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First–Principles Calculations of Band Offsets in GaAs/AlAs System

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ABSTRACT

The lattice-matched system $(GaAs)_n/(AlAs)_n$ superlattice is calculated for two different values of n=3 and 6 within *ab initio* pseudopotential density-functional theory using Quantum Espresso package of program exploiting the ultra-soft atomic pseudopotentials. Their band offsets, which is a well-known and inextricable problem at semiconductor interfaces, have been determined in this paper and were compared with experimental results. Discontinuities of valance and conduction bands were obtained as 0.46 and 0.25 eV, respectively. The averaged self-consistent potential $\bar{V}(z)$ across the [001] interface in GaAs is about 0.061 eV higher than its value in AlAs. The local density of states for both superlattices was also studied. The effect of different factors e.g. orientation, transitivity, and composition dependence is reported in this study. We found that, in the [110] direction of GaAs/AlAs superlattice, the dependence of the band offset on the orientation is negligible. The calculated band gap of $Al_xGa_{1-x}As/GaAs$ is linearly dependent on aluminum content.

1. Introduction

The electronic structure at semiconductor-semiconductor heterojunctions and superlattices plays a crucial role in the optical and transport characteristics of devices employing these interfaces. [1] These characteristics are mainly controlled by the magnitude of band offsets (BOs) at heterojunctions. [2] The basic mechanism responsible for heterojunction's band offset formation has been studied and discussed by different groups. Several factors like strain, stress, orientation, and composition may affect the band offset. These dependences were explored by different researchers on a variety of systems.[3] With advance growth techniques such as metal organic chemical vapor deposition (MOCVD), metalorganic vapour-phase epitaxy (MOVPE) and molecular-beam epitaxy (MBE), it is now possible to grow highly perfect synthetic semiconductors superlattices as well as short period superlattices (SPS) with high accuracy [4]. Under certain conditions, these structures demonstrated very interesting properties such as extremely high carrier mobility [5], ohmic contacts with exceptionally low resistance, and even negative differential resistance and mobility [6]. It is therefore of interest to study the physics of the short period superlattices.

The active region of electronic devices is composed of a small number of monolayers of different semiconductor materials. Since the bulk and interface properties of these monolayers are inextricably linked, they must be interpreted within the framework of an integrated microscopic approach in which the continuous crystal potential in the entire structure is totally considered.

It is clear that mono- and bi-multilayers should exhibit alloy behavior. However, as the superlattice period increases, the alloy characteristics should smoothly change to multi-quantum well (MQW) behavior. Gallium Arsenide (GaAs) and Aluminum Arsenide (AlAs) are among the most challenging semiconductors with direct and indirect band gaps, respectively.

Considering the direct band gap, the first one plays an important role in optical technology while the latter possess a special position in electronic semiconductors [7, 8].

The main part of this paper will address aspects of the physics related to the electronic band structure of $(GaAs)_n/(AlAs)_n$ heterojunctions with n = 3 and 6. The impact of various factors is also investigated.

2. Materials and Methods

As described by Bachelet et al. [9] a non-local norm conserving pseudopotential method within the Local Density Approximation (LDA) was employed to perform

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the calculations in a supercell geometry. However different forms of exchange-correlation potentials were tested, our reported results were obtained using the Hedin-Lundqvist [10] representation for the exchange-correlation potential. As introduced by Van der Waals [11], the spin orbit splitting effects were included. Although, it has been proven that the obtained conduction band energies employing LDA approximation are not precise, but we presume that LDA corrections are almost identical for both In As and GaAs, therefore in comparison with orientation and composition effects the impact of this approximation on the band offsets must be negligible

In order to determine the band offsets, the self-consistent potential across the interface structure was first calculated. Moreover the self-consistent potential was averaged within the forming components (A and B) and away from the interface region. The fundamental parameter in determining the band offset is known to be the difference between potential averages of these two regions, $\overline{\Delta V} = \overline{V_A} - \overline{V_B}$.

