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<td>Wang, Y; Zahid, F; Zhu, Y; Liu, L; Wang, J; Guo, H</td>
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Band offset of GaAs/Al$_x$Ga$_{1-x}$As heterojunctions from atomistic first principles

Yin Wang,1,a) Ferdows Zahid,1 Yu Zhu,2 Lei Liu,2 Jian Wang,1 and Hong Guo1,3

1Department of Physics and the Center of Theoretical and Computational Physics, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China
2Nanoelectronic Technologies, Brossard, Quebec J4Z 1A7, Canada
3Center for the Physics of Materials and Department of Physics, McGill University, Montreal, Quebec H3A 2T8, Canada

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Using an atomistic first principles approach, we investigate the band offset of the GaAs/Al$_x$Ga$_{1-x}$As heterojunctions for the entire range of the Al doping concentration $0 < x \leq 1$. We apply the coherent potential approach to handle the configuration average of Al doping and a recently proposed semi-local exchange potential to accurately determine the band gaps of the materials. The calculated band structures of the GaAs, AlAs crystals and band gaps of the Al$_x$Ga$_{1-x}$As alloys, are in very good agreement with the experimental results. We predict that valence band offset of the GaAs/Al$_x$Ga$_{1-x}$As heterojunction scales with the Al concentration $x$ in a linear fashion as $VBO(x) \approx 0.587x$, and the conduction band offset scales with $x$ in a nonlinear fashion. Quantitative comparisons to the corresponding experimental data are made.

The properties of III-V compound semiconductors and their heterojunctions have been relentlessly investigated for several decades due to their wide-ranging applications in electronic and optoelectronic technologies. One of the most important electronic properties of heterojunctions is the band offset which describes the relative alignment of the electronic bands across the junction interface.1 An accurate determination of the band offset is critical for understanding quantum transport properties of the heterojunction. For many III-V materials systems, the band offset has been carefully measured experimentally.2,3

Theoretical calculations of band offset have always been a serious challenge. This is because first principles method of density functional theory (DFT)2 with local-density approximation (LDA)3 and generalized gradient approximation (GGA)5 underestimates the band gap ($E_g$) of semiconductors. Without a correct calculation of $E_g$ for individual semiconductors, the calculated band offset between two semiconductors may be compromised. Advanced methods such as GW6 and/or hybrid functional7 can yield accurate $E_g$ for many systems but require significantly more expensive computation. Another difficulty is when there are impurities: the predicted physical results must be averaged over the multitudes of impurity configurations which is extremely costly in computation. Realistic semiconductors all have impurities and if the impurity concentration is small, one needs to compute systems of large number of host atoms in order to accommodate a few impurity atoms. Because of these issues, predicting band offset has persisted to be a challenging theoretical problem.

Considerable theoretical efforts have been devoted in the literature to correctly predict $E_g$. Apart from the GW6 and hybrid functionals7 for pure semiconductors, the recently proposed modified Becke-Johnson (MBJ) semilocal exchange potential was shown to give quite accurate $E_g$ values for many compounds with a computational cost similar to that of LDA.8 Even though MBJ is not a fundamental solution to the issue of electron correlation, it is practically useful for calculating $E_g$. To deal with the prohibitively large computation required for performing configuration average of doped semiconductors, one wishes to obtain the averaged physical quantity without individually computing each impurity configuration by brute force as in the super-cell approach. In this regard, a widely used technique is the coherent potential approximation (CPA)9 as implemented in Korringa-Kohn-Rostoker10 or linear muffin-tin orbital (LMTO)11 DFT methods. CPA is a statistical effective medium approach such that an atomic site has $x\%$ chance to be an impurity (e.g., dopant) atom and $(1-x)\%$ chance to be a host atom, the configuration average is carried out analytically hence disorder effect can be calculated for any concentration $x$. Very recently, Ref. 12 has combined CPA with MBJ and reported the calculation of $E_g$ for the semiconductor In$_x$Ga$_{1-x}$N, the results are in excellent agreement with the measured data for the entire range of $0 \leq x \leq 1$.

In this paper, we employ the CPA-MBJ approach to quantitatively calculate the band offsets of two semiconductors with impurity doping. In particular, we consider the most important heterojunction, between GaAs and Al$_x$Ga$_{1-x}$As, and calculate the band offset as a function of the Al concentration $x$. Even though this heterojunction has been the subject of extensive past investigations, theoretically the calculation was usually done at a few special values of $x$ where the super-cell approach could be applied. Here, the CPA-MBJ approach allows us to determine a continuous curve of the band offset for the entire range of $0 < x \leq 1$, which has not been derived before from atomic first principles. Our calculated $E_g$ of Al$_x$Ga$_{1-x}$As and the calculated band offsets of the heterojunctions for the entire $x$ range are quantitatively and excellently compared with the corresponding experimental data.

