements this peak would be observed for only a small range of emergent angles. From an electronic system consisting of broad bands of both occupied and unoccupied states, ILEED spectra would be made up of loss features, shoulders or peaks, whose intensity would vary with angle.[16] On the other hand, for the bands shown in Fig. 1(d), transitions to the critical point Z will occur for the complete range of Δk. In this case a variation of intensity with angle would be due only to a change in the matrix element for transitions from different parts of the occupied flat band,[9] or to a change due to different processes becoming important in the dielectric constant theory of ILEED for $\Delta k_{\parallel} \neq 0$.[5,6] The lack of appearance of fine structure that varies with angle means primarily that the electronic transitions excited in the loss processes are either from a flat valence band to a broad band of conduction states, or from a broad valence band to a flat conduction band. Combinations of these are ruled out by the lack of angular-dependent structure. Within the framework of Bauer's theory,[9] the two cases depicted in Figs. 1(c) and 1(d) are the only ones significant for the prediction of gross angular-dependent structure in ILEED. From the known energy resolution of the instrument, an upper bound of 0.25 eV can be placed on the total width of the flat band.

The intensities of the inelastically scattered maxima, relative to the elastic peak, effectively rule out multiple scattering as a significant source of these loss spectra.[11] Contributions to the spectra from phonon-assisted transitions are expected to be small, this being a second-order process.[15]

For the case of transitions from or to a flat band, the generalized joint density of states, which is proportional to $1/[\nabla_k(E_c - E_v)]$, is just the density of states of the broad band. To a first approximation, the broad peak in Fig. 1 is interpreted as a measure of a density-of-states curve. This approximation was first used by Ludeke and Esaki in a study of excitations from a core state.[11] Ruling out accidental cancellation of their effects, the slow angular variation of intensity in the broad peak is indicative of matrix elements that vary slowly with $\Delta k_{\parallel}$, and of a dielectric constant model also relatively insensitive to $\Delta k_{\parallel}$, for these experimental conditions.

B. Energy-level diagram

The data will be interpreted with the aid of an energy-level diagram which is constructed from known properties of this surface (Fig. 2). In this diagram the top of the bulk valence band is used as the reference level, 0 eV, and the vacuum level is at 5.0 ± 0.1 eV.[17,18] Photoemission measurements from two experiments[19,20] indicate that occupied surface states form a narrow band at 0.1 ± 0.2 eV. In these experiments a high-energy peak in the energy distribution of photoemitted electrons is observed for the (111) 7×7 surface, but not for this surface covered by an absorbed gas. This peak is attributed to emission from surface states.[19,20] The same method has been used for other surfaces, and seems well established.[21] No other explanation has been put forward for these observations. These surface states are shown in Fig. 2.

Other photoemission data have been interpreted in terms of surface states lying below the top of the valence band.[18] These states, other than one at -12 eV which is outside the energy range relevant to the present paper, were not observed in the gas adsorption photoemission experiments referred to above.[19,20] In the interpretation of the energy-distribution curve (EDC) of electrons ejected from a (111) 7×7 surface by 21.2-eV photons, the curve was taken to be made up of two parts, due to the density of bulk states, and surface states, respectively. The surface-state density curve was obtained by subtracting a function proportional to the density of bulk states from the EDC.[18] Since then, the theory of EDCs has been

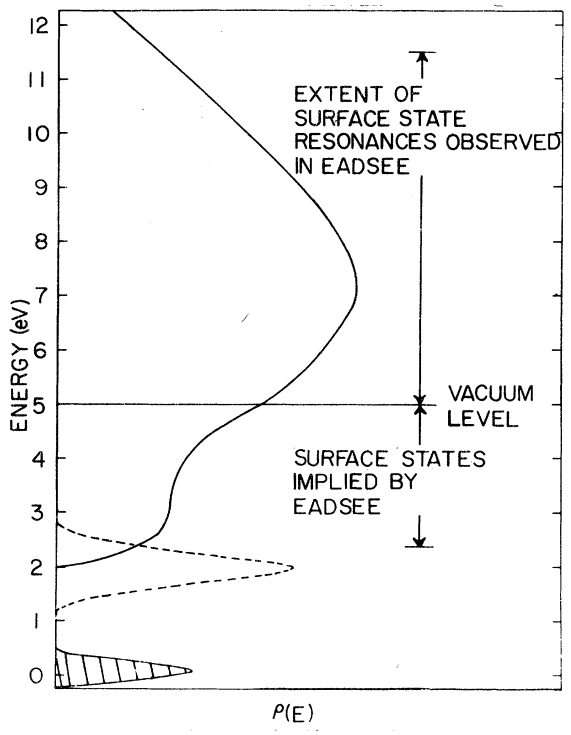

FIG. 2. Energy-level diagram for electron states in the silicon (111) 7×7 surface. The cross-hatched peak represents the occupied level observed in photo emission (Refs. 19 and 20), while the broad peak represents the density of states as interpreted from ILEED in this work. The exciton peak which was subtracted from the energy-loss data is shown by the dotted line.

advanced considerably.[22] For photon energies above about 30 or 40 eV, EDCs do reflect densities of occupied states. Below about 20-eV EDCs generally contain structure due to both the density of occupied states, and the joint density of states. Because of this, it is considered that the evidence for occupied surface states between 0 and −7 eV, derived from the EDC obtained with 21.2-eV photons, is inconclusive.