The electronic energies of the two bulk units are then obtained with respect to the average total potentials, and these are aligned, so the difference in the bulk average potential is equal to $\overline{\Delta V}$. The difference in the valence band maxima ($\Delta E_V = E_V^A - E_V^B$) is considered as the valence band offset. In addition, the band gap info is used to calculate the conduction band offset, $\Delta E_c = \Delta E_g - \Delta E_V$. The band offsets are calculated using the local density of states (LDOS) across the interface in agreement with the method which was proposed by Bass et al [12]. The effect of the periodicity on the offsets was then studied using the obtained band offset of superlattice by exploiting this method.

In the case of bulk electronic structure calculations of GaAs and AlAs with tetragonal unit cell containing four atoms, we found that the plane waves up to 12 Ryd is required. The convergence threshold was considered as 0.01 eV. The cells considered up to 24 atoms for the interface calculations, and plane waves with energies up to 6 Ryd were found to be sufficient to give converged average potentials, $\overline{\Delta V}$.

3. Results and discussion

The interface calculation is used to determine the difference in the average potentials of the two semiconductors' bulk like regions of GaAs and AlAs (Fig.1). The averaged self-consistent potential $\bar{V}(z)$ across the [001] interface is presented in Fig 1a. The dashed curves represent the corresponding bulk potentials. The horizontal dashed lines show the potential averages $\overline{V_{GaAs}}$ and $\overline{V_{AlAs}}$ respectively. Schematic diagram of the band lineup in $GaAs/AlAs$ is illustrated in Fig. 1b in which it summarizes the relative energies of the average potentials $\overline{V_{GaAs}}$, $\overline{V_{AlAs}}$ and valence and conduction band edges of this superlattice. The LDOS across the superlattice is used to calculate the valence band offset. The onset of these band offsets for two superlattice systems $(GaAs)_3/(AlAs)_3$, and $(GaAs)_6/(AlAs)_6$ is reported, The simulated LDOS for $(GaAs)_6/(AlAs)_6$ and $(GaAs)_3/(AlAs)_3$ are shown in Fig 2a and 2b, respectively which are in a good agreement with experiments and band gap is consistently calculated. This is performed by averaging over the LDOS of the atoms within a given distance range along the [001] direction. Density of states (DOS) of bulk GaAs and AlAs is depicted in Fig. 2b (dashed lines). It shows from top to bottom '*bulk-like*' layer and interface of AlAs, interface layer and *'bulk-like*' GaAs.

a) Factors Influencing Band offsets

The band offset of GaAs/AlAs with other lattice-matched heterojunctions is given in Table 1. By comparing the experimental values with the macroscopic and microscopic model predictions and self-consistent interface calculation (SCIC), it can be seen that the agreement is very good.

Because the model results only use bulk properties, this implies that the band lineup is solely controlled by the bulk band structure and that there is some natural lineup. On the other hand, a comparison with the SCIC shows that the agreement is best for cases where the charge transfer across the interface is small and the corresponding interface dipole has little influence in driving the band lineups. In systems where chemical bonding at the interface is important, such as at the GaSb/InAs interface, the dipole effect is noticeable [13]. Similarly, in some systems, other factors (e.g., an external high-frequency field [14]) can alter the interface dipole and contribute significantly to the offsets. We outline some of the factors that may have an impact on band lineups, excluding strain effects.

Table 1. The band offsets of GaAs/AlAs with other lattice-matched heterojunctions.

	I	*II*	*III*
AIP/Si	0.91/0.87	1.03	-
AIP/GaP	0.46/0.01	0.36	-
AlAs/Ge	0.87/0.7	1.05	0.65
AlSb/GaSb	0.38/0.09	0.38	0.45
GaAs/AlAs	0.55/0.03	0.46	0.55
GaP/Si	0.45/0.86	0.61	0.80
GaAs/Ge	0.32/0.67	0.63	0.56
GaSb/InAs	0.43/0.72	0.63	0.51
ZnSe/Ge	1.52/2.09	2.17	1.52
ZnSe/GaAs	1.20/1.42	1,07	1.10
CdTe/HgTe	0.51/0.00	0.27	0..35
CdTe/InSb	0.84	1.19	0.87
HgTe/InSb	0.33	0.91	-
InGaAs/InP	0.26	0.41	0.38

