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First-principles calculation of the AlAs/GaAs interface band structure using a self-energy–corrected local density approximation

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Abstract – We apply a self-energy–corrected local density approximation (LDA) to obtain corrected bulk band gaps and to study the band offsets of AlAs grown on GaAs (AlAs/GaAs). We also investigate the $Al_xGa_{1-x}As$/GaAs alloy interface, commonly employed in band gap engineering. The calculations are fully *ab initio*, with no adjustable parameters or experimental input, and at a computational cost comparable to traditional LDA. Our results are in good agreement with experimental values and other theoretical studies.

Introduction. – Group-III semiconductors have attracted close attention for their application in optoelectronics, operating from the infrared to the ultraviolet range, and in microelectronic devices. Indeed, due to its small electron effective mass, GaAs finds an important application in ultrafast transistors [1], where $Al_xGa_{1-x}As$ is commonly employed as the gate dielectric, thus making the AlAs/GaAs interface the subject of intense experimental [2–13] and theoretical [14–21] research. Band gaps and band offsets are material and interface parameters of great importance for the design and performance of heterojunction devices [22]. However, the quantitative theoretical prediction of these electronic properties can only be obtained with the help of computer-intensive perturbative approaches, such as GW [23], or from semi-empirical techniques. Among the latter it is worth mentioning tight binding and first-principles density functional theory (DFT) employing hybrid exchange-correlation functionals, where a linear combination of Hartree-Fock and local density functionals is fit to experimental data [24,25]. Recently, the LDA-1/2 technique for correcting the self-energy contribution to the particle excitation energy in the local density approximation (LDA) of DFT was introduced, with excellent results for the band gaps of several semiconductors and insulators [26], as well as for the band offsets of Si and SiO_2 [27]. The AlAs/GaAs interface is particularly interesting as a test to the LDA-1/2 technique because of its very small lattice mismatch, which excludes the spurious impact of interface stress due to mismatched interfaces (such as the Si/SiO_2) on the calculated electronic properties. In this paper we calculate the band gaps and band offsets of the interface AlAs/GaAs employing LDA-1/2. We also calculate the electronic properties of the interface between GaAs and the alloy $Al_xGa_{1-x}As$ with $0 \leqslant x \leqslant 1$. We show that, as previously found for the Si/SiO_2 interface [27], LDA-1/2 produces very accurate results for band gaps and band offsets at a computational cost comparable to that of standard DFT/LDA.

Theoretical methods. – *Zincblende* AlAs and GaAs slabs were used to construct our 128-atom AlAs/GaAs heterostructure along the (001) growth direction, with the computational unit cell defined by multiples of the experimental lattice constants [28] ($a = b = 3.995$ Å, $c = 180.8$ Å). As previously shown theoretically [15] and experimentally [6], this particular (001) direction does not limit our conclusions since the dependence of the valence band offsets (VBO) on interface models of common-anion, isovalent, lattice-matched

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semiconductors, is less than 0.1 eV. All interface calculations employed the Siesta code [29], while the WIEN2k [30] and VASP [31] codes were used to benchmark the bulk band gaps obtained with Siesta. Norm-conserving pseudopotentials of Troullier-Martins type [32] were used for both elements. Exchange and correlation were approximated by the LDA of Ceperley-Alder [33]. Ga *d*-electrons were included in the valence following Wei and Zunger [16] and García and Cohen [34] resulting in improved values for the VBO. Bulk GaAs calculations confirmed the importance of explicitly accounting for the Ga *d*-electrons, which improved the agreement with experimental lattice parameter by 5.3% with respect to *d*-electrons included in the core. Converged results were obtained by sampling the Brillouin zone with a $4 \times 4 \times 4$ or $6 \times 6 \times 1$ Monkhorst-Pack grid [35] for the bulk semiconductors and AlAs/GaAs heterostructure, respectively. All Siesta calculations employed the double-*zetas* plus polarisation (DZP) basis set.

The LDA-1/2 method follows the idea of Slater's "transition state" method [36], in which it is possible to calculate accurately the ionisation potentials of isolated atoms considering a state halfway between the ground state and the excited state. LDA-1/2 derivation for isolated atoms makes use of Janak's theorem [37], together with the fact that the Kohn-Sham (KS) eigenvalues depend almost linearly on the occupation number [38]. To apply it to crystals one adds to the crystalline potential a self-energy potential V_S defined as the difference between the Kohn-Sham atomic potential and that of the half-ion [26], repeated throughout the crystal lattice. In most cases, only the anionic self-energy potential is important because the valence band tends to be more localised. The self-energy potential range is limited employing a cutoff radius (CUT). This procedure is necessary to avoid that the self-energy Coulomb potential tail reaches the other atomic sites. The optimum CUT value is found at the maximum of the material bulk band gap, as shown in fig. 1. CUT is not an adjustable parameter since its relation with the band gap was obtained variationally [26].

