Quasiparticle Interpretation of Photoemission Spectra and Optical Properties of GaAs(110)

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We investigate the quasiparticle band structure and optical properties of a relaxed GaAs(110) surface using a first-principles Green's-function approach. The local fields and the dynamical correlation are fully incorporated in the evaluation of the electron self-energy operator. The results provide a quantitative interpretation of the photoemission, inverse photoemission, and reflectivity spectra observed for this surface. Implications of our theoretical surface band structure for the current controversy between various experimental results for the position of the empty surface band are discussed.

After two decades of extensive experimental and theoretical study, the atomic structure of the relaxed GaAs(110)-(1×1) surface[1-6] is now believed to be well understood. The surface relaxation is characterized by the rotation of the surface-layer As—Ga bond with As moving away from the surface. The most detailed description of the surface geometry is given by using low-energy electron diffraction (LEED) analysis.[1,2] Subsequent experiments[3] and theoretical studies[4,5] provide further evidence supporting this nonreconstructive, nearly bond-length–conserving relaxation model. It is generally agreed that the angle of rotation is 28° ± 2°.[1,3,5,6]

Despite the successful determination of the atomic geometry, the electronic properties and surface-state energies of this surface are not well understood. Semi-empirical tight-binding total-energy calculations which are successful in explaining the atomic displacement[2,6] fail to give a reliable description of the empty surface band.[7] Existing *ab initio* calculations[5,8] for this surface are based on the density-functional theory within the local-density approximation (LDA),[9] which suffers from the well-known "band-gap problem."[10,11] On the experimental side, the position of the empty surface states is currently under debate.[12-14]

In this Letter, we report the first thorough theoretical investigation for the electronic excited-state properties of this technologically important and theoretically prototypical surface, focusing on the surface quasiparticle band structure and the resulting photoemission and optical properties. Based on our calculation, we provide a consistent and quantitative interpretation of the surface-related excitation spectra as measured in photoemission[15] (PE), inverse photoemission[12-14] (IPE), electron energy loss[16] (ELS), and optical reflectivity[17-19] spectroscopies. It is shown that the many-body corrections to the LDA band energies for the surface states are substantial and similar to those found in bulk GaAs.

Generally, spectroscopic measurements of solids may be interpreted in terms of energy differences between quasiparticle states in a many-body system. In the

present work we use the Hybertsen-Louie scheme[10,20,21] which employs the *GW* approximation[22] for the electron self-energy to calculate the quasiparticle energies for the surface states. Both local field screening and dynamical correlation, which have been shown to be crucial for quasiparticle energies in semiconductors,[10,20,21] are taken into account in the present calculation. We have used a slab supercell geometry to simulate the surface with five layers of atoms and two layers of vacuum in the supercell. The topmost layer of atoms on both faces of the slab are relaxed according to the geometry given by a total-energy tight-binding calculation,[6] which agrees very well with *ab initio* total-energy calculations[5] and LEED data.[1,2] The uncertainty in the band energies associated with the structural model is estimated from the tight-binding calculation[4] to be ±0.1 eV. The wave
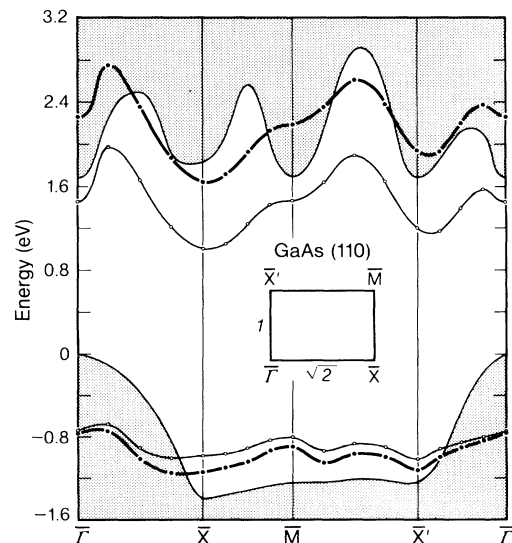

FIG. 1. The calculated surface band structure of relaxed GaAs(110): light line plus open circles, LDA; heavy line plus filled circles, quasiparticle theory. The shaded regions are projected bulk bands.

