First-Principles Calculations of Many-Body Band-Gap Narrowing at an Al/GaAs(110) Interface

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We calculate the quasiparticle electronic structure of a Al/GaAs(110) Schottky barrier as a function of distance from the interface, using the *GW* self-energy operator. The GaAs band gap is significantly narrowed near the metal, although the classical picture of image-potential narrowing is subject to large quantum corrections. The nature of these corrections is explored further using model calculations.

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The modification of the electronic structure of a semiconductor by the presence of a nearby interface with a metal provides an intriguing example of the different viewpoints taken by classical and quantum physics. Classically, the effect is straightforward: An electron is subject to an additional electrostatic potential describable by the interaction with an image charge in the metal, which lowers the electron's energy. In the language of energy bands, the conduction band is bent downwards near the metal. The potential energy of a hole is similarly lowered, so that the valence band is bent upwards. The magnitude of the bending in each case is $1/(4\varepsilon z)$, where ε is the static dielectric constant of the semiconductor and z the distance to the interface, so that the band gap narrows, changing by [1]

$$\Delta E_g^{\text{classical}} = -1/(2\varepsilon z)\,. \tag{1}$$

In the quantum theory of solids, however, an elementary description of a system is normally obtained using a single-particle or mean-field picture, which excludes the image-potential band-gap narrowing entirely. For example, in Hartree theory the electron is assumed to move in the electrostatic potential due to the static electron density together with that due to the nuclei. Since the image potential is essentially dynamical in origin and represents the instantaneous response of the surface to the presence of an extra electron, it is not part of the Hartree potential. Modern electronic structure calculations are normally performed within the framework of density-functional theory (DFT), in which all effects beyond Hartree theory are taken into account (in principle rigorously so far as the ground-state electron density is concerned) by a further potential known as the exchange-correlation potential. This potential will therefore contain a contribution from image effects, but is the same for occupied and unoccupied states and so does not describe band-gap narrowing. Moreover, practical calculations normally use the local-density approximation (LDA) for exchange and correlation, in which the exchange-correlation potential is assumed to depend only on the *local* electron density. In a Schottky barrier, the electron density near the interface will, except in the first atomic layer, differ very little from that of the bulk semiconductor, so that the image potential (and other such many-body effects due to the presence of the interface) is completely absent from LDA calculations.

Although the quantum-mechanical band bending must reduce to the classical image-potential form at large distances from the interface, there will be large quantum corrections (which, as explained above, are entirely of a many-body origin) near the interface. This was first investigated in model calculations by Inkson [2]. Our aim in this work is to investigate the image-potential band bending, and the quantum corrections to it, by studying the effect of an Al/GaAs(110) interface on the local electronic structure in the GaAs. Using a first-principles many-body technique allows us to calculate the behavior close to the interface. In addition, we do not have to assume a position for the image plane (the effective origin of the image potential), which is not known *a priori* for metal-semiconductor interfaces. We have also analyzed the properties of a simple model system to illuminate the physics underlying our results.

Our main calculations use the *GW* approximation for the self-energy operator [3]. This is the leading term in an iterative expansion of the self-energy operator in powers of the dynamically screened electron-electron interaction W, and has been shown to yield an excellent description of quasiparticle energies in semiconductors and simple metals [4,5]. Normally, the self-energy operator would be used to calculate the quasiparticle energies E_i of the whole system, using the quasiparticle equation

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) - E_i]\psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}')d\mathbf{r}' = 0\,. \tag{2}$$

