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QUASIPARTICLE CALCULATION OF VALENCE BAND OFFSET OF AlAs-GaAs(001)

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A first principles quasiparticle theory for band offsets of heterojunctions is developed and used to compute the valence band offset ΔE_v for the prototypical AlAs-GaAs(001) interface. The result $\Delta E_v = 0.53 \pm 0.05$ eV is in good agreement with recent experimental values and in particular with the most recent photoluminescence data $\Delta E_v = 0.56 \pm 0.03$ eV for an MBE grown sample. We show that there is a substantial many-body correction of 0.12 eV to the value of the valence band offset calculated using local density functional theory.

(AlGa)As-GaAs(001) is one of the most extensively studied heterojunctions.[1-3] The two lattices for this system are nearly perfectly matched making this a unique system for fundamental studies of heterojunction formation. One of the most important properties of heterojunctions is the valence or conduction band offset (ΔE_v or ΔE_c) which determines electronic transport behavior at the interface. Early experiments gave a large scatter for ΔE_v for this interface.[1-5] Nevertheless, a partitioning of the conduction and valence band offsets in the ratio of ΔE_c:ΔE_v = 85:15 later became well accepted.[4] A "common-anion rule" was suggested which states that the valence band offset of two semiconductors reflects primarily the energy differences between the anions, and would therefore nearly vanish for (AlGa)As-GaAs.[5] However, recent experiments done on MBE grown $Al_xGa_{1-x}As$-GaAs(001) quantum wells question this early accepted ratio and, instead, are consistent with a ratio ΔE_c:$\Delta E_v \approx$ 60:40.[6] Measurements on the MBE grown AlAs-GaAs(001) band offset also give[7-9] a larger value for the valence band offset ΔE_v = 0.45 - 0.56 eV. Recently, $\Delta E_v = 0.535 \pm 0.0125$ eV was reported by Dawson *et al.*.[10] Wolford performed a set of measurements on $Al_xGa_{1-x}As$-GaAs(001) using optical methods, he concluded that the ratio for the band offsets is 68:32 and $\Delta E_v = 0.560 \pm 0.03$ eV for $x = 1$.[11]

The band offset is essential for understanding interface phenomena of heterojunctions, superlattices and quantum well systems and for the design of novel semiconductor devices. Hence considerable theoretical effort has been made to attempt a prediction of this parameter.[12-20] Early empirical models[12-14] appeared to be in agreement with the "common anion rule". An early empirical pseudopotential calculation put ΔE_v = 0.25 eV for the AlAs-GaAs(110) interface.[15] Recently, local density functional calculation for the band offset using *ab initio* pseudopotentials[17] gave ΔE_v = 0.37 eV almost independent of the crystal orientation. An all electron calculation within the local density approximation (LDA) was carried out by Massidda *et al.*.[18] Meanwhile, Wei and Zunger[19] suggested that the failure of earlier tight-binding models is caused by the omission of the *d*-core levels. The *d*-core and valence electron interactions are included as non-local *d*-potential in *ab initio* pseudopotential calculations.[21]

In this paper, we propose that many-body effect plays an important role in the band offset problem. The discrepancy between LDA calculations and the experimental values for the band offset of AlAs-GaAs (001) interface is thus mainly caused by the inappropriate use of the eigenvalues obtained using LDA.

Our calculation is based on the quasiparticle theory[22-24] which has been successful in predicting the optical and photoemission spectrum of bulk semiconductors[23] and semiconductor surfaces.[25] The quasiparticle energy at the valence band maxima, E^{qp}_{vbm}, is calculated by solving

$$(T + V_{ext} + V_h)\psi_{nk}(\vec{r}) + \int d\vec{r}'\Sigma(\vec{r},\vec{r}';E^{qp}_{nk})\psi_{nk}(\vec{r}') = E^{qp}_{nk}\psi_{nk}(\vec{r}), \quad (1)$$

where V_h is the Hartree potential. The exchange and correlation contributions are included in the nonlocal energy-dependent self-energy operator Σ. In general, Σ is not Hermitian and E^{qp}_{nk} is complex with the imaginary part giving the lifetime. Σ within the GW approximation[22-24] is given by

$$\Sigma(\vec{r},\vec{r}';E) = i\int (d\omega/2\pi)e^{-i\eta\omega}G(\vec{r},\vec{r}';E-\omega)W(\vec{r},\vec{r}';\omega), \quad (2)$$