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functions are expanded up to $E_{cut} = 11.3$ Ry on the plane-wave basis, which ensures that the surface bands are well converged to 0.05 eV with the exception of $\bar{\Gamma}_c$ where the convergence is about 0.15 eV. The overall uncertainty for the quasiparticle energies in our calculation is about 0.10–0.20 eV. More details will be given in a future publication.[23]

The LDA and quasiparticle surface band structures of GaAs(110) along high-symmetry lines of the surface Brillouin zone (SBZ) are shown in Fig. 1. The quasiparticle band structure shows a substantial opening in the surface-state band gap and some other lesser modifications to the band dispersions compared to the LDA results. Table I summarizes the excellent agreement on the general descriptions of the surface-state energies between our quasiparticle theory and the experimental values deduced from PE data[15] and ELS.[16] We will discuss the comparison with the IPE data later.

Despite the relaxation of the surface, the overall many-body corrections for the surface states are not very different from those found in the bulk GaAs[21] or from those of the bulklike states in the slab.[23] This is not general result. In a previous calculation for the Ge(111):As surface[20] some surface states which have a mixed character of both conduction and valence bands are found to have distinctly different behavior from that of the bulk states. In the present case, the occupied and the unoccupied surface states are well localized on the top-layer As and Ga atoms, respectively, having the same character as the bulk states. This illustrates the importance of the wave-function sensitivity of the electron self-energy operator.

The placement of the empty surface-state band is currently a controversial topic.[12-14] It is important for understanding the clean surface, and its position may be relevant to Fermi-level pinning of metal-covered GaAs(110) surfaces which is currently of great interest. To our knowledge, there have been three experiments that directly measured the empty surface-state energies: IPE by Straub, Skibowski, and Himpsel[12] (hereafter re-

ferred to as IPE-1); IPE by Reihl et al.[13] (IPE-2); and an excite and probe PE measurement by Haight and Silberman[14] (two-step PE). Figure 2 shows the comparison of our quasiparticle surface band structure with the surface-state energies obtained from these three experiments. As can be seen from Fig. 2, our first-principles theoretical predictions agree to within 0.15 eV with the results from IPE-1. However, there are significant discrepancies between the results of IPE-1 and IPE-2.

In the two-step PE, an intense 1.78-eV source is first used to excite valence electrons to accessible conduction bands and then weak radiation of energy 10.72 eV is used to probe the valence and transiently photoexcited electrons.[14] At normal emission ($\bar{\Gamma}$), the first peak in the PE spectrum above the gap is at 1.4 eV while the theoretical energy for the surface state at $\bar{\Gamma}_c$ is 2.26 eV relative to the valence-band maximum. Since there is no direct evidence in the two-step-PE experiment that the observed feature is surface-state related, and theoretically we find that there is a strong resonance of a surface state with the bulk states at $\bar{\Gamma}$, we attribute this observed feature to the bulk conduction-band minimum at Γ which has enhanced surface sensitivity due to the resonance, instead of the surface-state assignment made in Ref. 14. This value of 1.4 eV agrees with the measured 1.43-eV minimum gap at Γ for bulk GaAs at room temperature. It may also be concluded that the surface-state energy at $\bar{\Gamma}_c$ is higher than the excitation energy 1.78 eV since there is no second peak found for the conduction band in the two-step-PE spectrum. This agrees qualitatively with our theory. At $\bar{X}_c$, the experimentally determined surface-state energy $E_s(\bar{X}_c)$ is 1.4 eV; our theoretical result is 1.64 eV. The difference is well

TABLE I. General features of the surface-state band structure of GaAs(110). E_{ss} is the average gap between surface states. E_{sb} is the average energy difference between the occupied surface states and the valence-band maximum. E_{bs} is the average gap between the valence-band maximum and the unoccupied surface states. W_s^c is the surface conduction-band width. (An 0.11-eV spin-orbit correction is included.) The units are in eV.