(Since the quasiparticle wave functions ψ_i are similar to those calculated using the LDA, this is usually done using perturbation theory in $\Sigma - V_{\text{xc}}^{\text{LDA}}$ [4,5].) However, in this work we are interested in the *local* electronic structure of different parts of the system. Therefore we define the *local* correction to the LDA band edge in the neighborhood of a point by first constructing from the LDA eigenfunctions of a wave packet which is maximally localized while retaining the character of the band of which it is a part [6]. The wave packet, rather than the LDA eigenfunction, is then regarded as the unperturbed wave function in

the application of perturbation theory. Our definition of the bandlike wave packet centered on the desired position z is

$$\phi_z(\mathbf{r}') = \mathsf{P} T_z(z')\psi(\mathbf{r}') , \tag{3}$$

where $\psi(\mathbf{r}')$ is the LDA eigenfunction, $T_z(z')$ is the "top-hat" envelope function

$$T_z(z') = \begin{cases} 1, & |z'-z| < a/2 , \\ 0, & \text{otherwise} , \end{cases} \tag{4}$$

repeated in each supercell (where a is the interlayer spacing: 2.0 Å in the GaAs and 1.4 Å in the Al), and P is a projection operator which projects (at the supercell $\mathbf{k}$ point in question) onto the set of 21 supercell bands centered on the original state ψ (a total energy range of about 2 eV), followed by normalization of ϕ_z. (A full discussion will be given in Ref. [7].) Using a narrow energy range of about 2 eV allows us to form wave packets which have either valence- or conduction-band character. When discussing the local electronic structure it is necessary to define such a "local band energy," a quantity that is not uniquely defined quantum mechanically. However, all sensible definitions (including ours) reduce to the correct bulk limit as the wave packets become delocalized, and we have also checked that our definition is meaningful over the length scale of 2 Å to which it is applied, by confirming that the results are insensitive to the details of the envelope function or projection operator used. Furthermore, our wave packet formulation has a clear relationship to local experimental spectroscopic techniques, in which a localized wave packet with either conduction- or valence-band character is involved in the spectroscopic process.

The calculation proceeds as follows. First, a LDA supercell calculation is performed, using norm-conserving pseudopotentials and a basis set of plane waves [8]. The structure used here is the "As short bond" structure, which has been used in earlier LDA calculations [9,10]. This consists of perfect bulk structures for both materials (except for a uniform 1.3% compression of the Al to accommodate the slight lattice mismatch), with the two materials aligned so that the As atom is bonded to the Al atom. The supercell is identical to that used in Ref. [9] and contains seven Ga, seven As, and ten Al atoms.

Second, the screened Coulomb interaction W is determined. The nonlocal, dynamic independent-electron polarizability $\chi_0(\mathbf{r},\mathbf{r}',\omega)$ is calculated, and W is obtained using the random phase approximation together with exchange and correlation included using the LDA [11]. The frequency dependence of each element of W in reciprocal space is fitted to a plasmon-pole form along the imaginary frequency axis [12], which we have checked is an excellent approximation even in this highly inhomogeneous system. Local field effects, which are of course crucial in describing the additional screening of the electron-electron interaction due to the presence of the interface, are included in full.

Third, the local band edge is calculated, as explained above, using

$$E_v(z) = E_v^{\mathrm{LDA}}(z) + \langle \phi_{vz} | \Sigma - V_{\mathrm{xc}}^{\mathrm{LDA}} | \phi_{vz} \rangle \tag{5}$$

(where v denotes the valence band edge; a similar expression holds for the conduction band edge), where ϕ_{vz} is the valence-band-like wave packet defined above, and $E_v^{\mathrm{LDA}}(z)$ is the local LDA band edge, which in turn is calculated from a bulk LDA calculation and the LDA effective potential V_{eff}:

$$E_v^{\mathrm{LDA}}(z) = E_v^{\mathrm{LDA}}(\mathrm{bulk}) + [\bar{V}_{\mathrm{eff}}(z) - \bar{V}_{\mathrm{eff}}(\mathrm{bulk})] , \tag{6}$$

where the overbar denotes a rolling average over one GaAs interlayer spacing as in Ref. [13]. $E_v^{\mathrm{LDA}}(z)$ is almost flat in the GaAs, varying by no more than ± 0.04 eV except within 1 Å of the interface. Therefore we have ignored the z dependence of $E_v^{\mathrm{LDA}}(z)$ in plotting the quasiparticle band edges, which also allows us to display clearly the transition of the local quasiparticle correction to its bulk Al value. Σ is the GW self-energy operator [3],

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{4\pi} \int_{-\infty}^{\infty} e^{i\omega\delta} W(\mathbf{r},\mathbf{r}',\omega') G(\mathbf{r},\mathbf{r}',\omega+\omega') d\omega' , \tag{7}$$

in which the one-particle Green's function G is approximated by the LDA Green's function [5]. Σ is evaluated at the corresponding bulk quasiparticle energy [14].

