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Control of Electrical Barriers at Semiconductor Heterojunctions by Interface Doping [and Discussion]

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Control of electrical barriers at semiconductor heterojunctions by interface doping

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From the results of self-consistent calculations on semiconductor heterojunction structures it has been shown that the band offsets depend on the potential lineup which in turn is determined by strain and charge transfer effects. The latter induces an electric dipole at the interface which can be altered by the introduction of suitable interlayers at or near the interface.

1. Introduction

The barriers to electrical transport across semiconductor interfaces play a crucial role in the construction of devices with particular characteristics. Because of this importance, much research has been directed at obtaining an understanding of the factors that influence the way the bands across the interface align. With a proper understanding it would be possible to engineer structures which gave desired electrical and optoelectronic properties without the need to grow combinations of different alloys and/or superlattices. Although the variation of the band edges across the interface is not abrupt, the concept of a well-defined discontinuity in the band edges has proved to be enormously useful in predicting the performance of a given device structure. Within the framework of this concept, the band offset at a heterojunction can be thought of as being derived from two contributions. The first is the alignment of some *reference levels* which, due to the long range nature of the Coulomb interaction, depends on the electronic charge distribution at the interface. The second contribution are the bulk band energies determined with respect to these reference levels. Over the years there has been much debate over the nature of these reference levels and the method for aligning them.

In the next section we give a brief overview of some of the different models for these reference levels and their alignment with particular emphasis placed on the approach we have taken in our calculations. This is followed by an analysis of how strain and alloy composition can be used as variables in controlling band offsets for a given system. We then turn our attention to the control of the band alignment by the introduction of thin interlayers at or near the interface focusing on both experimental and theoretical results.

2. Theories for aligning the band edges

Models for band alignment can be broadly classified in one of three categories. The early approaches like the electron affinity rule, transition metal impurity levels and the common anion rule were based on macroscopic properties and in general do not

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give good agreement with experiment for the whole range of heterojunctions (see, for example, Yu *et al.* 1992). Models based on the tight-binding approach (Harrison 1977) or bulk charge neutrality levels (Tejedor & Flores 1978; Tersoff 1984) although microscopic in origin, depend purely on the electronic properties of the bulk semiconductors. Although the observed band alignment in some systems could be explained by these models, there are severe limitations to using bulk properties to obtain band offsets. For example, band offsets based on these approaches would be independent of interface orientation and on the amount of strain in the constituent semiconductors. This is manifestly not the case and so the need to take into account the electronic structure of the interface and the concept of extrinsic and intrinsic charge neutrality levels is evident.

Self-consistent interface calculations (SCIC) by their very nature take account of the details of the interface as well as the strain in the system. Thus they provide a means of understanding the factors which influence the band alignment and the relative degree of each contribution. The band offsets are obtained by a two step process. The SCIC gives the difference in the average electrostatic potential on either side of the junction and this is used to align the bulk band structures which are determined with respect to the average bulk electrostatic potentials (Van de Walle & Martin 1987). The effect of strain and alloy composition is two-fold. The potential alignment in the SCIC is obviously affected by these factors. Also, the bulk band structures are altered with the band edges undergoing shifts with respect to their initial values. In addition to these effects, there is also a change in the absolute value of the average electrostatic potentials which should be considered. Below, we demonstrate how strain and alloy composition influences the band alignment by considering the GaAs–InGaAs heterojunction.

3. Effect of strain and alloy composition

To examine the influence of strain and composition on the band alignment at heterojunctions, self-consistent pseudopotential calculations of the various interface structures were performed (Oloumi 1990). A supercell geometry was used to model the structure. Non-local norm-conserving pseudopotentials (Bachelet *et al.* 1982) with the Hedin-Lundqvist (1971) form for the exchange correlation potential were used in the calculations. The spin-orbit interaction effects were added *a posteriori*. Once self consistency is attained, a plot of the average self consistent potential across the supercell $V(z)$ displays a discontinuity at the interface (see figure 1) with the difference between the average potentials in the two regions, $\Delta V = V_{\mathrm{InAs}} - V_{\mathrm{GaAs}}$, giving the reference level line-up. Thus, a knowledge of the energies of the band edges with respect to the average potential in the bulk gives the valence band offset directly.

As mentioned above, for lattice mismatched systems the bulk band edges are shifted with respect to the unstrained values. The biaxial strain can be separated into hydrostatic and uniaxial contributions, both of which cause a shift in the position of the valence band maximum denoted by $\Delta E_{\mathrm{v}}^{\mathrm{t}}$. The conduction band minimum is only affected by the hydrostatic component. The magnitude of the shifts are given in terms of the standard deformation potentials (Pollak & Cardona 1968). In addition to this, the average potential in the strained bulk also undergoes a shift, δV_{s}, due to a change in the local atomic volume (figure 2).