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where η is a positive infinitesimal; G and $W = v\epsilon^{-1}$ are the interacting Green's function and the dynamically screened Coulomb interaction, respectively.

The valence band offset can be rigorously written as the difference between the quasiparticle energies at the valence band maximum of the materials at the two sides of the interface,

$$\Delta E_v = E^{qp}_{vbm,GaAs} - E^{qp}_{vbm,AlAs}. \quad (3)$$

Using Eq. (1), E^{qp}_{vbm} can also be expressed as

$$E^{qp}_{vbm} = < \psi_{vbm} \mid (T + V_{ext} + V_h) \mid \psi_{vbm} > + < \psi_{vbm} \mid \Sigma(E^{qp}_{vbm}) \mid \psi_{vbm} > . \quad (4)$$

The corresponding LDA value is

$$\epsilon^{lda}_{vbm} = < \phi_{vbm} \mid (T + V_{ext} + V_h) \mid \phi_{vbm} > + < \phi_{vbm} \mid V_{xc} \mid \phi_{vbm} >, \quad (5)$$

where V_{xc} is the LDA exchange-correlation potential, $\mid \psi >$ and $\mid \phi >$ are the quasiparticle and LDA wavefunctions, respectively. Because the only difference in the Hamiltonian between quasiparticle theory and LDA is the exchange-correlation potential which is a very small fraction of the total interaction, the wavefunctions are overwhelmingly dominated by the kinetic energies, external and Hartree potentials. The overlap between $\mid \psi >$ and $\mid \phi >$ is more than 99.9 %. This argument is quite general and holds for bulk,[23] surface[25] and also holds for interface. We therefore use $\mid \phi >$ to replace $\mid \psi >$. The errors introduced by such approximation on the absolute values of E^{qp} are estimated to be less than 0.02 eV in the bulk and expected to be negligibly small for the difference of E^{qp} evaluated in Eq. (3). Combining Eqs. (4) and (5),

$$E^{qp}_{vbm} = \epsilon^{lda}_{vbm} + \Sigma^{vbm} - V^{vbm}_{xc}, \quad (6)$$

where $\Sigma^{vbm} = < \phi_{vbm} \mid \Sigma(E^{qp}_{vbm}) \mid \phi_{vbm} >$ and $V^{vbm}_{xc} = < \phi_{vbm} \mid V_{xc} \mid \phi_{vbm} >$. By use of Eq. (6), Eq. (3) becomes $\Delta E_v = \Delta E^{lda}_v + \delta_{vbm}$. The many-body correction δ_{vbm} is given as

$$\delta_{vbm} = (\Sigma - V_{xc})^{vbm}_{GaAs} - (\Sigma - V_{xc})^{vbm}_{AlAs}. \quad (7)$$

Since E^{qp}_{vbm}'s in Eq. (3) should be evaluated at large distances away from the interface and both Σ and V_{xc} are short range interactions, $(\Sigma - V_{xc})^{vbm}$ can be replaced by bulk values. To calculate the LDA band offset ΔE^{lda}_v, we use a similar approach to that of Van de Walle and Martin.[26] The averaged LDA local potentials, $\bar{V}$'s, in the bulk regions of GaAs and AlAs, and their difference, $\Delta\bar{V}$, are calculated using a superlattice. They are then used to line up bulk LDA eigenvalues. The many-body corrections will not affect $\Delta\bar{V}$ because this quantity only depends on the long range electrostatic potentials. These electrostatic potentials are known functions of the charge densities and are well determined by the LDA since the charge densities are known to be accurately given by the LDA (from comparison with X-ray form factors). Furthermore, surface energies and workfunctions which are quantities very sensitive to the surface electrostatic potentials have been accurately predicted within the LDA.