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a)Electronic mail: yinwang@hku.hk
The lattice constants of the zinc-blende AlAs and GaAs were individually relaxed by a projector augmented wave method with LDA as implemented in the VASP software, and the optimized lattice constant of 5.63 Å for GaAs was used for all the compounds in our calculations since the optimized lattice constant of AlAs (5.64 Å) is very close to that of GaAs. To calculate the band offset with Al doping, we apply the CPA-MBJ approach discussed above to the pure materials GaAs and AlAs with the MBJ functional, where the DFT is carried out within the TB-LMTO scheme under the atomic sphere approximation (ASA). For the technical details of the NANODSIM algorithm, we refer interested readers to Refs. 14 and 15.

In the DFT-CPA-MBJ calculations, the primitive cell of the zinc-blende structure was used to calculate the band structures and electronic packages. Figs. 1(a) and 1(b) show a perfect agreement of the valence bands and a good match of the conduction bands between these methods, confirming that the ASA employed in the TB-LMTO approach (NANODSIM) is accurate for calculating physical properties of these materials. It should be noted from Figs. 1(a) and 1(b) that the band gaps were underestimated by LDA. Next, we apply the MBJ functional to calculate the electronic structure again and the MBJ results are shown in Figs. 1(c) and 1(d). Compared with the LDA bands in Figs. 1(a) and 1(b), the opening of band gap is evident. From Figs. 1(c) and 1(d), the band gap values at Γ, X, and L points are listed in Table I. The MBJ band gaps are in good agreement with the experimental values at the Γ and X points, and within 7% for GaAs and 15% for AlAs to the experimental values at the L point.

Table I. Energies of the conduction band minima at the Γ, X, and L points.

<table>
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<tr>
<th>Material</th>
<th>$E_s$</th>
<th>$LDA'$</th>
<th>LDA</th>
<th>MBJ</th>
<th>Expt.</th>
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<tr>
<td>GaAs</td>
<td>0.493</td>
<td>0.761</td>
<td>1.518</td>
<td>1.519</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.334</td>
<td>1.346</td>
<td>1.960</td>
<td>1.981</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.948</td>
<td>1.100</td>
<td>1.691</td>
<td>1.815</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>2.014</td>
<td>2.300</td>
<td>3.099</td>
<td>3.099</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.312</td>
<td>1.307</td>
<td>2.258</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.086</td>
<td>2.191</td>
<td>2.835</td>
<td>2.46</td>
<td></td>
</tr>
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</table>

The band structures calculated with MBJ functional to calculate the electronic structure again and the MBJ results are shown in Figs. 1(c) and 1(d). Compared with the LDA bands in Figs. 1(a) and 1(b), the opening of band gap is evident. From Figs. 1(c) and 1(d), the band gap values at Γ, X, and L points are listed in Table I. The MBJ band gaps are in good agreement with the experimental values at the Γ and X points, and within 7% for GaAs and 15% for AlAs to the experimental values at the L point.

In contrast, the LDA gaps typically underestimate the values quite significantly which is a well known issue of LDA.

Having accurately determined the band structures for the pure materials GaAs and AlAs with the MBJ functional, we apply the CPA-MBJ approach discussed above to the alloy Al$_x$Ga$_{1-x}$As and the band offset of the heterojunctions.

![Image of band structures](image_url)
Having correctly determined the band gaps, dispersions and the direct-to-indirect gap crossover for the alloy Al<sub>1-x</sub>Ga<sub>x</sub>As, the band offset of the GaAs/AlGaAs heterojunction can be confidently analysed. The valence band offset (VBO) and the conduction band offset (CBO) of a heterojunction are defined as the difference between the energy values of the top of the valence bands and the bottom of the conduction bands of the two materials forming the junction, respectively. As already discussed, band offsets are of great importance for transport properties of the heterojunction. The band offsets can be calculated as

$$VBO, \ CBO = \Delta E_{x,c} + \Delta V,$$

where $\Delta E_{x,c} = \Delta E_x + \Delta E_c$ is defined as the difference between the top (bottom) of the valence (conduction) bands of two independent bulk materials that form the heterojunction, $\Delta V$ is the lineup of the potential through the heterojunction. When the two materials on either side of the heterojunction is extended long enough, $\Delta V$ is independent of the orientation of the two material interfaces.

Previously, by supercell method, the VBO of the GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As heterojunction was calculated at a few particular values of $x$, and several different scalings of VBO versus $x$ were reported. For instance, Ref. 23 reported VBO $\sim$0.564$x$ - 0.032$x^2$ (units eV); Ref. 24 reported VBO $\sim$0.41$x^2$; and Ref. 25 reported VBO $\sim$0.17$x$. Recently, Ref. 26 reported a calculation at $x = 0.5$ by the hybrid density functional method and obtained VBO = 0.26 and CBO = 0.42. However, first principles analysis of band offsets for the entire $0 < x \leq 1$ range is still lacking.

By the CPA-MBJ method discussed above, we have calculated VBO and CBO of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As heterojunction for the entire Al concentration range, results plotted in Fig. 3 versus $x$ in intervals of 0.1. The two insets of Fig. 3 plot the band alignment diagrams for $x = 0.5$ and 1.0. It is apparent that VBO is a linear function of $x$ while CBO is not. By fitting VBO linearly (solid red line), we obtain $VBO(x) \approx 0.587x$ eV which agrees quite reasonably with the experimental scaling of $VBO(x) \approx 0.55x$ eV.