The calculated quasiparticle band edges are shown in Fig. 1. Wave packets are created for the valence and conduction bands and combined with the local LDA band

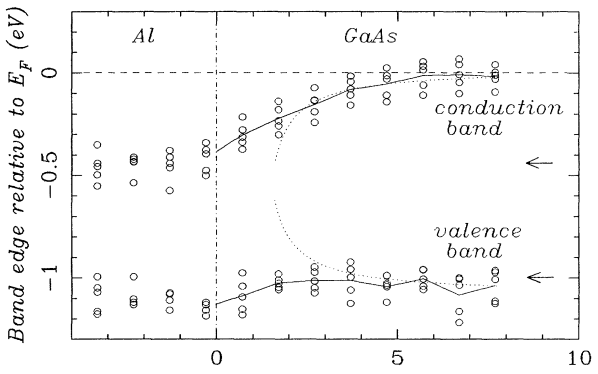

FIG. 1. The calculated local quasiparticle band edges near the Al/GaAs(110) interface. The families of circles correspond to different wave packets (see text) and the solid curve gives their average value. For comparison, the dotted line gives the classical band bending, $1/[4\varepsilon(z-z_p)]$, where the image-plane position z_p has been taken as 1 Å (see text). The GaAs interlayer spacing is 2.0 Å. The LDA band edges (see text) are denoted by the two arrows. The meaning of the "band edges" in the Al is explained in the text.

edge as in Eq. (5). The central state [$\psi(\mathbf{r}')$ in Eq. (3)] in the wave packet is varied over several different states within a few eV of each band edge, giving the families of points shown. The fact that each family of points lies close to a single curve demonstrates that the quasiparticle corrections, though very different for valence and conduction bands, are similar for different states in the same band. It is evident that there is significant band-gap narrowing close to the interface: The gap is reduced by about 0.4 eV from its bulk value. However, there are large corrections to the classical image-potential band-gap narrowing. [For illustration, the latter is shown as dotted lines with an image plane at 1 Å from the interface plane (the plane midway between the last plane of Al nuclei and the first plane of Ga and As nuclei). The value of 1 Å was chosen to be slightly greater than the corresponding distance from a jellium surface [15], because of the effective metallicity of the first layer of GaAs.] The band gap in the center of the GaAs is within 0.1 eV of its asymptotic value of 1.1 eV obtained in a comparable bulk GW calculation, which is as expected since the classical image-potential narrowing at that distance is only 0.1 eV, even after taking interfaces on each side into account. [The stated bulk value of the band gap differs from the low-temperature experimental value (1.5 eV) primarily because of the neglect of core exchange effects, which are not important for the band-gap narrowing studied here.]

As explained above, the local quasiparticle corrections to the LDA electronic structure are the differences between the plotted quantities and the LDA band edges denoted by the arrows. Figure 1 shows that in the Al these corrections rapidly (owing to the strong metallic screening) attain their bulk values, which, as expected for a simple metal, are small and similar for states both above and below E_F.

For an interface between a doped semiconductor and a metal, the usual electrostatic band bending occurs on a length scale of 100–1000 Å (depending on doping density) so as to align the Fermi levels on either side of the interface. Correspondingly, the majority carriers experience an energy barrier in traveling into the metal. The quantum corrections to the image potential have a negligible direct effect on the barrier height measured in conventional Schottky barrier experiments, since the top of the barrier occurs far from the interface [16] where the asymptotic image-potential narrowing is valid. The effects calculated here will be most readily observable in experiments that probe the excitation properties of the first few atomic layers of the semiconductor. [The band-gap narrowing will, however, change the charge density at the interface slightly from the LDA result. We expect this to have only a small effect on the barrier height, especially since most of the band bending occurs for unoccupied states which do not contribute to the charge density. (This is supported by the discussion of barrier-height changes in Ref. [17].) We expect the effect, in turn, on the band-gap narrowing itself to be even smaller.]