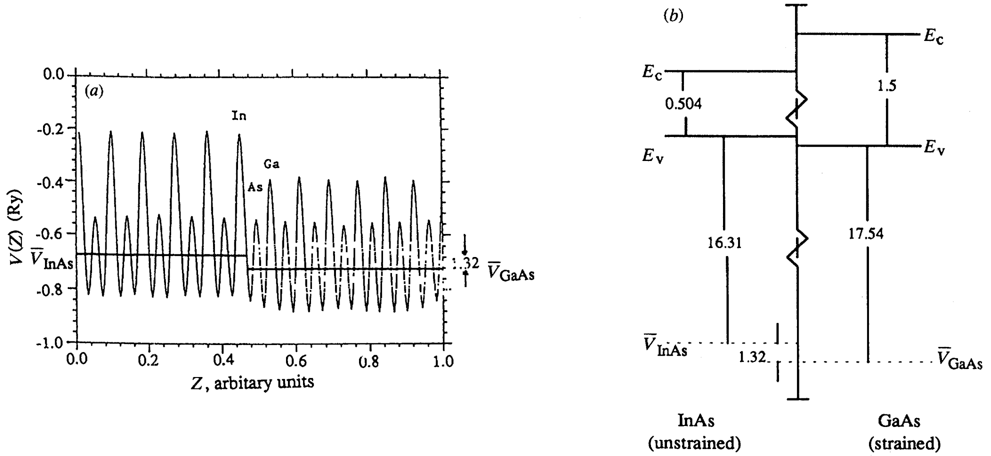


Figure 1. (*a*) Planar average of the self-consistent total potential across the InAs–GaAs (001) interface. (*b*) The band discontinuities obtained by aligning the band energies with respect to the respective $\bar{V}$.

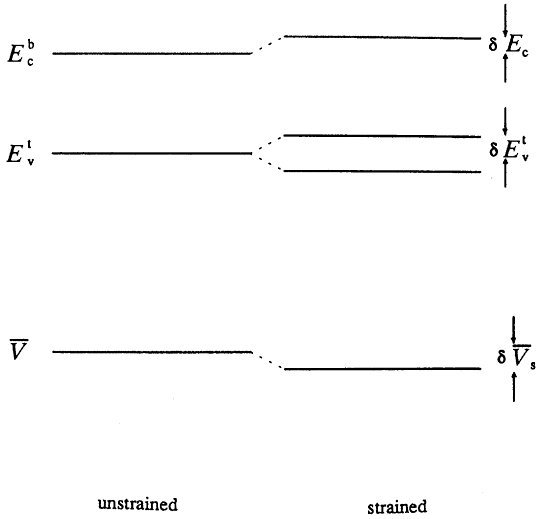


Figure 2. Schematic representation of the effect of biaxial strain on the band edges $(E_{\mathrm{c}}^{\mathrm{b}}, E_{\mathrm{v}}^{\mathrm{t}})$ and average potentials, $\bar{V}$. δE_{c} and $\delta E_{\mathrm{v}}^{\mathrm{t}}$ are given in terms of the deformation potentials (Pollak & Cardona 1968).

For the InAs–GaAs interface coherently strained on $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ substrates, the shifts in the bulk valence band edges and the average potentials are given in table 1. Also given are the $\Delta\bar{V}$ obtained from the interface calculations. The interesting point to note is that although the average potentials in the two regions undergo shifts, the difference between the two is nearly independent of the strain. Thus it is clear that there is a contribution to the potential alignment other than that arising from the bulk which is directly dependent on the interface details. The change in this interface electric dipole contribution, $\delta\bar{V}_{\mathrm{d}}$, can be attributed to the charge redistribution resulting from the movement of atoms from their original positions. From the results of these calculation we can conclude that the potential (reference level) line-up, defined by $\Delta\bar{V}$, depends on strain and on the electric dipole at the interface. For the

Table 1. *Shifts in the bulk valence band edge and average potential of InAs and GaAs strained on* $In_x Ga_{1-x} As$ *substrates*

(Also shown are the potential discontinuity across the InAs–GaAs junction. All energies in eV.)

	InAs		GaAs		
x	δE_v^t	δV_s	δE_v^t	δV_s	ΔV
0	0.19	−0.84	0	0	1.32
0.25	0.14	−0.65	0.13	0.25	
0.50	0.09	−0.36	0.25	0.43	1.25
0.75	0.05	−0.17	0.37	0.63	
1.00	0	0	0.50	0.77	1.27

InAs–GaAs system under biaxial strain, the shifts δV_s and δV_d are almost equal and opposite, hence the band alignment can be obtained directly from an observation of the relative shifts in the band edges.