I = Microscopic model [15], [16], *II* = SCIC [17], *III* = Expt. [18], [19]

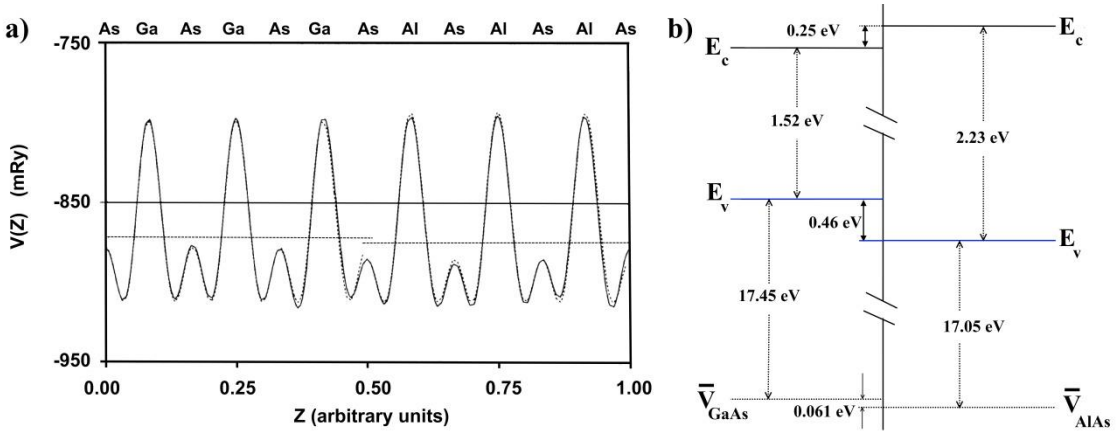

Fig. 1. (a) Averaged self-consistent potential $\bar{V}(z)$ across the [001] interface. (b) Illustrative diagram, relative positions of the average potentials $\overline{V_{GaAs}}$, $\overline{V_{AlAs}}$ and of the $GaAs/AlAs$ valence and conduction band edges.