Energy- and angular-dependent secondary electron emission (EADSEE) data for the 7×7 surface has been interpreted in terms of emission from surface-state resonances.[23] At the same time, angle-resolved secondary emission from bulk states of single-crystal tungsten have been investigated.[24] The model for secondary emission from bulk states, put forward by Kane,[25] has received substantial support by this work.[24] High-lying conduction states are occupied mainly according to their density, and the usual conservation laws are obeyed for electrons crossing an ordered surface. There is no way that this model can account for the EADSEE data referred to above.[23] In an evaluation of seven different processes that can contribute structure to EADSEE, that involving emission from surface-state resonances was found to be the only one that can satisfactorily account for the data.[26] Surface-state resonances have been observed from just above the vacuum level to 6.5 eV above the vacuum level,[23,26] as indicated in Fig. 2.

The dispersion curve of some of the surface-state resonances observed in EADSEE is accurately fitted with a nearly-free-electron model.[23] From this fit it was tentatively concluded that the bottom of the surface-state conduction band is at 2.4 ± 0.1 eV. A similar fit was observed for a dispersion curve derived from emission in the [10$\bar{1}$] azimuth.[26] Because non-free-electron behavior was also observed in EADSEE, the energy to which unoccupied surface states extend below the vacuum level cannot be inferred with confidence from this data. Nevertheless, it seems fairly sure that they would extend below the vacuum level, and as a first approximation the extent inferred from the free-electron model has been included in Fig. 2.

Other experiments have been performed on this surface,[27] none of which are qualitatively inconsistent with the diagram of Fig. 2. It is considered that the interpretations of these experiments are not as clear cut as for the experiments used to derive this diagram. Theoretical calculations of the surface-state band structure are not possible for this surface, as the atomic positions are not known with sufficient accuracy.[28]

When Rowe and Ibach first observed these loss features they interpreted the 1.9-eV peak as being due to the excitation of a transition from an occupied surface state just above the valence band, to an unoccupied state just above the bottom of the conduction band.[13] They recognized the 7-eV loss could be due to excitations from the same occupied state to higher-lying levels, or to the aforementioned unoccupied level from states below the top of the valence band. They later found that the 7-eV loss peak fitted the band model derived from their analysis of the EDC excited by 21-eV photons.[18] The present approach is similar: I will discuss how the 7-eV energy-loss feature is consistent with the band model derived from other experiments.

To summarize the situation to this point: the broad loss feature is indicative of transitions between a narrow and a broad band of states; the shape of the broad feature represents a density-of-surface-states curve; a narrow band of occupied surface states has been observed for this surface in photoemission experiments; a broad band of unoccupied surface states has been observed in EADSEE.

The broad maximum in the loss spectra is ascribed to transitions from the occupied state, observed in photoemission, to unoccupied states

whose existence is observed or implied by EADSEE (Fig. 2). The range of energies predicted for these transitions, from about 2 to 12 eV, is the energy over which the loss function has appreciable intensity (Fig. 1).

The 1.9-eV loss peak exhibits a larger angular dependence than the broad maximum. This peak has been subtracted from the broad maximum on the assumption that the peak is symmetrical, and that the lower energy half of the peak does not contain intensity contributions from the threshold of the broad maximum. When this is done (see Fig. 2) the broad feature has a steplike threshold at 2.3 ± 0.3 eV. This feature is interpreted as the density of unoccupied surface states. The density of states for a two-dimensional nearly-free-electron system is independent of energy.[29] The steplike threshold and subsequent plateau region of the broad feature, shown in Fig. 2, could be indicative of free-electron behavior near the bottom of this surface-state band. In that case the threshold at 2.3 ± 0.3 eV derived from the ILEED data is in agreement with the 2.4 eV predicted for the bottom of the conduction band from the analysis of the EADSEE data.

The weak shoulder in the density-of-states curve, at 4.9 ± 0.3 eV, is due to the slope of the curve decreasing above that energy. At the vacuum level, 5.0 ± 0.1 eV, new channels for surface-state decay come into effect. These extra channels could eliminate some surface states, thus explaining the change of slope of the density-of-states curve at this energy, as well as the eventual disappearance of these surface-state resonances above about 12 eV.

