

Tunneling spectroscopy of the Si(111)2×1 surface

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Abstract

Scanning tunneling spectroscopy has been used to observe electronic band features of the Si(111)2×1 surface, focusing on the size of the surface-state band gap. It is shown that peak positions in the normalized conductance, $(dI/dV)/(I/V)$, which are used to characterize the tunneling spectrum, are shifted slightly towards zero volts compared to the corresponding band structure features. A corrected band gap of 0.59 ± 0.04 eV is obtained for this surface.

The 2×1 reconstruction of the Si(111) surface, formed by cleaving in ultra-high-vacuum conditions, has been a prototypical system in both experimental and theoretical studies for many years. It is now well accepted that the π -bonded chain model correctly describes the atomic arrangement of the surface,[1] although a full understanding of the electronic structure, including excitonic effects, is still evolving.[2,3] This surface has provided an important test case for many-body computations of the surface-state band gap.[3] Experimentally, the surface-state gap of Si(111)2×1 was observed in early work using optical absorption spectroscopy,[4] and was found to be about 0.45 eV wide. Scanning tunneling spectroscopy (STS) measurements yielded a value for the surface gap of 0.50 ± 0.05 eV.[5-8] A combination of photoemission and inverse photoemission spectroscopy (PES/IPES) produced a value of 0.75 for this gap,[9,10] which was later refined to about 0.60 eV based on computations involving the finite resolution of the IPES spectrometer.[11] Because of the above mentioned importance of this surface in providing a test case for theoretical work, it is important to obtain an accurate as possible value for the surface band gap from the various experiments. For this reason, we consider in this work a particular correction to the tunneling spectroscopy result, which produces an increase by nearly 0.1 eV of the value directly observed in the experiments.

In STS studies, one measures the tunnel current I and differential conductance dI/dV as a function of the sample-tip voltage V . It is then conventional to compute a *normalized conductance*, $(dI/dV)/(I/V)$, and to compare this quantity to an expected surface density of states (DOS).[6,7] This normalized conductance provides a convenient means of characterizing the observed spectrum, yielding *e.g.* sharp, peaked features near the onsets of surface bands which provide a more well-defined indicator of the onset position than the relatively gradual turn-on of the current or differential conductance. Nevertheless, some deviations between the normalized conductance and the surface DOS can occur. Such deviations are apparent in the early computations of Lang *et al.* [*e.g.* compare the position of the DOS peak for Ca in Fig. 3 of Ref. 12 with the peak position in $(dI/dV)/(I/V)$], although at that time attention was not focused on these small shifts. Similarly, the previous results for the Si(111)2×1 surface-state band gap[5-8] have not considered possible deviations between the actual surface-state features and peaks in $(dI/dV)/(I/V)$. In this work we explicitly consider such shifts. We find that the peaks in $(dI/dV)/(I/V)$ tend to be shifted towards zero volts, by

an amount which depends on the peak position itself as well as the precise form of the falloff in current as one moves into the band gap.

To compute the correction to the observed peak values in $(dI/dV)/(I/V)$ for the Si(111)2×1 surface, we assume an explicit form for the surface DOS (as discussed below, the resulting correction values are relatively independent of the details of this assumed DOS). From dispersion curves for π -bonded chains given by the one-dimensional model of Ref. 2, the surface DOS, $\rho(E)$, is obtained in a straightforward way. We assume a constant DOS for the probe tip, and the tunnel current is then evaluated from

$$I \propto \int_{-\infty}^{\infty} dE [f(E-eV) - f(E)] D(E, k_{\parallel}) \rho(E) \quad (1)$$

where $f(E-eV)$ and $f(E)$ are Fermi-Dirac occupation factors in tip and sample respectively. For the transmission coefficient we use the result for a simple trapezoidal barrier,

$$D(E, k_{\parallel}) = \exp \left\{ -2s \left[\frac{2m}{\hbar^2} \left(\bar{\phi} - E + \frac{eV}{2} \right) + k_{\parallel}^2 \right]^{1/2} \right\} \quad (2)$$

where $\bar{\phi}$ is the average work-function between tip and sample, s is the tip-sample separation, and V is the bias voltage applied to the sample relative to the tip. The dependence of the component of the wavevector parallel to the surface, k_{\parallel} , on energy is evaluated through the assumed dispersion relationship.[2] From the tunnel current obtained by Eq. (1), we numerically compute the differential conductance dI/dV , and the normalized conductance $(dI/dV)/(I/V)$.

Results of our computations are shown in Figs. 1 and 2. Figure 1 shows the tunnel current and normalized conductance resulting from the assumed surface DOS. The onset of the surface band is taken to be at 0.3 eV. We use a tip-sample separation of 6 Å, and average work-function of 4 eV. By examination of the computed curve for $(dI/dV)/(I/V)$ it is clear that the maximum in this quantity occurs at a voltage significantly less than 0.3 V; the peak position is shifted by -0.047 V below the band edge. This value is not strongly dependent on the parameters used in the computations: varying the tip-sample separation or the work-function by 30% produces a change in the shift of less than 0.001 V, and similarly choosing a different model for the barrier (*i.e.* including the image potential) produces very little effect. If we choose a different form for the surface DOS, *e.g.* a step function with no dependence on k_{\parallel} , the shifts are nearly the same of for the π -bonded chain DOS. Results for these two models are shown by the solid and dotted lines, respectively, in Fig. 2. For band edges not too close to 0 V, the magnitude of the shift amounts to typically 10–20% of the band edge locations. Results for negative bias voltages (energies) are very similar to those shown in Fig. 2.

