PHYSICAL REVIEW B VOLUME 39, NUMBER 12 15 APRIL 1989-II

Silicon (111) 2×1 surface states: *K*-edge transitions and surface-selective $L_{2,3}VV$ Auger line shape

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(Received 6 July 1988; revised manuscript received 26 October 1988)

Transitions to unoccupied Si(111) 2×1 surface states have been observed at the silicon $1s$ absorption edge. The surface features are distinguished from bulk absorption by taking the difference between the absorption measured by monitoring the surface-sensitive *LVV* Auger decay (88 eV kinetic energy) and the bulk-sensitive *KLL* Auger decay (1610 eV kinetic energy). The difference curve reveals a surface peak which is centered 0.3 ± 0.15 eV above the conduction-band minimum and which disappears upon exposure of the clean surface to atomic hydrogen. By tuning the photon energy to the energy of this surface peak and selectively exciting the surface, we have extracted the contribution of the 2×1 surface to the total Si $L_{2,3}VV$ Auger line shape. We find that the surface contribution to the Si $L_{2,3}VV$ Auger line shape lies 0.5 ± 0.1 eV kinetic energy above the total contribution due to the presence of the Si(111) 2×1 occupied dangling-bond surface states, and the intensity of the bulk plasmon loss at 70 eV kinetic energy is suppressed due to the presence of the 2×1 π-bonded surface. Formation of the Si(111)-(1×1)H surface produces changes in the Auger spectra which are consistent with the removal of the occupied dangling-bond surface states from the band gap, the introduction of a Si—H bonding level 6.5 eV below the valence-band maximum, and the enhancement of the bulk-plasmon loss. We also find that the intensity of the high-energy Auger satellite at 103 eV kinetic energy is sensitive to the excitation photon energy within the vicinity of the silicon *K* edge and present a viable mechanism which accounts for this phenomenon.

I. INTRODUCTION

Due to their technological importance, semiconductor surfaces have been studied extensively in recent years using a variety of experimental and theoretical techniques. Among the most extensively studied surfaces are the Si(111) 2×1 structure, which is produced by cleaving Si crystals in vacuum, and the Si(111) 7×7 structure, which is produced by thermal treatment of a Si(111) surface. This paper focuses on the Si(111) 2×1 surface both before and after exposure to atomic hydrogen.

A variety of experimental techniques have already been applied to the study of the Si(111) surfaces, and a variety of structural models currently exist. The reader is referred to a review by Haneman[1] for a more thorough discussion of recent work. The most popular model of the 2×1 surface which is consistent with the available data is the π-bonded chain model originally proposed by Pandey.[2] In this model the silicon surface atoms reconstruct to form π-bonded chains through the mutual interaction of the dangling-bond p_z orbitals which are produced upon cleaving. In this work we report the first Si $1s$ x-ray-absorption spectra close to the Si $1s$ absorption edge for the clean Si(111) 2×1 surface and the hydrogen-terminated Si(111)-(1×1)H surface. The x-ray-absorption spectra are an important new input towards the understanding of these surfaces since the data may be used to distinguish between the existing structural models.

In the dipole approximation,[3] the probability of the absorption of x rays by a *K*-shell initial state is given by

$$W_{i\rightarrow f}(\omega)\sim\omega^{-1}|\langle i|\epsilon\cdot\mathbf{p}|f\rangle|^2\rho(E_f)\ .$$

In this equation ω is the frequency of the incoming x ray, ϵ is the x-ray electric field vector, $\mathbf{p}$ is the momentum operator, $\langle i|$ is the *K*-shell initial state of s symmetry, $|f\rangle$ is the final unoccupied state of p symmetry, and $\rho(E_f)$ is the partial density of states per unit energy of p symmetry at the energy of the final state E_f. Close to the edge, barring excitonic effects, the $1s$ absorption spectra are strictly proportional to $\rho(E_f)$ since the matrix elements are slowly varying and the final state lies in the bottom of the conduction band. The $1s$ absorption spectrum should therefore be directly sensitive to the unoccupied surface dangling-bond states due to the favorable dipole coupling between states of s and p character. By studying the absorption spectra in both bulk- and surface-sensitive modes, we have observed $1s$ absorption into a surface-state band which we determine to lie 0.3 ± 0.15 eV above the bulk conduction-band minimum. This finding is in agreement with calculations performed for the π-bonded chain model by Pandey[4] and by Northrup and Cohen[5] for the position of the unoccupied surface-state band relative to the conduction-band minimum. These calculations are also in agreement with the surface-state dispersion curve as derived from angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) for this surface.[6]

Si(111) 2×1 surface states have been observed previously at the Si $2p$ absorption edge;[7] however, our data afford a simpler interpretation since the $1s$ core level lacks the added complexity of the spin-orbit-split *L*-shell initial state and directly probes the density of p antibonding states at the surface which are produced upon cleaving. Si(111) 2×1 surface states have been observed in the inverse photoemission spectra reported by Straub *et al.*,[8] and our data are in agreement with their findings. It is also important to point out that since the 1s absorption spectra as recorded in both bulk- and surface-sensitive modes agree so closely with the inverse photoemission spectra, excitonic effects are of little importance in the understanding of the gross absorption features. This observation is apparent due to the fact that inverse photoemission adds an electron to the system rather than creating an electron-hole pair. We further note that the absorption data recorded with the radiation's electric polarization vector aligned parallel (normal incidence) to the surface show a reduction in the surface-state absorption intensity when compared with data recorded with the polarization vector aligned normal (glancing incidence) to the surface. Due to the dipole coupling of the absorption process, this result is consistent with the notion that the dangling-bond p_z states reside in the vacuum and not within the plane of the surface. This result further validates our conclusion that we have observed transitions to the unoccupied Si(111) 2×1 dangling-bond surface states rather than surface-enhanced excitonic transitions to the conduction-band minimum.

Due to its dependance on the density of occupied valence-band states, much experimental and theoretical effort has been given to the understanding of the silicon $L_{2,3}VV$ Auger line shape. In the independent-hole one-electron approximation,[9] the probability of a core-valence-valence Auger transition is given by

$$J(E)\sim\sum_{j,L_1,L_1',L_2,L_2'}\int d\omega\,\rho_{L_1L_1'}(E-\omega,Z_j)\times\rho_{L_2L_2'}(E+\omega,Z_j)\times W_{L_1L_1'L_2L_2'}(E,Z_j)\;.$$

In this equation $\rho_{LL'}(E,Z)$ is the one-electron occupied local-density-of-states matrix at an atomic depth Z from the surface; $W_{L_1L_1'L_2L_2'}(E,Z)$ is the matrix element for the Auger process involving two electrons with orbital angular momenta L_1,L_2 and exchange. W contains corrections for the electron-escape depth at layer Z as well. Since the Auger current appears as the weighted convolution of the valence-band density of states, the natural linewidth of a core-valence-valence Auger transition is twice the valence-band width, $2W$. Features of the spectra lying outside this region cannot be accounted for in the independent-hole one-electron picture and are thus assumed to be of many-body origin. The above equation fails to take into account the interaction, U_{eff}, between the two final-state valence holes and other many particle effects. U_{eff} is typically expressed as $U_{\text{eff}}=F-R$,[10] where F is the bare repulsive interaction of the two holes, and R is the attractive interaction of one hole with the polarization cloud of the other. U_{eff} serves to reduce the energy position of an Auger peak since it represents the energy required to remove the ejected Auger electron from the field of the additional valence hole. Values for U_{eff} are typically deduced from comparison of the experimental Auger-peak energy positions with the Auger energies calculated from the experimental valence and core photoelectron binding energies.