For both AlAs and GaAs, we found that only modifying the pseudopotential of As *p*-orbital —As(*p*)— is important, leaving the Al and Ga pseudopotentials unchanged. We labeled the arsenic pseudopotential with half-ionised *p*-orbital as As-05*p*. While relativistic corrections to the Ga and As pseudopotentials have proved essential (fig. 1) the same correction applied to the Al pseudopotential leads to negligible change in the AlAs bulk band gap. Indeed, without relativistic correction we found a maximum GaAs band gap of 2.1 eV around a CUT value of 3.8 atomic units (a.u.), while with relativistic correction we found a maximum band gap of 1.6 eV at the same radius, which is in much better agreement with the experimental value of 1.52 eV [28]. Employing the same As(*p*) self-energy–corrected pseudopotential in the calculation of the AlAs band gap we obtained 2.48 eV, slightly higher than the experimental value of 2.23 eV [28]. It is worth

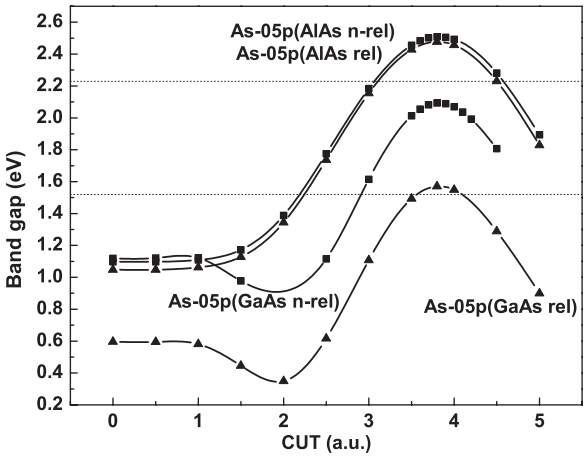

Fig. 1: Dependence of the GaAs (AlAs) band gap on the LDA-1/2 cutoff radius (CUT) used to limit the As self-energy potential (As-05*p*) range. The optimum CUT value is found variationally at the maximum value of the band gap. With (triangles) and without (squares) scalar relativistic correction applied to the pseudopotentials. The horizontal lines mark the experimental band gaps. Lines connecting symbols are guides to the eye.

mentioning that because the self-energy correction is applied to the same atom across the interface, the CUT value shall not differ considerably for AlAs and GaAs, as previously shown in ref. [26] and confirmed in our work. The calculated band gaps can be further improved by taking into account the spin-orbit (SO) energy (not included explicitly in our calculations) which up-shifts the GaAs and AlAs valence bands by ~ 0.11 eV, resulting in band gaps of ~ 1.49 eV and ~ 2.37 eV, respectively. Relativistic pseudopotentials are employed for all species throughout this paper.

Results. – Table 1 summarises the band gaps of GaAs and AlAs calculated with the LDA and LDA-1/2 approaches. It also shows the calculated lattice constants and the bulk moduli for both materials. The Siesta band gap values agree well with our VASP-PAW results.

Figure 2 shows the band gaps and band offsets calculated with LDA and LDA-1/2. The band edges correspond to the highest occupied and lowest unoccupied eigenvalues calculated projecting the density of states (PDOS) on one atom of each atomic plane, for all planes, along the AlAs/GaAs heterostructure, similarly to Bass *et al.* [39]. This approach is especially useful when dealing with localised interface states and/or large periodic super cells. We have employed a large enough super cell so that spurious quantisation effects resulting from the reduced dimensionality of the slabs at each side of the interface are negligible. Therefore, the band gaps obtained from the stack calculations are the same as their corresponding bulk values. The LDA valence band offset (VBO) is 0.32 eV, while the LDA conduction band offset (CBO) is close to zero. The LDA-1/2 band offsets are better

Table 1: Bulk structural and electronic parameters for AlAs and GaAs. All results obtained without spin-orbit coupling; "d" and "i" stand for direct and indirect band gap, respectively.