Despite the relative insensitivity of the above results on the parameters of the computation, we do find that the computed results are sensitive to one aspect of the assumed model, namely, the manner in which the tunnel current decays into the surface-state band gap. For the model of Eq. (1), the variation in the current is governed by the occupation factors for the electrons, leading to an inverse slope for $\ln(I)$ vs. V of magnitude $kT=0.025$ eV in the band gap region. Reducing the temperature leads to a reduction of the shift between the band onset at the peak in $(dI/dV)/(I/V)$: at 77

K the shift becomes -0.033 V. More importantly, we find from a close examination of the experimental data that the decay of the tunnel current into the gap is substantially slower than that expected from Eq. (1). For example, for the relatively high quality data of Ref. 6, we find an inverse slope of $\ln(I)$ vs. V of about 0.040 eV. The slope of these band tails vary at different points on the sample surface, and we tentatively associate them with disorder induced states existing on the surface, likely associated with buckling of the π -bonded chains. Indeed, the images of Fig. 4 in Ref. 5 illustrate such states quite directly. We note that one factor which we do *not* consider to be relevant in this apparent smearing of the band edges is tip-induced metallicity of the surface states. For tip-sample separations significantly *less* than those used in the data acquisition in Refs. 6–8 we do indeed observe the formation of a metallic conduction (linear behavior in I vs. V) within the surface gap, but for the data shown in Refs. 6–8, and with which the surface gap is determined, this metallic conduction does not play a role. We have also considering the possibility of phonon-assisted tunneling transitions, and their effect on the form of the band onset; we find that such processes will shift the $I(V)$ characteristic near the onset, but do not produce a significant change in the inverse slope in the gap region.

In an effort to estimate the effect of this apparent band edge smearing on our estimate of the shift between $(dI/dV)/(I/V)$ and the band edge position, we have included some broadening in our assumed surface DOS. To match the experimental results we use exponential broadening [of the form $\exp(|E|/\Delta E)$], and show results in Fig. 2 for broadening amounts of $\Delta E=0.020$ and 0.040 eV. The broadening produces a small change in the computed shifts. For larger amounts of broadening we find the shifts to be rather sensitive to the precise form and amount used for the broadening. In that case, a more complete understanding of the physical origins and appropriate functional form of the broadening would be required.

Summarizing our computational results, we find that the location of peaks in the normalized conductance are shifted, generally towards zero volts, relative to the location of the edge of a surface band. For the case of the Si(111)2 \times 1, with band onsets at -0.3 and $+0.2$ V, we find a total correction to the band gap value of about 0.080 ± 0.02 eV, where the uncertainty is estimated by considering the various curves in Fig. 2. Combining this result with our best value of the band gap from peaks $(dI/dV)/(I/V)$ based on a reanalysis of the data of Ref. 6, 0.51 ± 0.03 eV, yields a corrected gap value of 0.59 ± 0.04 eV (combining the errors in quadrature[6]). As previously discussed, this value should be compared with the *minimum* band gap on the surface, which appears to be *indirect* for the case of Si(111)2 \times 1.[3,8] Our result is in good agreement with the theoretical indirect gap of 0.58 eV,[3] and also compares favorably with the PES/IPES results of 0.60 eV for the direct gap[9-11] (about 0.04 eV high then the indirect gap according to theory[3]). Our results thus support the current view of excitonic effects accounting for the ≈ 0.15 eV difference between these energies and the optical absorption onset of 0.45 eV.[3,4]