By dividing the electronic charge into atomic and overlap components while taking into account matrix-element effects in the above approximation, Jennison[11] was able to successfully calculate the experimental Auger line shape associated with a clean Si(100) 2×1 surface. The agreement between theoretical and experimental work suggested that surface and many-body effects are quite small. The questions one must address, however, are, first, due to the inherent surface sensitivity of the LVV transition, what is the contribution, if any, of the surface to the total line shape? And, second, if many-body effects are indeed present, e.g., hole-hole or electron-electron interactions, how would the presence of the surface affect them?

By selectively tuning the photon energy to the 1s-to-surface-state transition, we have extracted the surface contribution to the Si $L_{2,3}VV$ Auger line shape and show that it differs significantly from the bulk contribution. In fact, due to the presence of the occupied Si(111) 2×1 surface states, the surface contribution to the Si $L_{2,3}VV$ Auger line shape lies 0.5 ± 0.1 eV kinetic energy above the total contribution, and, due to the presence of the 2×1 π-bonded surface, the intensity of the bulk-plasmon loss at 70 eV kinetic energy is reduced. We present a classical picture which is based on the differences between the surface- and bulk-electronic and geometric structures to explain these results. We also note that the effective interaction of the two final-state valence holes is negligible on both the 2×1 and (1×1)H surfaces and in the bulk, and is independent of the exact nature of the interaction. This conclusion is based on the fact that in all cases the Auger-peak energy positions are well accounted for by their valence and core photoionization energies.

In an earlier study of clean and hydrogen-terminated Si(100) 2×1 surfaces, Madden *et al.*[12] concluded that a feature 17 eV below the main Si $L_{2,3}VV$ Auger peak, which was enhanced upon hydrogen adsorption, was due to a two-hole valence state localized in a Si—H surface bond. This assignment was based on the fact that the feature lies outside of the spectral width predicted by the self-convoluted total-density-of-states curve and its agreement with the hydrogen electron-stimulated-desorption (ESD) threshold. We present evidence that this state is actually a bulk-related phenomenon which is not unique to the hydrogen-terminated surface. We suggest that this feature may be more simply explained classically as the bulk-plasmon loss originally reported by Mularie and Rusch[13] for silicon, but enhanced due to the adsorption of hydrogen. Apparently, hydrogen removes the effects of the surface which serve to screen the intensity of this feature.

By studying its electron-stimulated threshold, Rowe and Christman[14] identified a feature in the Si $L_{2,3}VV$ Auger spectrum, which was previously believed to be a plasmon-gain process,[15] as a high-energy Auger satellite due to a doubly ionized L-shell initial state. We go on to demonstrate that the intensity of this feature, which occurs in our Si(111) 2×1 spectrum at 103 eV kinetic energy, is sensitive to the stimulating photon energy within the vicinity of the Si *K* edge and present a viable mechanism which accounts for this phenomenon.

II. EXPERIMENT

The Si(111) 2×1 surface was prepared by cleaving a lightly doped *p*-type silicon single crystal *in situ* in a standard ultrahigh-vacuum chamber ($p < 5\times10^{-11}$ Torr). The chamber was equipped with low-energy electron diffraction (LEED) optics, a double-pass cylindrical mirror analyzer (CMA) with an internal electron gun, and a 90% transmission copper grid combined with a total-yield (TY) detector upstream of the sample. The total current emitted from the grid was used for flux normalization. The Si(111)-(1×1)H surface was prepared by exposing the 2×1 surface to approximately 1×10^{-6} Torr of H_2 gas for 15 min in direct line of sight of a white-hot tungsten filament. The 2×1 surface showed a predominantly single-domain 2×1 LEED pattern with sharp diffraction spots. After hydrogen exposure, LEED showed a sharp 1×1 pattern indicative of the 2×1-to-(1×1)H surface reconstruction. Auger-electron spectroscopy (AES) showed no traces of either carbon or oxygen after all other data had been collected.

All data were taken at the Stanford Synchrotron Radiation Laboratory using the "Jumbo" double-crystal monochromator.[16] The absorption data were taken in constant-final-state (CFS) mode[17] by setting the CMA voltage at either 1610 eV kinetic energy (the *KLL* bulk-sensitive Auger decay) or 88 eV kinetic energy (the *LVV* surface-sensitive Auger decay, which is a direct product of the *KLL* decay since a *KLL* decay leaves two core holes in an *L* shell) and collecting the Auger electrons emitted from the sample's surface as a function of photon energy. The Si *LVV* and *KLL* Auger lines have been used previously in the measurement of the Si absorption cross section.[18] All absorption data were normalized to the incident flux. A pair of InSb crystals were used for monochromatization and gave a resolution of 1 eV full width at half maximum (FWHM) at the silicon *K* edge ($h\nu = 1840$ eV). For the absorption data, the only instrumental broadening is due to the monochromator. The Si $L_{2,3}VV$ Auger line-shape data were taken by scanning the CMA's voltage and measuring the number of electrons emitted from the sample's surface as a function of kinetic energy while keeping the photon energy fixed. For the Auger measurements, the CMA resolutions was 0.5 eV. Other than the spectrum taken at normal incidence, all data were taken with the radiation's electric polarization vector aligned within a few degrees of the sample's normal (i.e., glancing incidence).

III. RESULTS

Figure 1(a) shows the Si(111) 2×1 1*s* absorption edge taken with CFS kinetic energies 88 eV (*LVV*) and 1610 eV (*KLL*). The curves have been scaled to make the absorption at photon energies $h\nu = 1836$ and 1846 eV equal. At these energies the absorption features are qualitatively the same, and conduction-band final-state effects should be negligible. What is clear from the figure is that the general features of both the *LVV* and *KLL* absorption edges are quite similar, except for the extra intensity of the *LVV* edge in the vicinity of its inflection point and the extra intensity of the *KLL* edge at its peak.

Figure 1(b) shows the Si(111) 2×1 scaled *LVV* absorption edges taken with the radiation's electric polarization vector aligned perpendicular to the surface (glancing incidence) and parallel to the surface (normal incidence). Shown also in the figure is the *KLL* absorption edge (dotted line) for reference. The extra intensity of the *LVV* edge in the vicinity of its inflection point is suppressed at normal incidence.

Figure 1(c) shows the scaled *LVV* and *KLL* absorption edges after exposure of the 2×1 surface to atomic hydrogen. For the Si(111)-(1×1)H system the only difference between the *LVV* and *KLL* edges is the extra intensity of the *KLL* edge at its peak. The extra intensity of the *LVV* edge in the vicinity of its inflection point is now gone.