	GaAs[a]		AlAs	
	Siesta	Exp.[b]	Siesta	Exp.[b]
a (Å)	5.654	5.653	5.636	5.661
B (GPa)	76.4	75.4	75.6	74(4)
Band gap[c]	0.54(d)	1.52(d)	1.07(i)	2.23(i)
Band gap[d]	1.60(d)		2.48(i)	

[a]Using Ga(d) in valence.
[b]Reference [28].
[c]Band gap: LDA. Using scalar relativistic (rel) PPs.
[d]Band gap: LDA for Ga(rel), Al(rel), LDA-1/2 for As(rel)-05p, and experimental lattice constants.

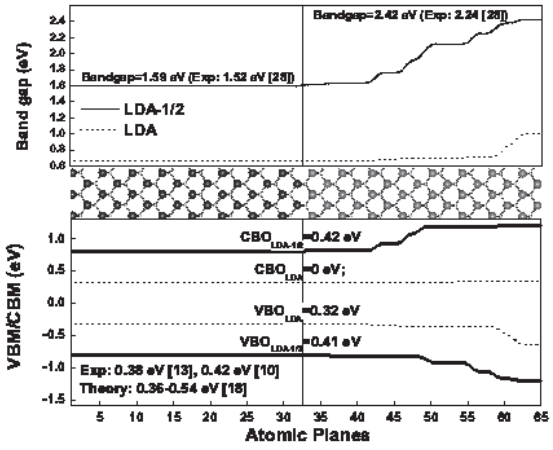

Fig. 2: Top: LDA (dotted line) and LDA-1/2 (solid line) band gaps along the AlAs/GaAs heterostructure; middle: heterostructure model with GaAs on the left and AlAs on the right; bottom: LDA (dotted line) and LDA-1/2 (solid line) valence band maximum (VBM) and conduction band minimum (CBM) along the AlAs/GaAs heterostructure. Conduction/valence band offsets (CBO/VBO) are indicated. In all cases, self-energy correction was only applied to the As p-orbital. The vertical line indicates the physical interface. The distance between atomic planes is ~ 1.4 Å.

balanced, with CBO = 0.42 eV and VBO = 0.41 eV, close to 0.38 eV measured by Katnani and Bauer [13] and 0.42 eV measured by Sorba *et al.* [10] and in the range of theoretical values calculated by Wang *et al.* [18] employing the atomic sphere approximation in the linear muffin-tin orbital band structure method.

Next, we investigated the effect of alloying the AlAs film with Ga, forming $Al_xGa_{1-x}As$, on its band gap and band offset with GaAs. In our simplified alloy model we replaced entire layers of Al for Ga since there is only one Al atom per layer, the number of replaced layers setting the Ga concentration in the slab. Moreover, the $Al_xGa_{1-x}As$/GaAs interface in the alloy side is always formed by an AlAs layer, followed by a GaAs layer

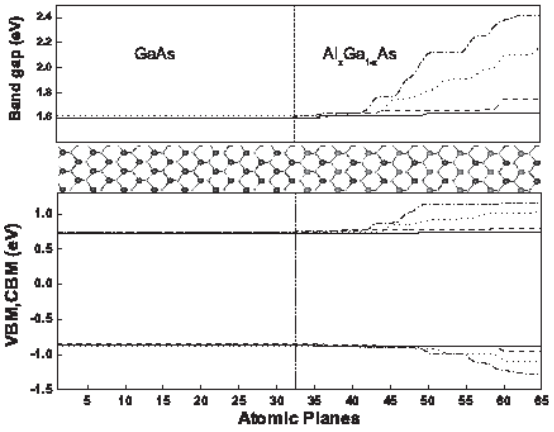

Fig. 3: Top: LDA-1/2 band gaps along the $Al_xGa_{1-x}As$/GaAs heterostructure for different values of Al concentration (dot-dashed line: $x = 100\%$; dotted line: $x = 75\%$; dashed line: $x = 50\%$; solid line: $x = 25\%$); middle: heterostructure model with GaAs on the left and $Al_xGa_{1-x}As$ on the right; bottom: LDA-1/2 valence band maximum (VBM) and conduction band minimum (CBM) along the $Al_xGa_{1-x}As$/GaAs heterostructure for different values of Al concentration (line styles have the same meaning as in the top figure). In all cases, self-energy correction was only applied to the As p-orbital. The vertical line indicates the physical interface. The distance between atomic planes is ~ 1.4 Å.