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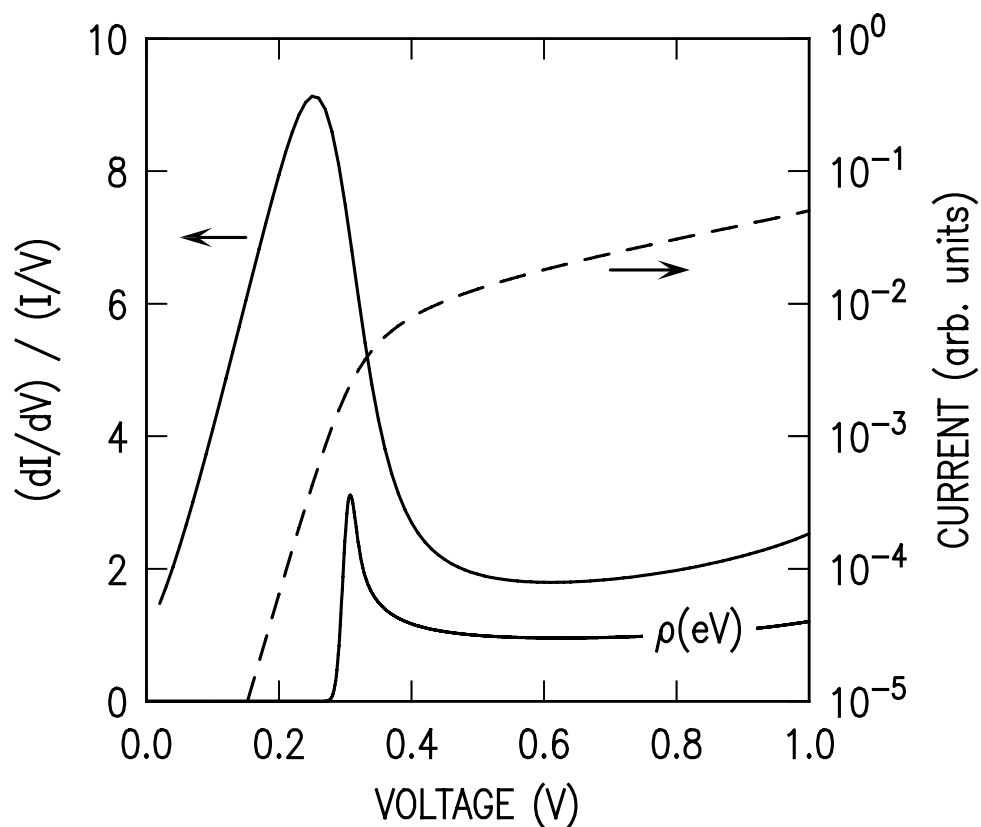


Figure 1 Computed tunnel current (dashed line) and normalized conductance $(dI/dV)/(I/V)$ (solid line), for the assumed surface DOS, $\rho(eV)$, for π -bonded chains as shown in the lower part of the figure. For plotting purposes, the surface DOS has been broadened using a Gaussian with FWHM of 0.02 eV.

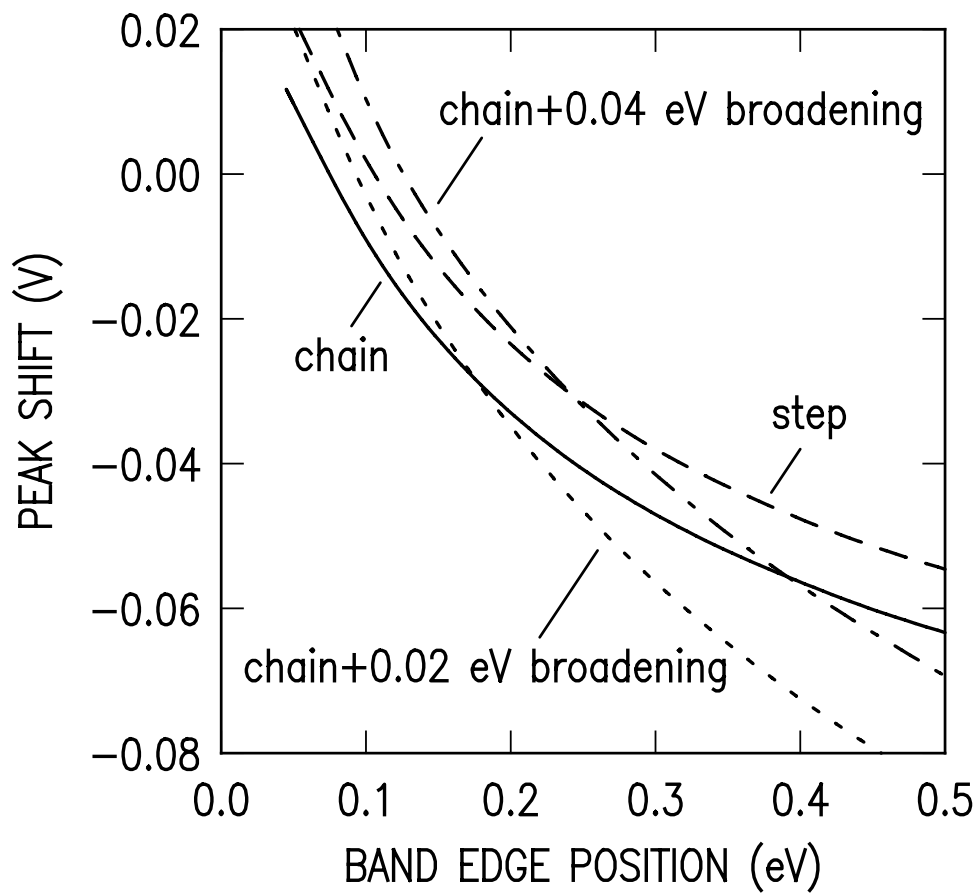


Figure 2 Results for peak shift in $(dI/dV)/(I/V)$ relative on the position of the edge of a surface band. Several cases are considered: π -bonded chain DOS, step-function DOS, and π -bonded chain DOS with various amounts of exponential broadening.