Figure 1(d) shows the difference between the *LVV* and *KLL* absorption edges ($LVV-KLL$) for both surfaces. The zero level is indicated by the dotted line. As can be seen from this figure, the difference between the two absorption edges corresponding to the Si(111) 2×1 surface is a peak centered at $h\nu = 1840.3$ eV, which is 0.3 ± 0.15 eV above the 1*s*-to-conduction-band-minimum threshold. The energy position of the 1*s*-to-conduction-band-minimum threshold was determined by extrapolating the straight portion of the *KLL* absorption edge to zero absorption. This procedure, which is valid under the assumption that excitonic processes may be neglected, a result which we have found to be the case for silicon,[19] gives the energy of the 1*s*-to-conduction-band-minimum threshold as 1840 eV for this particular monochromator setting. Note that the peak at photon energy $h\nu = 1840.3$ eV is not present in the difference curve corresponding to the Si(111)-(1×1)H surface. What is also evident from Fig. 1(d) is that both difference curves exhibit two resolved negative-going features at photon energies $h\nu = 1842$ and 1843 eV which may be accounted for by the extra intensity of the *KLL* absorption edge within this photon-energy region. The intensities of these features are nearly identical both before and after exposure to atomic hydrogen, while the intensity of the peak at photon energy $h\nu = 1840.3$ eV has disappeared. We note that the width (FWHM) of the $h\nu = 1840.3$ eV peak is 1.7 eV.

Figure 2(a) shows the background-corrected Si $L_{2,3}VV$ Auger spectra from the Si(111) 2×1 surface taken with excitation photon energies $h\nu = 1840.3$ and 1845 eV. The first photon energy corresponds to the energy of the surface peak maximum of Fig. 1(d), while the second photon energy is 5 eV above the 1*s* absorption edge. All the spectra shown in Fig. 2 have been background corrected by subtracting a third-degree polynomial which was fitted to the particular raw $N(E)$ spectrum between the kinetic-energy ranges of $30 < E < 50$ and $120 < E < 140$ eV. The spectra have been normalized to the same height and offset in the figure for clarity. The characteristic features of each spectrum were insensitive to which of the different backgrounds were used in the subtraction.

Apparent from Fig. 2(a) is the following: both spectra

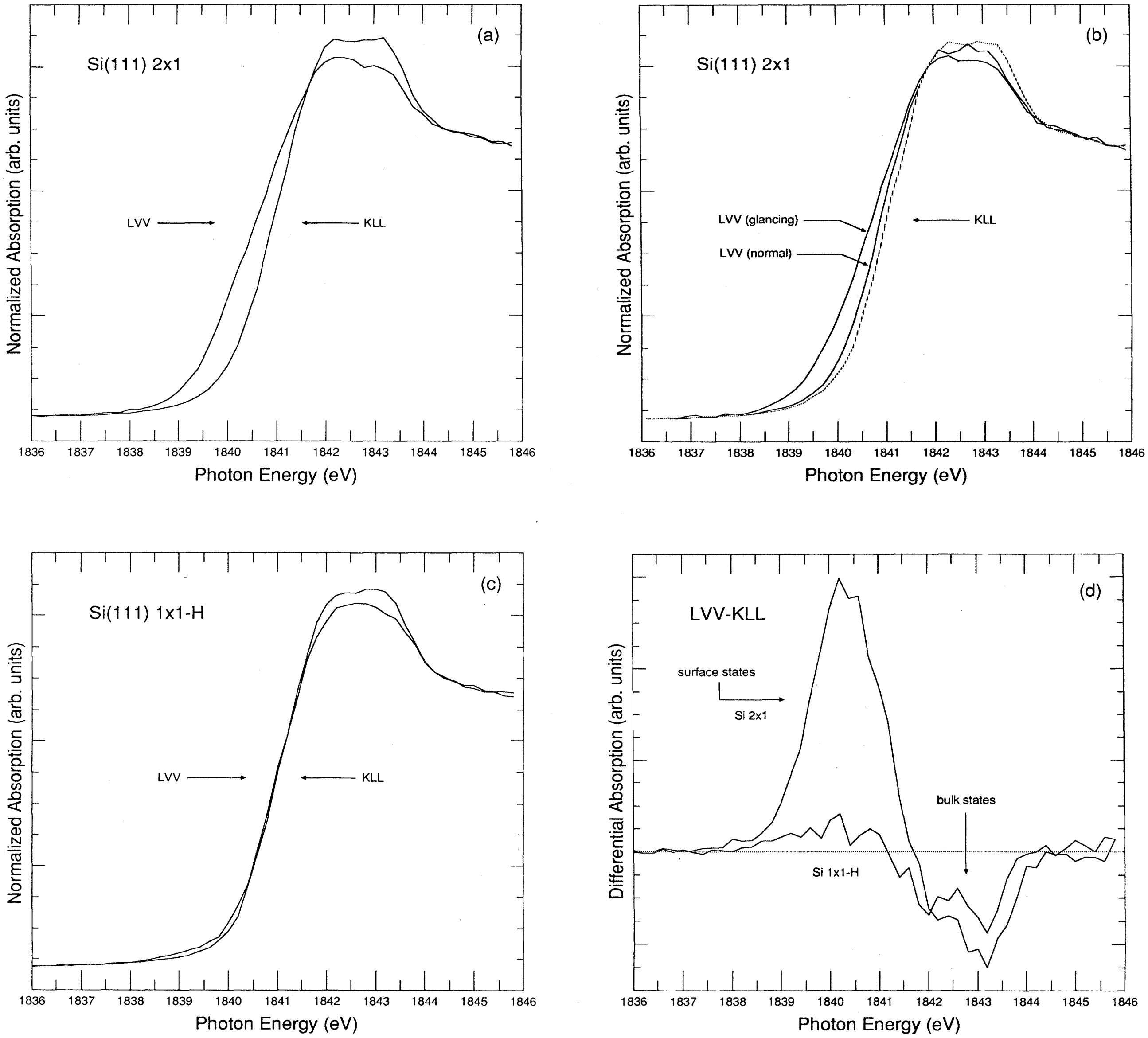

FIG. 1. (a) *LVV* and *KLL* Si 1*s* absorption edges from the Si(111) 2×1 surface. (b) *LVV* Si 1*s* absorption edges from the Si(111) 2×1 surface taken at normal and glancing incidence. Shown also is the *KLL* 1*s* absorption edge (dotted line) for reference. (c) *LVV* and *KLL* Si 1*s* absorption edges from the Si(111)-(1×1)H surface. (d) Difference curves (*LVV*−*KLL*) of the data from (a) and (c). Absorption curves were scaled to make the absorption both above and below the edge equal.

are qualitatively the same, except for the energy position of the main peak at 88 eV kinetic energy and the relative intensity of the shoulder at 70 eV kinetic energy. The negative-going edge of the main peak in the spectrum taken with photon energy $h\nu = 1840.3$ eV is shifted 0.5 ± 0.1 eV towards higher kinetic energy relative to the negative-going edge of the main peak in the spectrum taken with photon energy $h\nu = 1845$ eV. The shoulder at 70 eV kinetic energy in the spectrum taken with photon energy $h\nu = 1845$ eV is notably enhanced. We note that the main peak in the $h\nu = 1840.3$ eV spectrum is narrower than the main peak in the $h\nu = 1845$ eV spectrum. Both spectra also exhibit a second but smaller peak which appears as a shoulder at 81 eV kinetic energy.