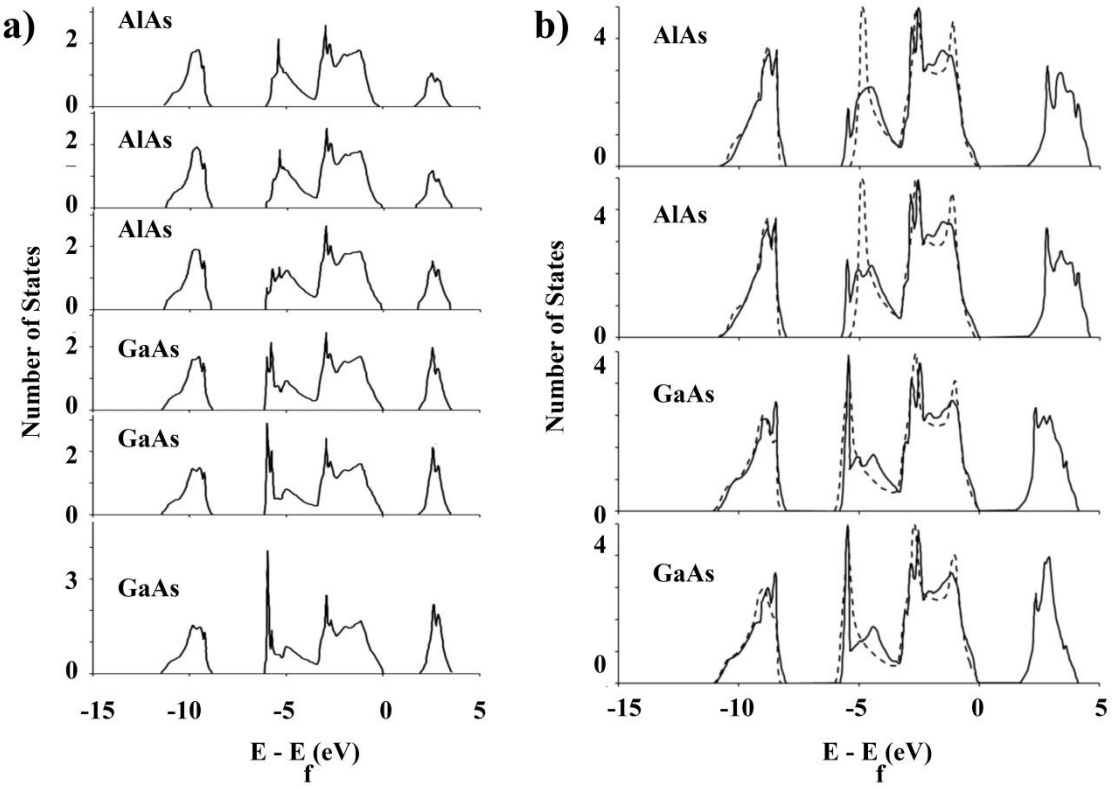

Fig. 2. a) The LDOS of $(GaAs)_6/(AlAs)_6$, b) The LDOS (full lines) of $(GaAs)_3/(AlAs)_3$ superlattices with the corresponding bulk DOS of GaAs and AlAs (dashed lines).

b) Orientation effects

In the [110] direction, the dependence of the band offset on orientation has been studied in GaAs/AlAs system. It is clear that for the majority of systems, the observed differences in offsets for different interface orientations are very small and acceptable within the experimental or calculation error (which is only 0.02 eV from that found for the [001]). Linear models that rely solely on bulk properties predict no orientation dependence. The transitivity of band offsets is normally written as follows:

$$T(A,B,C) = \Delta E_V(A/B) + \Delta E_V(B/C) - \Delta E_V(A/C) \qquad (1)$$

Transitivity is fulfilled when T = 0. Christensen [20] performed calculation (using the LMTO method) for a number of lattice-matched heterostructures and found that T was very close to zero in systems including GaAs or AlAs (see Table 2).

c) Composition Dependence

The $Al_xGa_{1-x}As/GaAs$ system is one of the most studied heterojunctions. Over the entire range of *x* values, the band offsets have been obtained both numerically and

experimentally. The change in the band gap is linearly related to x in the region where $Al_xGa_{1-x}As$ is a direct gap material ($x < 0.37$)

$$\Delta E_g = 1.255x \qquad [eV] \tag{2}$$

The conduction band offset has been measured to be approximately a constant fraction of the difference in band gaps for this range of composition.

$$\Delta E_c = 0.62\ \Delta E_g \tag{3}$$

Or

$$\Delta E_c = 0.78x \qquad [eV] \tag{4}$$

Table 2. Transitivity of the band offsets

A/B	B/C	A/C	ΔE_v (A/B)	ΔE_v (B/C)	ΔE_v (A/C)	T (A, B, C)
AlAs/GaAs	GaAs/Ge	AlAs/Ge	0.53	0.46	1.03	-0.04
ZnSe/GaAs	GaAs/Ge	ZnSe/Ge	1.07	0.46	1.58	-0.05
ZnSe/AlAs	AlAs/Ge	ZnSe/Ge	0.60	1.03	1.58	0.05
CuBr/GaAs	GaAs/AlAs	CuBr/AlAs	0.82	-0.53	0.50	-0.21
CuBr/ZnSe	ZnSe/GaAs	CuBr/GaAs	-0.32	1.07	0.82	-0.08

4. Conclusion

Electronic structure calculations were performed on the $(GaAs)_n/(AlAs)_n$ superlattices for n = 3, 6. We performed self-consistent calculation to drive explicit results for the interface structure of the system by minimization of the total energy. Two different theoretical methods were employed and a comparison with other theoretical and experimental methods was made. The lineup of band structures has been calculated, so the discontinuities of valance and conduction bands ($\Delta E_v, \Delta E_c$) was calculated. These findings, along with other computed factors, were in good agreement with the reported experiments.

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