Since the direct-to-indirect gap crossover is where the conduction band minima at $\Gamma$ and $X$ have the same energy value, it would be very useful to plot band structures of the Al<sub>1-x</sub>Ga<sub>x</sub>As alloy. This is however not possible because when Al is randomly doped into GaAs, the material is disordered and momentum is no longer a good quantum number. Nevertheless, one can plot the calculated density of states (DOS) as a function of the momentum $k$ and energy $E$ as shown in the inset of Fig. 2 which is for the alloy Al<sub>0.36</sub>Ga<sub>0.64</sub>As. This inset reveals a broadened “band structure” of the disordered alloy where the “bands” are no longer infinitely sharp lines as that of crystals due to impurity broadening. The broadened “bands” trace out the energy minima and dispersion from which we found that the “conduction band” minima at $\Gamma$, $X$, and $L$ points have essentially the same energy value for this alloy, thus, confirming that the theoretical crossover point is at $x \approx 0.36$.

FIG. 2. The calculated band gaps of Al<sub>1-x</sub>Ga<sub>x</sub>As versus $x$ by the CPA-MBJ approach. The two solid lines are fitting to the data in the two ranges of $x$. Inset: the calculated DOS for the alloy Al<sub>0.36</sub>Ga<sub>0.64</sub>As in logarithmic scale as a function of momentum $k$ and energy $E$, revealing a broadened “band structure.”

FIG. 3. Valence band offset (red dot) and conduction band offset (blue square) at different concentration $x$. The red line shows the linear fitting of the VBO. The GaAs/Al<sub>0.5</sub>Ga<sub>0.5</sub>As heterojunctions have the straddling type gap—the valence band maximum (VBM) of GaAs is higher, while its CBM is lower. Insets: band alignment diagrams of GaAs/Al<sub>0.5</sub>Ga<sub>0.5</sub>As (on the left) and GaAs/AlAs (right). The VBO (CBO) values are with respect to the VBM (CBM) of GaAs in units of eV.
calculated VBO values in Fig. 3 agree very well with the previous experimental and theoretical reports, namely, at $x = 0.3$, the calculated VBO is 0.167 eV, to be compared with the experimental value of 0.17 ± 0.04 eV. Concerning CBO, it was known experimentally that CBO appears to fit an approximate relation $CBO \approx 0.6 \Delta E_g^T$ where $\Delta E_g^T$ is the band gap difference of the two parts of the heterojunction. The linear increase of the CBO in the direct gap range in Fig. 3 is very close to this relation. Near and beyond the direct gap range, the calculated CBO decreases with increasing of $x$, which is also in good agreement with the experimental results.

In summary, using the DFT-CPA-MBJ first principles approach, we have calculated the band offset of the GaAs/Al$_{1-x}$Ga$_x$As heterojunctions for the entire range of the Al dopant concentration $x$. The calculated offset scales with the Al concentration $x$ in a linear fashion as $VBO(x) \approx 0.587x$, and the conduction band offset scales with $x$ in a nonlinear fashion. In our calculations, the impurity doping is handled by the CPA while accurate band structures and band gaps of the materials are obtained by the MBJ semilocal exchange potential. Our atomicistic calculations of the band structures of GaAs and AlAs are obtained by the MBJ semilocal exchange potential. Our atomicistic calculations of the band structures and band gaps of the materials appear to fit an approximate relation $CBO \approx 0.6 \Delta E_g^T$ where $\Delta E_g^T$ is the band gap difference of the two parts of the heterojunction. The linear increase of the CBO in the direct gap range in Fig. 3 is very close to this relation. Near and beyond the direct gap range, the calculated CBO decreases with increasing of $x$, which is also in good agreement with the experimental results.

We thank Dr. J. N. Zhuang, Dr. B. Wang, Dr. H. T. Yin, and Mr. R. G. Cao for useful discussions, and CLUMEQ for providing computation facilities. This work was supported by the University Grant Council (Contract No. AoE/P-04/08) of the Government of HKSAR and NSERC of Canada (H.G.).

13. G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993); G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996). An energy cutoff of 400 eV was used in the plane wave, a $20 \times 20 \times 20$ mesh was used to sample the Brillouin Zone for the primitive cell.
16. Using the self-consistent DFT-CPA-MBJ iterations, Ga and As 3d electrons are treated as core electrons and the 4d orbitals are included in the self-consistent process.
17. Our further calculations showed that (001) and (110) supercells give the same band offset, indicating that the value of band offset is independent of interface orientation as previously reported by Wei and Zunger, see: S. H. Wei and Z. Zunger, Appl. Phys. Lett. 69, 2719 (1996).
20. The optimized $c$ parameters used in the MBJ functional for calculating the GaAs and AlAs materials are: (a) For GaAs crystal, $c = 1.09$ for the atoms and 1.34 for the vacancy spheres. (b) For AlAs crystal, $c = 1.04$ for the atoms and 1.44 for the vacancy spheres. These values are used for all other calculations presented in this work.