Figure 2(b) shows the background-corrected and normalized Si $L_{2,3}VV$ Auger spectra from the Si(111)-(1×1)H surface taken with the same photon energies as for the clean 2×1 surface. Unlike the spectra corresponding to the 2×1 surface, these spectra are insensitive to the stimulating photon energy. The overall line shapes of the data of Fig. 2(b) are similar to the line shapes of the data of Fig. 2(a), except for the position of the main peak, which now occurs at 86 eV kinetic energy, and a significant increase in the intensity of the shoulder at 70

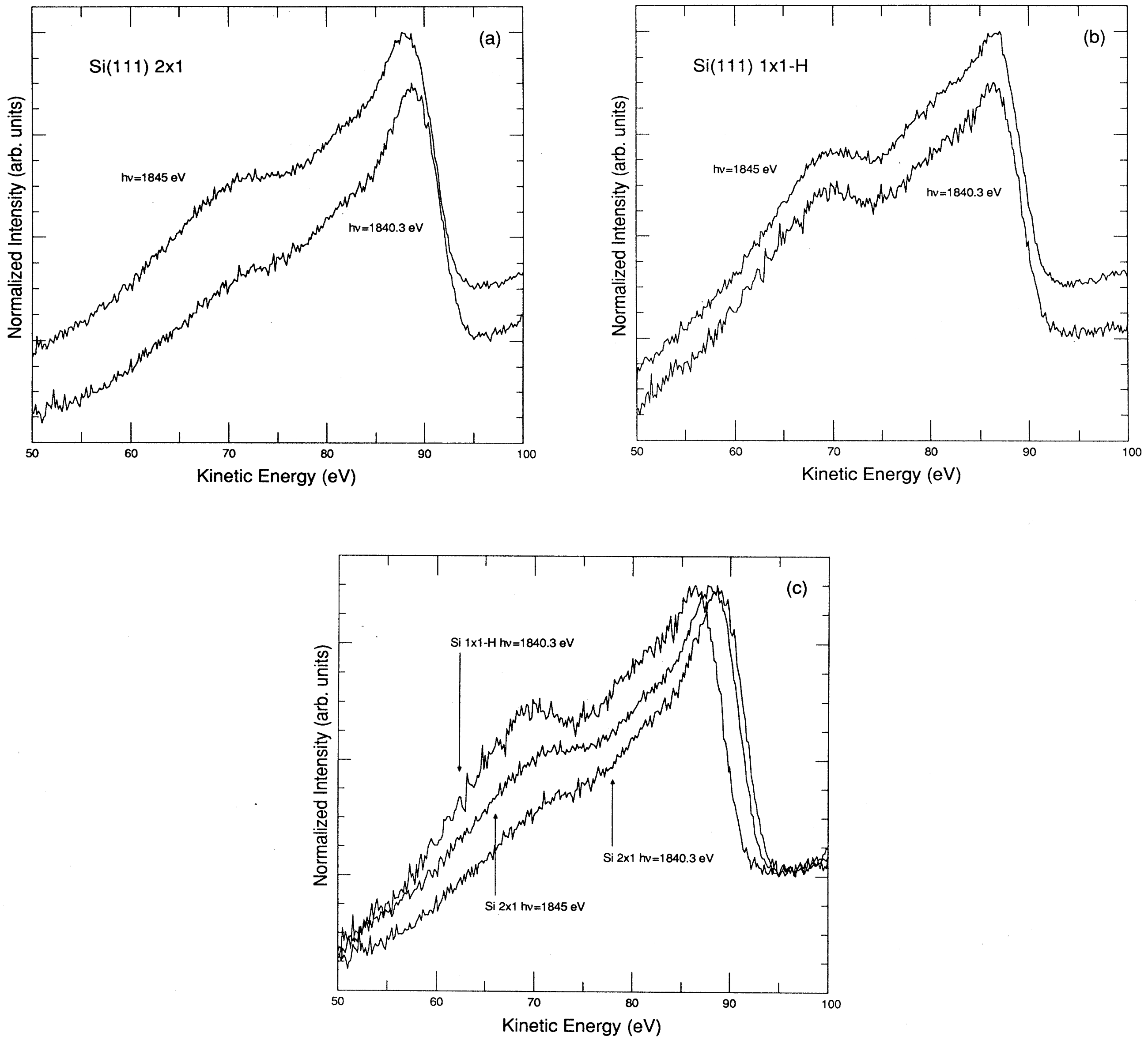

FIG. 2. (a) Si $L_{2,3}VV$ Auger line shape from the Si(111) 2×1 surface taken with photon energies $h\nu=1840.3$ and 1845 eV. (b) Si $L_{2,3}VV$ Auger line shape from the Si(111)-(1×1)H surface taken with photon energies $h\nu=1840.3$ and 1845 eV. (c) Si $L_{2,3}VV$ Auger line shape from the Si(111) 2×1 surface taken with photon energies $h\nu=1840.3$ and 1845 eV and the Si $L_{2,3}VV$ Auger line shape from the Si(111)-(1×1)H surface taken with photon energy $h\nu=1840.3$ eV. The line-shape curves were corrected for background and scaled to make their total heights equal. They have been offset in (a) and (b) for clarity.

eV kinetic energy. The negative-going edge of the main peak of the Si(111)-(1×1)H surface taken with either photon energy is shifted 1.7±0.1 eV towards lower kinetic energy relative to the negative-going edge of the main peak of the Si(111) 2×1 surface taken with photon energy $h\nu=1845$ eV. There also appears to be extra intensity in the kinetic-energy range 75–85 eV which serves to wash out the shoulder previously within this region.

Figure 2(c) shows the Auger spectra from the 2×1 surface taken with photon energy $h\nu=1840.3$ eV, $h\nu=1845$ eV, and the Auger spectrum from the (1×1)H surface taken with photon energy $h\nu=1840.3$ eV. The narrowing and shift of the main feature as a function of photon energy and surface preparation may be more directly observed in this figure. Also apparent is the filling in of the features in the region 75–85 eV kinetic energy and the growth in intensity of the shoulder at 70 eV kinetic energy. The intensity of the shoulder at 70 eV kinetic energy is suppressed at the 2×1 surface for $h\nu=1840.3$ eV, enhanced at the 2×1 surface for $h\nu=1845$ eV, and even larger at the (1×1)H surface for either photon energy. What will be central to our argument is that the 2×1 spectrum taken with photon energy $h\nu=1845$ eV appears as the average of the 2×1 spectrum taken with photon energy $h\nu=1840.3$ eV and either of the (1×1)H spectra. By average we mean that the kinetic-energy position of the main peak and the intensity of the feature at 70 eV kinetic energy lie between those of the other two spectra.

Figure 3(a) shows the Si $L_{2,3}VV$ line shapes from the 2×1 surface taken with photon energy $h\nu=1837$ eV (3 eV below the Si K edge) and photon energy $h\nu=1845$ eV (5 eV above the Si K edge). Figure 3(b) shows the same data from the (1×1)H system. These spectra cover a greater kinetic-energy range and have not been corrected for background, but, rather, they have been scaled to make equal the number of counts above and below the pertinent spectral features. Only the high-energy feature near 103 eV kinetic energy is sensitive to the excitation photon energy. For both surfaces, this feature is notably enhanced at the higher photon energy.