C. Surface exciton

It is assumed that the 1.9-eV loss peak is associated with the broad maximum at higher energies, although its angular dependence, implying $\Delta k_{\parallel} = 0$, distinguishes the associated electronic transition from transitions to ordinary surface conduction-band states. It is noted that the energy of the peak is close to that of the lowest bulk conduction state L $(k_{\parallel} = 0)$.[30]

The peak is interpreted as an exciton peak, this being the only interpretation consistent with all of the observations. Because the bound electron-hole pair of an exciton travel together, $\Delta k_{\parallel} = 0$ for such an excitation. No other single-particle excitation from a flat band can have this Δk dependence. The value of the exciton binding energy deduced from the spectra, 0.4 ± 0.2 eV, does depend on the assumptions made in the peak resolution procedure described above.

In the dielectric theory of inelastic scattering,[5,6] peaks in an energy-loss spectrum need not occur at the same energy as the corresponding optical excitations, although the difference cannot be large for a narrow peak. Using the formula for the binding energy of a three-dimensional exciton,[31] a simple calculation can be used to deduce that the effective relative dielectric constant of the region in which the exciton is formed is between 5 and 8.[32] No theory has been published for the binding energy of a surface exciton. Surface excitons associated with a core hole have been reported for GaAs.[33]

D. Further discussion

That completes our discussion of the present data. It is believed that the band model depicted in Fig. 2 should be appropriate to the interpretation of surface sensitive experiments other than those discussed here. Appearance potential spectra (APS) represent one such experiment, being a surface sensitive probe of unoccupied states.[34] The APS from polycrystalline silicon[35] does not match that calculated from the density of unoccupied bulk states.[36] It is suggested that these measurements be extended to the Si (111) 7×7 surface, and the conduction states depicted in Fig. 2 incorporated into the appropriate model for calculating the spectra.

One unsatisfactory feature in our understanding of the electronic structure of this surface is the lack of band-structure calculations, due to insufficiently precise knowledge of the atomic arrangements.[28] With the additional experimental information reported here, there might be another approach to the problem. As mentioned above, the deduced density-of-states curve is not like that expected for a two-dimensional free-electron system. Two factors effecting surface-state densities can be implied from the EADSEE and ILEED studies: State densities in excess of free-electron values are observed in regions of E-k space near the boundary where matching between surface and bulk states is possible[23]: Decay into the vacuum effectively removes surface states. If models can be found to quantitatively account for these two types of behavior it might be possible to construct the density-of-states curve semiempirically, as the bottom of the free-electron-like band is known, as is the disposition of states in the two bounding media.[30]

III. SUMMARY AND CONCLUSIONS

This paper consists of three main parts: one is the first report of experimental observations of ILEED spectra due to the formation of single-particle excitations; two, the interpretation of this data within the framework of the theory described by Bauer; and three, the fitting of the derived data to a band model constructed from the results of earlier experiments. In the first part, the enhancement of surface losses in ILEED spectra for

conditions of a near grazing-emergence-diffracted beam is in accordance with the theory of Mills. Actually, that theory was for $\Delta k_{\parallel} = 0$ processes involving an electron path symmetric with respect to the surface normal. The extension of the theory to the present situation of a nonsymmetric path is trivial. It increases the variety of predictable experimental conditions for which surface losses can be observed in ILEED experiments.

Two types of ILEED features due to single-particle excitation have been observed: those that are dependent on angle, and those that are virtually independent of angle. This exhausts the possibilities. The apparatus was originally set up with the belief that angular-dependent fine structure in ILEED would provide more detailed information about single-particle excitations. One of the surprising features of the work, then, is the large amount of information derived from those parts of the ILEED spectra which show virtually no angular-dependent fine structure. Within the framework of Bauer's theory the interpretation of this part of the data is unambiguous.

The ILEED data are consistent with the surface electronic structure information derived from the photoemission and EADSEE experiments. It is probable that the density-of-states information found from the ILEED data will be of use in interpreting the results of other experiments, such as APS measurements.

The presence of the exciton in the excitation spectra is indicated primarily by the angular dependence of the associated loss peak, indicating a $\Delta k_{\parallel} = 0$ process. It is noted that observation of the optical absorption spectra over the same energy range as the present ILEED data would not immediately lead to such a clear cut interpretation of the exciton peak. It is the different angular behavior of the 1.9-eV loss peak from that of the rest of the spectra that distinguishes it as an exciton peak. The distinction is valid for single-particle excitation from, or to, a flat band: it does not depend on the details of the model used to interpret the rest of the spectrum. In the course of these ILEED and EADSEE experiments several hundred distinct spectra have been recorded from the one surface. The strength of these methods is due to the detailed data they can obtain, and the fairly well defined theories that exist for their interpretation.

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