We find that the many-body correction is significant. *i.e.* $\delta_{vbm} = 0.12 \pm 0.02$ eV for the AlAs-GaAs(001) interface. It is more than 29 % of the LDA value for the valence band offset which is $\Delta E^{lda}_v = 0.41$ eV. Therefore, our calculated value for the valence band offset is $\Delta E_v = 0.53 \pm 0.05$ eV. This value is in very good agreement with the most recent experimental values of 0.53 - 0.56 eV.[10,11]

A fully converged LDA calculation of ΔE^{lda}_v was carried out by use of *ab initio* scalar-relativistic pseudopotentials[27,28] for the electron-ion interaction. Ten special k-points in the irreducible Brillouin zone are used to obtain the self-consistent charge density for the bulk materials.[29] The wavefunctions are expanded in a plane wave basis up to kinetic energies of 16 Ry. A 56-Ry energy cutoff is used to calculate the charge density. All the bulk calculations were done at the atomic volume of GaAs corresponding to an MBE growth of AlAs on a GaAs substrate. The valence band maxima are converged to within 0.02 eV at this energy cutoff which introduces an uncertainty of 0.005 eV in the result for the LDA valence band discontinuity. The relative position of the averaged potentials is calculated in the superlattice using 6 k-points for the Brillouin zone sum.[30] An energy cutoff of 12 Ry is used for the plane wave expansion in the superlattice calculation. The calculation was iterated until the potential is self-consistent to within 10^{-5} Ry and $\Delta\bar{V}$ was stable within 0.002 eV.

To investigate the convergence for $\Delta\bar{V}$, an energy cutoff of 10 Ry for a 2x2 superlattice and an energy cutoff of 12 Ry for 2x2 and 3x3 superlattices (corresponding to 8 and 12 atoms/cell respectively) are used. It appears that $\Delta\bar{V}$ is well converged beyond 2x2 superlattice at a 12 Ry cutoff; this is consistent with other LDA calculations. From these results, we estimate the uncertainties for ΔE^{lda}_v to be less than 0.02 eV. The spin-orbit splitting Δ_0 shifts the valence band maximum by $1/3\Delta_0$ upward. This gives rise to an increase in the valence band offset by 0.02 eV for[31] $\Delta_{0,GaAs} = 0.34$ eV and $\Delta_{0,AlAs} = 0.28$ eV. Therefore, our result for the LDA valence band discontinuity after taking into account the spin-orbit splittings is $\Delta E^{lda}_v = 0.41 \pm 0.03$ eV.

We proceed using the method of Ref. 23 to calculate the self-energy Σ in Fourier space. The Green's function G is approximated using the LDA wavefunctions and spectrum with subsequent update to include the quasiparticle effects. The static dielectric matrix $\epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q};\omega = 0)$ is obtained within the random-phase approximation by use of the Adler-Wiser formulation[32] and extended to finite frequencies using a generalized plasmon pole model. In this model, we use two δ-

functions to represent the spectrum of $\epsilon_2^{-1}{}_{\vec{G},\vec{G}'}(\vec{q};\omega)$. Therefore, the complete dielectric matrix is determined uniquely by use of Kramer-Kronig relation, the f-sum rule and basic symmetry requirements. No adjustable parameters are used. The size of the dielectric matrix is determined by the reciprocal space cutoff $G_{\max} = 3.2$ *a.u.*, and 100 lowest energy bands within an energy range of about 100 eV are included in calculating ϵ^{-1} and the self energy operator Σ.