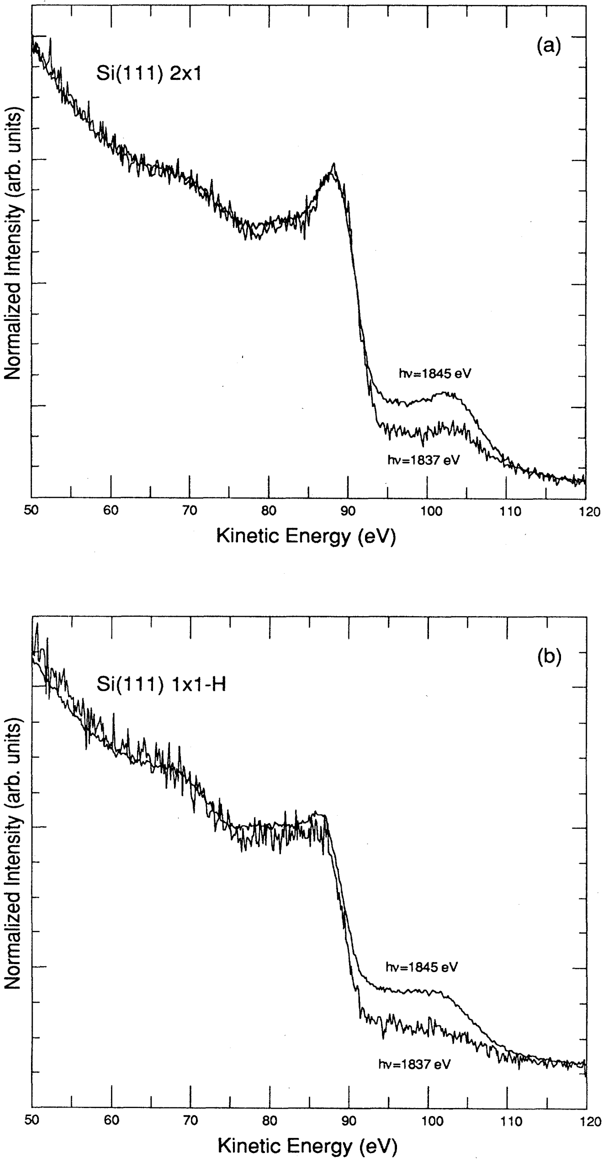

FIG. 3. (a) Si $L_{2,3}VV$ Auger line shape from the Si(111) 2×1 surface taken with photon energies $h\nu=1837$ and 1845 eV. (b) The Si $L_{2,3}VV$ Auger line shape from the Si(111)-(1×1)H surface taken with photon energies $h\nu=1837$ and 1845 eV. These line-shape curves cover a wider kinetic-energy range than those of Fig. 2 and have not been corrected for background, but, rather, they have been scaled to make their intensity above and below the main spectral features equal.

IV. DISCUSSION

A. Silicon 1*s* absorption

1. Si(111) 2×1

Due to the extremely small mean free path of 88-eV electrons (~ 5 Å),[20] the LVV absorption edge is a measure of the absorption within ~ 10 Å of the surface, whereas, due to the increased mean free path of 1610-eV electrons (~ 25 Å),[20] the KLL absorption edge is a measure of the absorption within ~ 50 Å of the surface. By subtracting the KLL from the LVV absorption edge, the surface contribution to the total absorption is obtained. As can be seen from the expanded difference curves of Fig. 1(d), for the clean 2×1 surface, the difference is a peak centered at $h\nu=1840.3$ eV. Taking the position of the conduction-band minimum to be 1840 eV on this curve, we attribute this extra absorption to excitation of the 1*s* electron into the unoccupied Si(111) 2×1 surface-state band which we determine to lie 0.3 ± 0.15 eV above the conduction-band minimum. These results are consistent with the band-structure calculations performed for the π-bonded–chain model by Pandey[4] and by Northrup and Cohen.[5] The calculations reveal an empty surface-state band centered just above the conduction-band minimum with a bandwidth of roughly 1.5 eV. Unlike the work of Morar *et al.*[21] for the diamond (111) 2×1 surface which was performed with the higher resolution available at the lower photon energies, our experiment shows no resolvable structure. Thus we cannot comment on the nature of the surface critical points, although the symmetric nature and width of the surface peak is suggestive of a single band with a bandwidth of 1.3 eV, a result which is also in agreement with the above-mentioned calculations. In determining this value, we have taken the Si 1*s* core-hole lifetime to be 0.4 eV (Ref. 22) and assumed a simple Gaussian broadening.

It is important to mention that other processes, such as surface enhancement of the core excitonic binding energy, which would be due to an increased Coulomb interaction at the surface, could account for these absorption results. Figure 1(b) shows that the LVV absorption edges recorded at glancing and normal incidence have different intensities near threshold. Since the p_z states of the π-bonded chain have their largest component perpendicular to the surface, due to the dipole coupling between states of *s* and *p* character, the surface-sensitive absorption data should exhibit the observed polarization dependence with respect to the incident-photon beam. Since the average acceptance angle of the CMA is the same at these two polarizations, so is the surface sensitivity of the measurement. We can therefore rule out surface enhancement of the core excitonic binding energy as well as bulk processes as being the cause of these absorption results. In a similar measurement performed at the Si $L_{2,3}$ absorption edge, no enhancement of the LVV absorption edge was observed at threshold.[7] Rather, it was argued that the surface-sensitive absorption data showed an additional state of s symmetry 2.3 eV above the conduction-band minimum which was attributed to back antibonding orbitals in the first layer. The empty dangling-bond surface states which are mainly of p symmetry were not seen. If, in fact, our data reflected surface enhancement of the core excitonic binding energy, the $L_{2,3}$ edge should show a larger effect near threshold since the resolution available at the L edges is significantly greater than at the K edge.

2. *Si(111)-(1×1)H*

Clearly, after hydrogen adsorption, the peak at $h\nu = 1840.3$ eV disappears, a result which further validates its assignment as a surface feature. This result is consistent with the picture that hydrogen saturates the surface dangling bonds and allows the surface atoms to return to their "bulk" positions. The surface energy levels split away from the Fermi level and lie deep in the bulk valence and conduction bands.[23] Such a conclusion is consistent with our LEED observation, which indicates that the surface transforms from a 2×1 to a 1×1 unit cell. It is important to point out that while the surface-state transitions are reduced by an order of magnitude upon hydrogen adsorption, the two negative-going features at $h\nu = 1842$ and 1843 eV remain virtually unaffected. We attribute these features to the two bulk-density-of-states maxima present above the conduction-band minimum.[24] Since these features appear negative in the difference curve ($LVV - KLL$), they do not exist on the surface. We have previously demonstrated that features in the Si 1s absorption spectra result from transitions to these states.[19] The negative nature of these features reflects the redistribution of conduction-band state density from the bulk to the surface levels and is a result of the difference in the surface- and bulk-electronic structures. Our absorption measurements indicate no other hydrogen-induced changes in the conduction-band density of states other than a decrease in the conduction-band density of states at the bottom of the conduction band. In other words, only the surface-state peak is removed. This finding is in agreement with the $L_{2,3}$ core-level characteristic loss spectra (CLS) reported in Ref. 25 for the conduction band, but is in contrast to the photoemission spectra reported in Ref. 26 for the valence band. Along with the decrease in the density of states at the top of the valence band due to the removal of the surface states from the band gap, a peak 6.5 eV below the valence-band maximum in the valence-band spectrum was observed upon hydrogen adsorption and is attributed to charge density in Si—H surface bonds. Our absorption results are of particular interest since, based on the results of Ref. 26, one would expect to observe transitions to the corresponding unoccupied Si—H antibonding levels which do not appear in the Si 1s absorption spectra. This anomaly may reflect the differences between the surface s and p density of states.