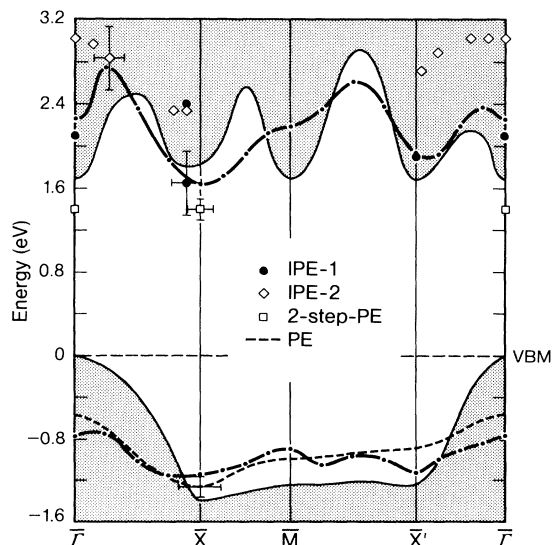|	E_{ss}	E_{sb}	E_{bs}	W_s^c
LDA	2.2	−0.89	1.3	0.85
Present Work	3.1	−0.99	2.0	0.85
Expt.	3.1 [a]	−0.93 [b]	1.9 [a]	1.0 [a]

[a]Reference 16.
[b]Reference 15.

FIG. 2. Comparison of quasiparticle surface band structure with various experimental data: PE (Ref. 15), IPE-1 (Ref. 12), IPE-2 (Ref. 13), and two-step PE (Ref. 14).

within the combined experimental and theoretical error bars. Both values are in good agreement with 1.65 eV from IPE-1.

In the projected bulk band, $\bar{X}_c$ is derived from the bulk X_c. Our bulk calculation gives a band-edge energy $E_b(X_c) = 1.83$ eV; the experimental value is 2.01 eV. Together with the above experimental results for the surface-state energy $E_s(\bar{X}_c)$ and our theoretical $E_s(\bar{X}_c)$, we conclude that $E_s(\bar{X}_c)$ lies below $E_b(X_c)$. This has been clearly verified in the process of performing IPE-1, but is in direct conflict with the results of IPE-2 which give $E_s(\bar{X}_c) = 2.34$ eV, significantly higher than $E_b(X_c)$. There is in fact an overall trend that IPE-2 overestimates the surface optical band gaps, as pointed out by the authors themselves. We suspect this may be due to an experimental uncertainty in positioning the valence-band maximum in IPE-2. The overall surface-state dispersions from $\bar{\Gamma}_c \rightarrow \bar{X}_c$ and $\bar{\Gamma}_c \rightarrow \bar{X}_c'$ from this experiment are, however, in fairly good agreement with our theory: $E_s(\bar{\Gamma}_c) - E_s(\bar{X}_c) = 0.64$ eV and $E_s(\bar{\Gamma}_c) - E_s(\bar{X}_c') = 0.28$ eV, compared with the calculated values of 0.62 and 0.32 eV. We also note that the IPE-2 data do not show a band valley at $\bar{\Gamma}_c$. This is rather difficult to reconcile with the projected bulk band.