Table 1. Many-body correction δ_{vbm} versus number of q-points used in the Brillouin zone sum.

N_q	3	10	14
δ_{vbm} (eV)	0.082	0.116	0.121

Table 1 summarizes the many-body correction δ_{vbm} to the LDA band offset as defined by Eq. (7) for the different numbers of q-points N_q used in the Brillouin zone sum for Σ. Numerically, δ_{vbm} is well converged to 0.12 eV at $N_q = 14$ to within 0.005 eV. A systematic trend for the valence band is observed in Figure 1 in which $E^{qp}_{nk} - \epsilon^{lda}_{nk}$ for both GaAs and AlAs

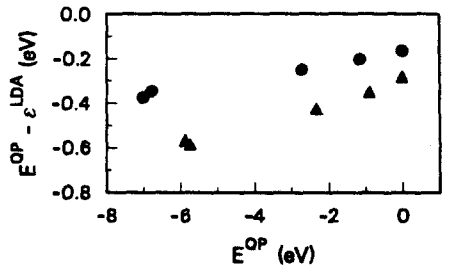

Figure 1. $E^{qp}_{nk} - \epsilon^{lda}_{nk}$ is shown as a function of the quasiparticle energy E^{qp}_{nk} for both GaAs (filled circles) and AlAs (filled triangles) p-like valence bands.

p-like valence bands was plotted as a function of the quasiparticle energy E^{qp}_{nk}. A consistent 0.1 - 0.2 eV difference in the correction to the LDA eigenvalues of GaAs and AlAs is observed for the valence band states. From Table 1 and Figure 1, the many-body correction to the valence band offset, δ_{vbm}, is determined to be 0.12 ± 0.02 eV. The uncertainty of 0.02 eV includes possible influences from the various cutoffs mentioned earlier.

The sign of δ_{vbm} can be understood by examining the self-energy at the valence band maxima. It may be divided into three terms – bare exchange, screened exchange and Coulomb hole components which are given in Table 2. Expressions for the three terms are given in Ref. 23. A more negative bare exchange energy is found for AlAs which is 0.3 eV lower than for GaAs. The exchange hole in AlAs is therefore deeper and narrower than that in GaAs. This is consistent with a more localized valence band wavefunction for AlAs. The occupied p-like band of AlAs is found to be about 1.1 eV narrower than GaAs. The screened exchange term reduces the bare exchange in both GaAs and AlAs but has little effect on their difference. However, the Coulomb hole energy competes with the exchange energy and reduces the difference by about 0.2 eV. A larger negative Coulomb hole energy in GaAs is consistent with more effective screening ($\epsilon_{\infty,GaAs} = 10.9$ and $\epsilon_{\infty,AlAs} = 8.16$[31]). Since LDA gives almost identical exchange-correlation potential V_{xc} for GaAs and AlAs, the many-body correction to the LDA is more negative in AlAs; this leads to a positive δ_{vbm}. This conclusion agrees with previous results for C, Si, Ge, and LiCl[23] where the many-body correction to the valence band maximum increases as the wavefunctions become more localized.

In conclusion, using the quasi-particle theory[23], we have determined the valence band offset for the AlAs-GaAs(001) interface. Although LDA is a powerful method for many ground state properties, it can not be used for an accurate prediction for the band offsets. We expect the many-body correction to play an even more important role in determining the band offsets for those heterojunctions made from materials with less chemical similarities than GaAs and AlAs.

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Table 2. The bare exchange Σ_x, screened exchange Σ_{sex}, Coulomb hole Σ_{coh}, self-energy Σ, and the LDA exchange and correlation potential V_{xc} at the valence band maximum for GaAs and AlAs in electron volts (eV).

	Σ_x	Σ_{sex}	Σ_{coh}	Σ	V_{xc}
GaAs	-12.638	8.987	-8.280	-11.931	-11.759
AlAs	-12.936	8.992	-8.110	-12.054	-11.761

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