B. Si $L_{2,3}VV$ Auger line shape

1. *Si(111) 2×1*

The absorption edges of Fig. 1(a) show that for the photon energy corresponding to the surface-peak maximum ($h\nu = 1840.3$ eV), the ratio of the surface (LVV) to bulk (KLL) absorption is enhanced by nearly a factor of 2. Since the density of states at the conduction-band minimum is zero, the photon energy $h\nu = 1840.3$ eV is great enough to excite 1s electrons into the unoccupied surface-state band, while not being great enough to excite an appreciable number of 1s electrons into the bulk conduction band. Thus, at this photon energy, excitations will be concentrated at the surface. Because the Auger process probes the local density of states at the atom on which the original core hole was created,[27] by preferentially exciting surface core holes, the Si $L_{2,3}VV$ Auger line shape taken with photon energy $h\nu = 1840.3$ eV should be more surface sensitive than the measurement made with photon energy $h\nu = 1845$ eV. Since the photon energy $h\nu = 1845$ ev is great enough to excite all 1s electrons deep into the bulk conduction band, the Auger line shape obtained at this photon energy should correspond to more common measurements which include both bulk and surface contributions. This last observation is apparent since the LVV and KLL absorption edges of Fig. 1(a) are qualitatively identical at this photon energy.

Before we discuss the surface and many-body contributions to the Auger line shape, it is important to elucidate the independent-particle contributions. The calculated silicon valence-band density of states shows three dominant structures,[24] which in our discussion we shall call V_1, V_2, and V_3. These states occur 2.9, 7.0, and 9.6 eV below the valence-band maximum. The energy positions of these structures agree well with the experimental data; however, the experimental data show less detail, as one would expect due to experimental broadening. Using the approximation that the energy of an Auger electron due to a core-valence-valence decay may be described by the simple formula $E_{ij} = E_c - V_i - V_j$ gives, for the transitions $L_{2,3}V_1V_1$, $L_{2,3}V_2V_2$, and $L_{2,3}V_3V_3$, 88, 80, and 75 eV, respectively. Here, i and j denote the two valence levels involved in the transition, and E_c is the $L_{2,3}$ core-level binding energy. All energies have been referenced to the vacuum level, and we have used the average core-level binding energy for the L_2 and L_3 subshells. Since the Auger spectra show no structure narrower than 10 eV, and since the L-shell spin-orbit splitting is only 0.6 eV, this additional approximation is valid. We therefore attribute the main peak in the experimental Auger spectrum at 88 eV to $L_{2,3}V_1V_1$ transitions and the shoulder at 81 eV to $L_{2,3}V_2V_2$ transitions. $L_{2,3}V_3V_3$ transitions would lie in the region of 75 eV and are not observed in the data. Transitions involving V_i and V_j for $i \neq j$ would lie intermediate in energy to transitions for $i=j$ and naturally add to the Auger current.

The above-calculated values are based entirely on a singly ionized L-shell initial state and a doubly ionized final state which consists of two valence holes and in no way account for the hole-hole interaction, U_{eff}, which tends to lower the observed Auger energies. This term arises from the fact that the ejected Auger electron must leave the atom in the presence of the attractive field due to the additional core hole in the valence band. The presence of one core hole is accounted for by the fact that we have used the single-particle valence and core-level binding energies in the calculation. Due to silicon's effective screening ($\epsilon \sim 12$), U_{eff} should tend to zero.[28] This result has also been demonstrated by Jennison.[29] The relative intensities of the transitions may be accounted for in the above approximation by noting that the density of states which contributes to the atomic charge at the top of the valence band is predominantly of p character, while at the bottom of the valence band it is predominantly of s character; thus, due to the angular momentum and parity selection rules,[9] combined with Jennison's arguments,[11] the contributions from V_3 would be suppressed compared to the contributions from V_1. The width of the main feature, 10 eV, is also in accord with the simple theory since it corresponds to twice the width of the valence feature V_1.

The fact that the main Auger peak in Fig. 2(a) is narrower and shifted towards higher kinetic energy for photon energy $h\nu = 1840.3$ eV may be attributed to transitions involving the occupied dangling-bond states associated with the clean 2×1 surface again in the independent-hole one-electron picture. Since the surface states lie above the valence-band maximum as determined by ultraviolet photoelectron spectroscopy (UPS),[30] the electron emitted during a core-valence-valence Auger transition would naturally lie at higher kinetic energy, an effect indeed observed in the more surface-sensitive spectrum ($h\nu = 1840.3$ eV). The less surface-sensitive spectrum ($h\nu = 1845$ eV) lies at lower kinetic energy and is broadened due to the contribution of the lower-kinetic-energy bulk LVV electrons. The shift of the more surface-sensitive Auger spectrum towards higher kinetic energy should correspond to twice the surface valence-band shift minus the surface core-level shift. The valence-band spectrum corresponding to the clean Si(111) 2×1 surface[26] shows that the difference between the energy position of the surface-state maximum and the first bulk valence-band maximum (V_1 in the above discussion) is 2.1 eV. The $2p$ surface core-level shifts have been decomposed into a center-of-gravity shift of 0.15 eV towards lower binding energy due to the relaxation of the surface layer relative to the bulk.[31] The surface contribution to the main Auger peak should thus lie 4.1 eV above the bulk contribution. The discrepancy between the calculated (4 eV) and the experimental (0.5 eV) differences may be resolved by noting that, due to the inherent surface sensitivity of the LVV transition, the spectrum taken at photon energy $h\nu = 1845$ eV contains equal contributions from the surface and from the bulk,[32] while, due to lifetime broadening and finite monochromator bandpass, the surface-selective spectrum taken at $h\nu = 1840.3$ eV still contains contributions from the bulk. The observed peak positions in both spectra therefore appear as the weighted averages between the surface and bulk contributions. We will return to this dilemma in the discussion concerning the Si(111)-(1×1)H surface.

It is once again important to mention that other processes, such as resonant shakeup, could account for the change in the LVV line shape near threshold. Such an effect has been observed at the Si KLL Auger line in SiO_2;[33] however, the same work found the effect to be an order of magnitude smaller in Si due to the lack of localization of the core exciton in the narrow-band-gap material. We would therefore not expect to see resonant-photoemission effects at the Si LVV Auger line. Our Auger measurements indicate that for the Si(111)-(1×1)H surface there are no changes between the LVV line shapes recorded at the same photon energies as for the clean Si(111) 2×1 surface. The apparent suppression of these Auger effects in the presence of hydrogen favors the role of surface states in the deexcitation process.