The reflectivity of this surface shows strong polarization dependence which is believed to be associated with the anisotropy of the atomic structure. The differential polarized reflectance (PR) has been measured by several groups[17-19] using different methods. It is defined as

$$(\Delta R/R)_{\text{pol}} = (R_\parallel - R_\perp)/R_\parallel , \qquad (1)$$

where $R_\parallel$ is the reflectance for light polarized along $[\bar{1}10]$, the direction of the zigzag chain of the surface, and $R_\perp$ is for [001]. We evaluate this quantity using the three-layer model[24] for the transitions between surface states only. By considering the surface to be a separate phase from the bulk substrate as a starting point of this model, the bulk-surface (from bulk state to surface state) transitions are neglected. In cases such as Si(111)-(2×1), because surface states lie within the projected bulk band gap, there are no complications resulting from the bulk states[18] in this small energy range. In the present case, however, our calculation indicates that there is a strong interference between the features from both bulk-bulk and surface-surface transitions in the PR spectrum.[23]

In the calculation of $(\Delta R/R)_{\text{pol}}$, the quasiparticle band structure in the full SBZ is obtained by a tetrahedral-like linear interpolation after $E_{\text{qp}}(\mathbf{k})$'s are calculated at sixteen $\mathbf{k}$ points in the irreducible part of the SBZ. The same procedure is followed to obtain an expression for the optical matrix elements in the full SBZ. The calculation of the imaginary part of the surface dielectric function, $\text{Im}\epsilon(\omega)$, is then straightforward. The real part of ϵ is calculated from the Kramers-Kronig relations.[25] The bulk ϵ is taken from experiment.[26] Our results, to-

gether with the experimental data, are given in Fig. 3. Two observations about this spectrum are as follows: First, the theoretical $(\Delta R/R)_{\text{plot}}$ spectrum generally has contributions from both bulk-bulk and surface-surface transitions with comparable intensities[23] even after we ignore the surface-bulk transitions. Second, in the present special case of GaAs(110), we find that the peak at 2.8 eV in the theoretical PR spectrum is purely surface-surface related, and moreover, has a definitive polarization, $R_\perp = 0$.

At this time, there is no quantitative accord between theory and experiment or between results from the two available experiments for $\Delta R/R_{\text{pol}}$. But there appears to be some general qualitative resemblance between the theoretical and the two experimental curves. The features above 3 eV are found to have contributions from both bulk-bulk and surface-surface transitions with polarization preference. We find, however, that the common peak of the three curves (although it is rather broad in the results of Ref. 17) at ∼2.8 eV only involves surface-surface transitions and has an absolute transition selection rule, i.e., $R_\perp = 0$ at this energy, as stated above. This peak arises from transitions at the $\bar{X}$ point and in its vicinity in the SBZ, and the corresponding dipole matrix elements are subject to a strong symmetry requirement. This fact has been observed in the work by Berkovits et al.,[19] and is well reproduced here. Smaller but similar disagreement in the intensities of the peaks in the reflectance spectra between theory and experiment is also found in bulk calculations.[27] These are attributed in part to neglecting the excitonic effects and local fields in the screening in the calculation of the optical response function.

To summarize, we have applied a first-principles Green's-function theory to determine the quasiparticle excitation energies at the relaxed GaAs(110)-(1×1) sur-
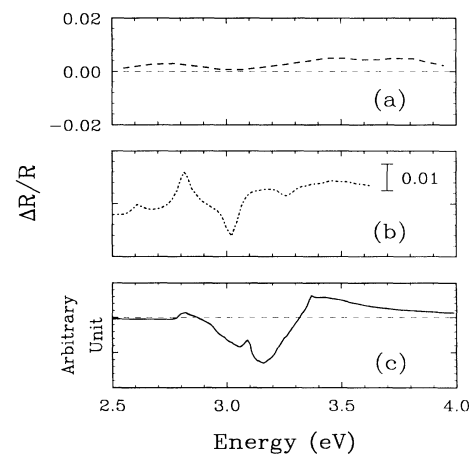

FIG. 3. The differential polarized reflectance as defined in the text. (a) Experimental data from Ref. 17; (b) experimental data from Ref. 19; (c) present calculation.

face. We obtained a quantitative agreement with a spectrum of experimental data. Meanwhile the theory casts some doubts on results from several recent experiments. We conclude that our quasiparticle results give an accurate description to the spectroscopic properties of this surface.

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