The p-type Schottky barrier height is the difference between the Al Fermi energy and the GaAs valence band edge several angstroms to the right of the interface. (Variation in the local band edge in the first few angstroms has no effect on the barrier height, because of the existence of metal-induced current-carrying states in the band gap.) In the structure shown the LDA barrier height is 1.1 eV (in reasonable agreement with Ref. [10]). The GW barrier height may be evaluated either from the local band-edge corrections or by combining quasiparticle calculations for the two bulk materials with the results of the LDA supercell calculation. The good agreement between the two values obtained, 1.1 and 1.2 eV, respectively, gives further confirmation of the validity of our local band edge. (The small difference reflects the fact that the wave packet contains components of wave functions other than the valence band edge.) As is evident from Fig. 1, the n-type Schottky barrier height for this system is negative (-0.1 eV in the GW calculations; -0.5 eV in the LDA), since the Fermi energy is above the bulk position of the conduction band. We have estimated the effect of the occupation of these conduction-band states (which have a very low weight because of the small effective mass) on the screened interaction and hence on the band-gap narrowing, and conclude that it is negligible. Similarly, the long-range electrostatic band bending caused by the occupation of the conduction bands is not significant on the length scale of our calculations.

We have also repeated the GW calculations for a structure in which some of the Al atoms in the bulk and at the interface are displaced. These results show very similar behavior to the band-gap narrowing, suggesting that the narrowing is insensitive to the details of the interface bonding and the structure of the metal, although the Schottky barrier height is remarkably sensitive to the structure of the interface [18,19].

The image-potential band-gap narrowing was first investigated quantum mechanically by Inkson [2] using a mathematical model. Inkson showed that the proper long-distance limit was obtained using a GW expression for the self-energy operator, with W taken to be that corresponding to the additional static density response in a dielectric medium when a distant interface with the metal is introduced, and G the simple noninteracting Green's function of a model semiconductor in a two-band approximation. He also investigated the band-gap narrowing close to the interface by modeling the wave-vector and energy dependence of W. We have extended Inkson's model to describe more accurately the behavior in this region by taking the space and energy dependence of W into account more completely [7]. We find that the major change in the band-edge positions as one approaches

the interface, in comparison with the classical image-potential values, is a reduction in the upwards bending of the valence band, and an enhancement of the downwards bending of the conduction band, over the length scale of a few GaAs lattice constants. This result agrees with our full calculations (see Fig. 1). The quantum correction arises from the frequency dependence of the additional screened interaction due to the presence of the interface (thus including information about the interface plasmon modes) which makes a significant contribution to the self-energy operator for electrons close to the interface. Other terms, such as the effect of the change in the screening near the metal owing to the occupation of the MIGS (metal-induced gap states) in the band gap, have only a very small effect on the band bending.

These conclusions from our model calculations are rather general, and we have tested them further by repeating our main GW calculations but using plane-wave wave functions in G and in constructing the wave packets. The results are similar to the main calculations and consistent with the model, although the magnitude of the band bending for states representing the valence band and conduction band is less than 50% of that in the full calculation. This demonstrates that the character of the wave functions, as well as the nature of W, is responsible for the band-gap narrowing near the interface.

In conclusion, a first-principles GW calculation of the local quasiparticle electronic structure of a Al/GaAs-(110) interface, together with analysis of a corresponding model system, has allowed us to investigate the quantum-mechanical analog of the classical image-potential band gap narrowing that is valid in the long-distance limit. The band gap is substantially reduced, but the band bending is primarily in the conduction band near the interface, rather than equally distributed between the bands as predicted by the classical model. It should be possible to detect these effects in suitably designed optical experiments on metal-semiconductor interfaces. The correction to the classical picture arises largely from the energy dependence of the screening of the electron-electron interaction by the interface.

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