In order to determine the effect of the 2×1 surface on the many-body contributions to the Auger line shape, we turn our focus towards the feature which lies outside the kinetic-energy region of twice the valence-band width. As it is suppressed in the more surface-sensitive spectrum, the shoulder at 70 eV kinetic energy must be a bulk-related phenomenon which cannot be associated with the clean 2×1 surface. This feature was first identified as a bulk-plasmon loss in the Auger spectrum by Mularie and Rusch.[13] It was later observed in the electron-energy-loss spectra (EELS) by Ibach and Rowe.[26] In the free-electron model the energy of the plasma oscillations of the valence electrons is given by $\omega_p = (4\pi n e^2/m)^{1/2}$.[34] Here n, e, and m are the electron density, charge, and mass, respectively. Assuming four valence electrons per atom, the value $\omega_p = 16.6$ eV is obtained for silicon. Since this feature occurs 17 eV kinetic energy below the main Auger peak, we find the observed silicon plasmon frequency to be in excellent agreement with the calculated value. Following the arguments of Ritchie,[35] the surface plasmon should exist at a frequency $\omega_s = \omega_p/\sqrt{2} = 11.7$ eV. This result is due to the boundary condition imposed on the solutions of Maxwell's equations that the normal component of the electric displacement vector be continuous across the surface. Since the surface plasmon lies so close in energy to the bulk plasmon, and since it lies within the valence-band contribution to the Auger line shape, it is not resolved in our data; however, it occurs in EELS spectra at 12 eV.[26] This value is again in excellent agreement with theory. Since the surface possesses its own distinct plasmon frequency, the bulk plasmon should not exist on the surface; hence, as one would expect, the shoulder at 70 eV kinetic energy is suppressed in the more surface-sensitive spectrum ($h\nu = 1840.3$ eV). Since the LVV spectrum contains roughly equal surface and bulk components, clearly the intensity of the shoulder at 70 eV kinetic energy would be greater in a pure "bulk" spectrum (surface not included) than in our $h\nu = 1845$ eV spectrum. In other words, our findings indicate that the presence of the 2×1 π-bonded surface reduces the intensity of the bulk-plasmon loss by a factor of 2 in the Si $L_{2,3}VV$ Auger line shape.

2. *Si(111)-(1×1)H*

As has already been mentioned, there are no significant differences between the two Auger line shapes of Fig. 2(b) from the Si(111)-(1×1)H surface. These spectra are insensitive to the exciting photon energy. As can be seen from the absorption edges of Fig. 1(c), after hydrogen exposure the bulk and surface absorption are qualitatively identical, except for the peak of the "white line." Thus, there is no preferential excitation of the surface atoms between these two photon energies, and, hence, the Auger line shapes taken at these two photon energies appear the same. Apparently, hydrogen adsorption removes the observed surface effects and our ability to preferentially excite the surface.

The shift of the main peak towards lower kinetic energy upon hydrogen adsorption has previously been explained by the narrowing of the density of states at the top of the valence band due to the saturation of the occupied surface dangling bonds,[25] a result in agreement with UPS spectra[26] and with the line shapes calculated from the theoretical density-of-states curves for Si(100) surfaces.[25] In his work on the Si(100) 2×1 surface, Madden[25] reported a shift of the main Auger peak 1.5 eV towards lower kinetic energy upon hydrogenation. This shift is to be compared with our value of 1.7 eV for the Si(111) 2×1 surface. This shift is analogous to the 0.5-eV shift observed for the clean 2×1 surface as we varied the contributions of the surface and the bulk by changing the photon energy, and is too large to be attributed to band bending. Upon hydrogen adsorption, the Auger line shape apparently becomes more "bulk-like," and the removal of the occupied surface states from the band gap accounts for the shift of the main Auger peak towards lower kinetic energy. Chemical shifts of the 2*p* core level also cannot account for the magnitude of the observed effect since they average to 0.15 eV (Ref. 31) and are modified upon hydrogen adsorption.[7]

Intuitively, it is clear that the highest-energy features in the Auger spectra originate from the highest-energy features in the valence band. For the clean 2×1 surface the highest valence-band features are the occupied surface states. On the other hand, since hydrogen adsorption removes the occupied surface states from the top of the valence band and places them 6.5 eV below the valence-band maximum,[26] for the hydrogen-terminated surface, the highest-energy Auger features originate from the bulk. Since we have demonstrated that the Auger spectrum from the 2×1 surface taken with photon energy $h\nu=1845$ eV appears as the average of the Auger spectrum from the 2×1 surface taken with photon energy $h\nu=1840.3$ eV and the Auger spectrum from the (1×1)H surface taken with either photon energy, we conclude that the actual peak position of the main feature would be closer to 86 eV kinetic energy in a pure "bulk" Auger spectrum (i.e., surface not included). Such a conclusion accounts for the dilemma discussed in the preceding section.

As already mentioned, the calculated difference between the 2×1 surface and bulk contributions to the main Auger peak is 4.1 eV. This estimate is close to the observed 2.2-eV difference between the main Auger peak from the 2×1 surface taken with photon energy $h\nu=1840.3$ eV and either of the spectra from the hydrogen-terminated surface. Such an error is well within the scope of our analysis. One must realize, however, that the highly surface-sensitive Auger spectrum ($h\nu=1840.3$ eV) still contains contributions from the underlying bulk since the ratio of the LVV to KLL absorption is enhanced by only a factor of 2 at this photon energy; thus, it is tempting to speculate that the main peak of the more surface-sensitive Auger spectrum would lie closer to 90 eV if it were to contain no bulk component. Our estimate would then be in perfect agreement with the experimental value. We have also noted that there is a filling in of the feature in the kinetic-energy region of 75–85 eV. Since hydrogen introduces bonding states 6.5 eV below the valence-band maximum[26] (3.6 eV below the state which we have called V_1), the extra intensity observed in this region upon going from the clean 2×1 surface to the hydrogen-terminated (1×1)H surface may be attributed to Auger transitions involving Si-H valence charge. Again from the simple formula, Auger transitions from these states would lie in this kinetic-energy range.

The above discussion indicates that the independent-hole one-electron picture adequately accounts for the experimental line shape for both the 2×1 and (1×1)H surfaces and for the bulk within the energy region of twice the valence-band width once the contributions from the appropriate occupied surface states have been accounted for. In order to determine the effect of the (1×1)H surface on the many-body contributions, we once again turn our focus to the feature which lies outside of the region of twice the valence-band width. What is clear from Fig. 2(b) is that the intensity of the feature at 70 eV kinetic energy is greatly enhanced upon hydrogen adsorption. Assuming that this feature is the bulk-plasmon loss, this result is as expected since the adsorption of hydrogen removes the effects of the surface which serve to screen its intensity.

Figure 2(c) shows the key differences between the Auger spectra more clearly. What is essential to observe is that the line shape from the 2×1 surface taken with photon energy $h\nu=1845$ eV actually appears as the average of the line shape from the 2×1 surface taken with photon energy $h\nu=1840.3$ eV and either of the line shapes from the (1×1)H surface. We have argued that the spectrum from the 2×1 surface taken with photon energy $h\nu=1845$ eV is the average of the surface and bulk line shapes and that the intensity of the shoulder at 70 eV kinetic energy is reduced in the 2×1 spectra due to the presence of the 2×1 π-bonded surface. Clearly, then, the intensity of the bulk-plasmon loss in a pure "bulk" silicon spectrum would more closely resemble the intensity of the bulk-plasmon loss observed in the spectra from the (1×1)H surface. These results suggest that the shoulder at 70 eV kinetic energy in the (1×1)H spectra is not a two-hole localized valence state as proposed by Madden *et al.*,[12] but rather is the same bulk-plasmon loss observed for the clean 2×1 surface intensified due to the adsorption of hydrogen. Theoretical calculations give evidence that the adsorption of hydrogen removes the Si(111) surface dipole moment.[36] Under such conditions, the macroscopic electric field outside of the crystal would vanish and Maxwell's equations would allow surface-plasmon oscillations at the bulk-plasmon frequency.[37] This phenomenological description implies that, when terminated with hydrogen, the surface no longer screens the bulk-plasmon loss and the intensity of the feature at 70 eV kinetic energy is representative of the plasmon intensity in the underlying bulk.