(except when $x = 1$). Within this model we varied the $Al_xGa_{1-x}As$ film stoichiometry setting x as 0.00, 0.25 ($L1_2$ arrangement), 0.50 ($L1_0$), and 0.75 ($L1_2$). For the sake of simplicity we did not relax the atomic positions of the system for each value of x which is expected to have little consequence on the results, as these semiconductors are almost lattice matched. We also kept the GaAs in-plane lattice parameters fixed for the interface structure regardless the alloy composition.

Figure 3 shows the variation of the $Al_xGa_{1-x}As$/GaAs band gap between GaAs and the alloy, as well as the band edges along the structure for different values of Al concentration. Notice that the valence band transition from GaAs to $Al_xGa_{1-x}As$ is much smoother than the conduction band transition. Indeed, visual inspection suggests that for all Al concentrations, the conduction and valence band transition onsets take place in the range 7–10 Å and ~ 20 Å away from the physical interface, respectively. The step-like conduction and valence transitions shown in the figure are not due to our particular choice of alloy model, since it is also present in fig. 2 where there is no alloying, but are actually due to the Gaussian broadening of the eigenvalues taken near the band edges.

Figure 4 summarises the results for the band edges as a function of Al concentration x. A linear fit yields VBO = $0.34x$ in agreement with Ji *et al.* [40]. However, we find that a quadratic fit better describes our results. In this case we obtain VBO = $0.41x^2$. The departure from linearity may be due to the simplicity of our alloy

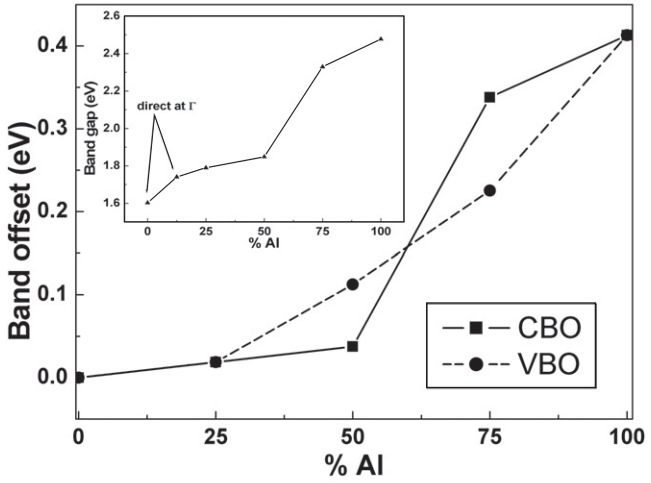

Fig. 4: LDA-1/2 conduction/valence band offsets (CBO/VBO) for the $Al_xGa_{1-x}As/GaAs$ interface and different Al concentrations in GaAs. Lines connecting symbols are guides to the eyes. Inset: $Al_xGa_{1-x}As$ bulk band gaps as a function of Al concentration.

model. The inset of fig. 4 shows the band gap increase while changing the concentration of Al and Ga in the *bulk* alloy. With this calculation we intend to show that LDA-1/2 not only accurately shifts the band extrema, but the whole band structure as well. We found a band gap transition from direct to indirect occurring in the range of 12.5–25% Al concentration, lower than experimentally observed (38–45%) [1,2,11]. Although this disagreement deserves a more detailed investigation, it is also possibly due to the simplicity of our alloy model.

Concluding remarks. – In summary, we have calculated the AlAs/GaAs interface band offset using a self-energy–corrected LDA/DFT technique. We found band gaps of 1.49 eV for GaAs and 2.37 eV for AlAs after including *a posteriori* the spin-orbit contributions, which reduce the two band gaps by 0.11 eV. The calculated valence and conduction band offsets for AlAs grown on GaAs along the (001) direction were 0.41 eV and 0.42 eV, respectively, in the range of experimental and theoretical values reported in the literature. The $Al_xGa_{1-x}As$ band gaps and $Al_xGa_{1-x}As/GaAs$ band offsets were calculated for different concentrations x of Al in an attempt of alloying one side. We found a direct to indirect bulk band gap transition for x between 12.5 and 25%, which is lower than experimentally reported possibly due to the simplicity of our alloy model. A linear fit to the VBO dependence on x agrees well with previous results, though a quadratic fit seems more appropriate. These results demonstrate that, at a modest computational cost, the first-principles LDA-1/2 technique is accurate for band offset prediction for this class of materials.

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