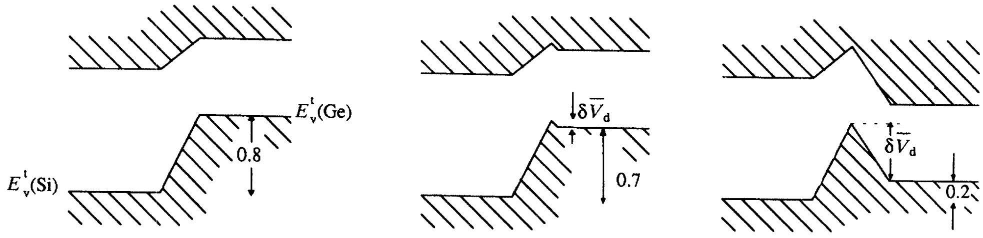
Calculations in $In_x Ga_{1-x} As$ strained on GaAs and GaAs strained on $In_x Ga_{1-x} As$ suggest that the potential lineup (ΔV) varies linearly with the indium content suggesting that both the strain and dipole contributions vary linearly with composition.

4. Control of band alignment: experimental

Although the use of strain effects and compound (ternary and quaternary) semiconductors gives great flexibility in modifying band offsets, the values are limited to ranges determined by the constituent semiconductors. Therefore, altering the electrical dipole at the interface can lead to even greater flexibility and appears to be the way forward in achieving true band offset engineering.

Capasso *et al.* (1985) showed that the electrical dipole can be altered by introducing sheets of donors and acceptors on either side of the interface. The valence band offset is modified by an amount equal to the potential difference between the two charged sheets. The dipole can also be altered by using a single sharply defined doping layer, or δ-doped layer, placed near the heterointerface on the low gap side (Muller *et al.* 1989). This structure causes an asymmetry in the potential at the interface as the electron charge densities in the individual subbands in the quantum well are displaced from the centroid of the ionised donor sheet.

Shen *et al.* (1991) showed that p-type (Be) δ-doping layer close to the n-isotype InAs–GaAs interface alters the effective barrier at the heterojunction. More recently, Bratina *et al.* (1992) demonstrated that the valence and conduction band discontinuities at the AlAs–GaAs heterojunction can be continuously tuned by the introduction of pseudomorphic elemental Ge or Si layers of controlled thickness at the interface. They also showed that the local interface dipole associated with the interlayer can be added (or subtracted) from the natural band offsets depending on the growth sequence. Furthermore, the observed dipole was found to be three times as large for Ge as for Si per interlayer atom. However, they also found that the change in the valence band offset increased with the Si layer thickness with the maximum dipole achieved for half a monolayer.



No interlayer

with In interlayer

with Sb interlayer

Figure 3. The effect of an interlayer at the Si–Ge interface is to alter the difference in the average potential, ΔV, by an amount δV_d determined by the change in charge transfer. This in turn causes a modification of the band offsets. All energies are given in eV.

5. Control of band alignment: theoretical

As the alignment of the reference levels is determined by the amount of charge transfer across the interface through the electric dipole potential, an obvious way by which the band discontinuities at a heterojunction could be altered is by modifying this dipole. This modification can be achieved by a number of means. The dipole depends on the kind of atoms at the interface and the interatomic spacings both of which influence the charge transfer. Thus, in lattice mismatched systems the strain not only induces shifts in the band edges but also alters the dipole because the relative positions of the atoms at the interface are changed. The introduction of interlayers at or near the interface alters the dipole by controlling the amount of charge transfer alone and thus is a simpler control than when strain is involved.

There has been much theoretical interest in understanding precisely how the dipole is altered and the dependence of this potential on the kind of atoms and the number of layers. Munoz *et al.* (1990) demonstrated the a bilayer of Ge at a GaAs homojunction induces a relative shift in the bands either side of the interlayer. Peressi *et al.* (1991) predicted changes in band offsets of the order of 1 eV when group III–V interlayers were inserted at IV–IV junctions.

Bass & Matthai (1991) showed that metallic monolayers at the Si–Ge interface greatly affected the band alignment. However, the modification depends on the kind of atom involved. For example, whereas indium hardly altered the band alignment, a monolayer of antimony reduced by the valence band offset to a quarter of its original value. These results can be understood in terms of the charge transfer between the atoms at the interface. The Sb layer gives more electrons to silicon atoms than to the germanium atoms resulting in a modified dipole potential, $\Delta V - \delta V_d$ (see figure 3). Indium on the other hand takes almost equal number of elections from the silicon and germanium atoms leaving the dipole potential virtually unchanged, i.e. δV_d is very small.