Two additional forms of evidence exist which support the above conclusion. First, we note that, upon hydrogen adsorption, the intensity of the surface plasmon in the EELS spectrum of the Si(111) 2×1 surface disappears, while the intensity of the bulk plasmon increases.[26] One would expect to observe a corresponding effect in the Auger spectrum as well. Second, we note that, upon hydrogen adsorption of the Si(111) 7×7 surface, an increase in the intensity of the second-order plasmon loss at $2\omega_p$ accompanies the increase in the intensity of the first-order plasmon loss at ω_p.[38] Thus, the peak at 70 eV kinetic energy may not be attributed to a different process coincident in energy since the intensities in the first- and second-order plasmon losses must be correlated. That is, the intensity of the first-order plasmon loss cannot increase without the accompanying increase in the intensity of the second-order plasmon loss and vice versa.

3. *Two-hole core localization*

We now turn our focus to the effect of two-hole core localization on the Si $L_{2,3}VV$ Auger line shape. The data of Fig. 3(a) for the 2×1 surface show that only the feature at 103 eV kinetic energy, which is outside of the region of twice the valence-band width, is sensitive to the excitation photon energy above and below the Si *K* edge. As previously mentioned, the *LVV* decay is a direct consequence of a *KLL* decay since a *KLL* decay leaves two core holes in a 2*p* shell. For photon energies above the Si *K* edge, the 2*p* photoionization cross section is smaller than the 1*s* photoionization cross section; thus, a majority of *L*-shell core holes will be created as a consequence of a *KLL* decay. For photon energies below the Si *K* edge, there should be no *KLL* decays and all *LVV* electrons will be emitted as a consequence of direct 2*p* photoionization. The difference in the two processes, photoionization of a 2*p* electron resulting in a *LVV* decay, versus photoionization of a 1*s* electron resulting in a *KLL* decay which then results in a *LVV* decay, is the presence of an additional 2*p* core hole during the *LVV* decay in the latter case. The final state described in the former case consists of two valence core holes and a *LVV* electron, while in the latter case it consists of a 2*p* core hole, two valence core holes, and a *LVV* electron. These two processes are illustrated in Fig. 4. The doubly ionized *L* shell and the corresponding electron which contributes to the satellite Auger peak are denoted by an asterisk. Auger satellites are due to Auger transitions involving doubly or triply ionized inner shells.[39] In our case the doubly ionized inner shell is the 2*p* core level. The latter process is consistent with the satellite observed in the Auger spectrum of silicon by Rowe and Christman.[14] It was found that the satellite in their spectrum was due to a doubly ionized *L*-shell initial state which was ionized by the incident-electron beam. The enhancement of the satellite peak evident in our data is due to prior *KLL* decays for photon energies above the Si *K* edge.

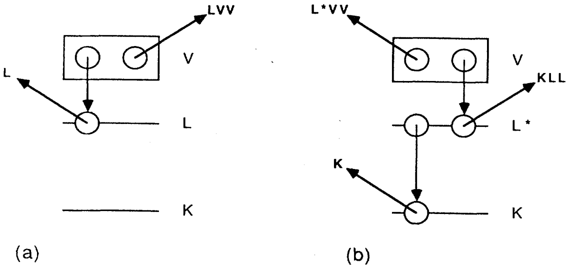

FIG. 4. Diagrams for the Si $L_{2,3}VV$ Auger decay. (a) Standard *LVV* decay which follows a 2*p* photoionization. (b) Satellite *LVV* decay which follows a *KLL* decay. The doubly ionized *L* shell and corresponding satellite *LVV* electron are denoted with an asterisk.

In Fig. 3(a) the peak at 103 eV kinetic energy shows an enhancement when excited by photons with energy $h\nu=1845$ eV, which is 5 eV above the Si *K* edge, than when excited by photons with energy $h\nu=1837$ eV, which is 3 eV below the Si *K* edge. For the 2×1 system the energy difference between the main peak, 88 eV kinetic energy, and the satellite peak, 103 eV kinetic energy, is 15 eV. The (1×1)H system [Fig. 3(b)] shows the same energy difference between the two peaks, although each is shifted 2 eV towards lower kinetic energy for reasons already discussed. Thus, 15 eV is roughly the energy difference between a singly and doubly ionized Si 2*p* core level. This energy difference is due to the presence of the extra "spectator" core hole in the Si 2*p* core level during the *LVV* decay. The presence of this "spectator" core hole causes modifications in the electron wave functions and an effective increase in the 2*p* core-level binding energy. We note that, in contrast to the plasmon loss at 70 eV kinetic energy, the effect of surface structure on the intensity of the two-hole core localization is negligible. This result is as expected since the enhancement is due to the prior *KLL* decay for photon energy above the Si *K* edge, which is an atomic rather than a geometric effect. In contrast, the collective electron interactions associated with a plasmon loss are sensitive to surface geometry, since both the plasmon energy and the plasmon intensity are directly correlated with the valence electronic structure.

V. CONCLUSION

Electronic transitions from the Si 1*s* core level to the unoccupied 2×1 surface states have been observed at the Si *K* edge. Their sensitivity to electron-escape depth and hydrogen adsorption have been demonstrated. The observed surface differential absorption peak lies 0.3±0.15 eV above the conduction-band minimum, a result which agrees with calculations performed for the π-bonded–chain model for this surface.[4,5] The effects of the 2×1 and (1×1)H surfaces on the Si $L_{2,3}VV$ Auger line shape have been addressed. By preferentially exciting the 2×1 surface, we find that the surface contribution to the Si $L_{2,3}VV$ Auger peak lies 0.5±0.1 eV kinetic energy above the total contribution, and the presence of the 2×1 π-bonded surface reduces the intensity of the bulk-plasmon loss. The former result has been explained in terms of an independent-hole one-electron model, while the latter result has been explained in terms of the collective interactions of the valence-electron gas. Hydrogen-induced changes in the Auger spectrum are consistent with the removal of the surface states from the band gap, the introduction of a Si—H bonding state 6.5 eV below the valence-band maximum, and the enhancement of the bulk-plasmon loss. These changes have been explained in terms of the above pictures as well. The sensitivity to photon energy of the peak at the high-energy side of the main $L_{2,3}VV$ Auger transition has been explained by the localization of two 2*p* core holes following a *KLL* decay. Unlike the plasmon loss, the intensity of this feature is not sensitive to the surface geometry since it is an atomic rather than a geometric effect. The features in the Si(111) 2×1 and (1×1)H $L_{2,3}VV$ Auger spectra within the kinetic energy range 75–95 eV have thus been accounted for by an independent-hole one-electron model, while the features outside this region have been accounted for by many-body phenomenon. More specifically, the shoulder at 70 eV kinetic energy is due to the collective interactions of the electron gas, while the peak at 103 eV kinetic energy is due to the localization of two 2*p* core holes.

ACKNOWLEDGMENTS

This work was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the U.S. Department of Energy under Contract No. DE-AC03-82ER13000 (Division of Chemical Sciences and Division of Materials Science of the Office of Basic Energy Sciences).

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