The results of calculations on InAs–GaAs interface structures with Ge interlayers yields even more information about the nature of the interface dipole. By considering various interlayer configurations Shen & Matthai (1992) found that the band alignment depended greatly on the position and on the thickness of the interlayer. When a bilayer of Ge was placed between In and As atoms (Type 2) the discontinuity in the average potential across the interface increased by 1.68 eV whereas for the Ge bilayer placed between As and Ga (Type 1) the change in the discontinuity was −1.72 eV. These findings can also be understood in terms of charge transfer and

Table 2. *Changes to the average potential discontinuity and the valence band offset*, ΔE_v, *at the* InAs–GaAs *interface with a* Ge *interlayer*

(All energies in eV.)

type of interlayer	ΔV	ΔE_v
no. interlayer	1.32	0.10
bilayer, type 1	−0.4	1.6
bilayer, type 2	2.9	1.7
monolayer	0.9	−0.3

consequently the dipole potential. At the InAs–GaAs junction the As atom receives less charge from the Ga than from the In atom resulting in a positive value for the potential discontinuity, ΔV. When the Ge bilayer is placed at the interface, the charge transfer from the In to the Ge atom in the Type 2 interface is similar to that transferred from Ga to Ge in the Type 1 interface. Hence the *changes* to the original interface dipole are of similar strengths with the difference in sign being attributed to the direction of the dipole. For a monolayer of Ge replacing the As layer at the interface, as Ge would be expected to take less charge compared with As, the magnitude of the dipole would be correspondingly reduced and this is confirmed by the self-consistent calculation. The changes to the valence band offset with the Ge interlayers are summarised in table 2.

6. Discussion

From the self-consistent calculations, we have shown that the band alignment at semiconductor heterojunctions is crucially dependent on the amount of charge transfer across the interface which is in turn influenced by the positions of the atoms and their relative electron affinities. The resulting dipole potential can be altered by strain or by the introduction of interlayers at the interface which alter the electric dipole. Experimentally the dipole change can be realized by the explicit introduction of charge sheets, near interface δ-doping causing an asymmetric change in the charge distribution or by interlayers thereby affecting the amount of charge transfer.

Much of the work described here is based on work done jointly with Dr J. Bass, Dr M. Oloumi and Dr T.-H. Shen. Thanks also to Kirstin Saynor for help in preparing the typescript.

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Discussion

G. P. SRIVASTAVA (*University of Exeter, U.K.*). Dr Matthai's work has examined the factors which affect the band line-up at semiconductor heterojunctions. By considering $(\mathrm{Si})_n(\mathrm{Ge})_n$ and $(\mathrm{GaAs})_n(\mathrm{InAs})_n$ his work shows that a stable value for band offset can be extracted by considering $n = 6$. Some time ago Baldereschi's group maintained that as low as $n = 4$ may be adequate for extracting band offset values. Perhaps different values of n are required for different directions of growth?

He has also shown that the band offset at Si–Ge and GaAs–InAs is affected by bulk properties as well as strain and introduction of suitable interlayers at the interface. Last year Resta and Baroni showed, using basically the same theoretical technique as his, that the band offset at strained Si–Ge interfaces is a bulk property, depending only upon the macroscopic strain present in the two materials far from the interface and independent of any interface feature, e.g. abruptness, interface strain or buckling. Could he comment on the conclusions reached by these workers?

C. C. MATTHAI. Based on our calculations on the $(\mathrm{Si})_n(\mathrm{Ge})_n$ and $(\mathrm{GaAs})_n(\mathrm{InAs})_n$ systems, the minimum value of n which is required to extract meaningful band offsets depends on the system under consideration and on the growth direction. This is intrinsically tied to the decay of the states at the band edges from one semiconductor into the other.

With reference to the results of Resta and Baroni for the Si–Ge system, we arrived at essentially the same conclusion. However, of the systems we studied we found this to be true only for this system. For example, for the InAs–GaAs system, the interface dipole which depends on the interface geometry crucially affects the line-up. The Si–Ge system is special because the amount of 'charge transfer' does not appear to depend on the Si–Ge bond length!

D. W. PALMER (*University of Sussex, U.K.*). Is there good agreement between band-offset magnitudes obtained in Dr Matthai's calculations (for particular assumed atomic positions at the interfaces) and those found experimentally? If so, can he therefore deduce the positions of the interface atoms in the structures experimentally studied?

C. C. Matthai. Yes, there is good agreement between calculated and measured band offsets. However, because of the number of degrees of freedom involved, it would not be possible to deduce the positions of the interface atoms from band offset measurements.