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The interface electronic states and valence band offsets of the Si/GaP heterojunction

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Abstract. The electronic structures of Si/GaP(111), Si/GaP($\bar{1}\bar{1}\bar{1}$) and Si/GaP(110) interfaces have been calculated using a self-consistent extended Hückel theory combined with the cluster and slab models. The values of the valence band discontinuities could be derived from the calculated band structures and are found to be dependent on the crystal orientation, i.e. $\Delta E_v = 0.88$ eV, 0.97 eV and 0.87 eV for Si/GaP(111), Si/GaP($\bar{1}\bar{1}\bar{1}$) and Si/GaP(110), respectively. The results are in good agreement with the experimental observations. The interface electronic states are significantly different for the (111), ($\bar{1}\bar{1}\bar{1}$) and (110) interfaces and have a strong influence on the energy band structure.

The energy band line-up is the most important property of a semiconductor heterojunction. Since the discontinuity of the valence band or conduction band plays a crucial role in determining the transport behaviour of a heterojunction and ultimately the performance of heterojunction devices, accurate knowledge of these band offsets is essential for the designing of novel semiconductor devices.

Until recently, many general theories of heterojunction band line-ups were based on the idea of linearity, i.e. the valence band discontinuity of a heterojunction could be expressed as the difference of two terms determined by the two component semiconductors (Kroemer 1985). Of these theories, the midgap energy model of Tersoff (1984) appears to be particularly successful in estimating band discontinuities with good accuracy. Tersoff postulated that there is an energy called the midgap energy E_B associated with each semiconductor. Any discontinuity in E_B at the interface will give rise to a charge-transfer dipole. The net result is that the discontinuity in E_B is screened by the dielectric constant of the semiconductor. If the dielectric constant is large enough, the self-consistent band line-up should be given by aligning E_B at the interface. Although this model agrees well with the experimental results for a number of III–V and elemental semiconductor pairs, there still remain some possible problems to be clarified. Like all the linear band offset theories, Tersoff's model neglected the details of the microscopic interface charge distribution which might affect the values of band offsets. As has been demonstrated by recent experiments, the line-up would be modified by controlled interface contamination (Niles *et al* 1985, 1986). The idea that the band offsets are regarded as resulting from 'intrinsic' bulk properties of the component materials independent of the junction boundary conditions seems conceptually questionable.

Another school of thought is the self-consistent interface potential (SCIP) theories which treated the heterojunction as a whole assembly to investigate the true band edge

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shift across the interface. This provides a possible approach towards the solving of the electronic interface dipole shift problem which has been ignored in linear theories. The calculations were based on a reasonable physical background but were a formidable computer task. The earlier work by Baraff *et al* (1977a, b), Pickett *et al* (1978), Pickett and Cohen (1978) and Ihm and Cohen (1979) was focused on the non-polar (110)-oriented heterojunctions. The band line-ups predicted by SCIP calculations were in even poorer agreement with reliable observations than were the linear theories. Recently, Van de Walle and Martin (1985, 1986a, 1987) extended further a self-consistent *ab initio* pseudopotential method to study systematically a wide variety of interface systems and they (Van de Walle and Martin 1986b) also extended to the lattice-mismatched Si/Ge system by taking into account the strain effect which has never been considered in the linear theories.

As a preliminary approach to the physics of band discontinuities from theoretical calculations, the present work aims at studying the role of interface states and its relation to the values of band offset. The calculations place more emphasis on the global character of the problem, while the search for high accuracy is somewhat neglected. In this work the self-consistent extended Hückel theory (EHT) is used in treating both cluster and slab models. With the Si/GaP interface as prototype, encouraging results are obtained. This is a semi-empirical method in which the parameters are mostly adopted from those used in previous work on surface chemisorption or reconstruction with considerable success. The computational effort required for this method is remarkably reduced compared with the SCIP method. This is practically useful for 'single-shot theories' in which each semiconductor pair should be calculated individually.

To simulate the Si/GaP(111) or Si/GaP($\bar{1}\bar{1}\bar{1}$) interface, an atomic slab containing six layers of Si and six alternately stacked layers of Ga and P was employed, as shown in figure 1(*a*). At the interface, the Si atoms are bonded to Ga and P atoms in the case of Si/GaP(111) or Si/GaP($\bar{1}\bar{1}\bar{1}$) with the bond length between Si and Ga (or P) taken to be the same as that in the bulk Si or GaP since this is a lattice-matched system. On both sides of the slab, the dangling bonds of Si and P (or Ga) were saturated with pseudo-atoms Si′ and Ga′ (or P′); the atomic orbitals of these were taken to be s like. By treating such an interface structure as a whole assembly, the detailed information about the interface states and their correlation to the valence band edges of the component materials could be derived.

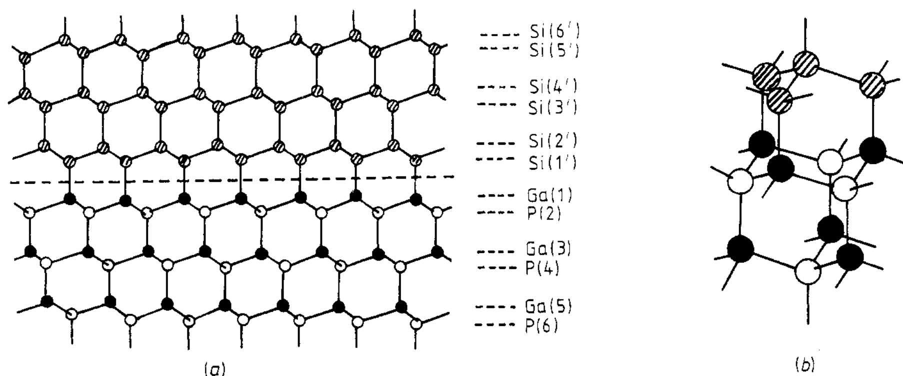

Figure 1. (*a*) A slab model and (*b*) a cluster model of a Si/GaP heterojunction (Si/GaP(111)): ▨, Si; ●, Ga; ○, P. Si′ means a Si pseudo-atom, A′ a P pseudo-atom, B′ a Ga pseudo-atom. For Si/GaP($\bar{1}\bar{1}\bar{1}$), Ga and P, and A′ and B′, are interchanged.

In order to save the computer time, we did not carry out the self-consistent calculation on the slab. Instead, the charge self-consistent calculations were first carried out on the cluster models. A $Si_{10}Si'_6$ cluster and a $Ga_4P_6Ga'_{12}P'_4$ (or $Ga_6P_4Ga'_4P'_{12}$) cluster was employed to simulate the bulk Si and GaP, respectively. The total density of states (TDOS) calculated from the self-consistent EHT agreed well with the result obtained by a first-principles calculation, if the adjustable empirical parameter set K_{ij} were chosen suitably. The next step was to carry out the self-consistent EHT calculation on a larger cluster $Si_4Ga_6P_4Si'_7Ga'_4P'_9$ (or $Si_4P_6Ga_4Si'_7P'_4Ga'_9$) as shown in figure 1(*b*), which could be used to simulate the Si/GaP interface system. The charge transfers obtained are $0.1e^-$ from Ga to Si at the Si/GaP(111) interface and $0.2e^-$ from Si to P at the Si–GaP($\bar{1}\bar{1}\bar{1}$) interface; both of these are smaller than that from Ga to P ($0.46e^-$) in bulk GaP. The

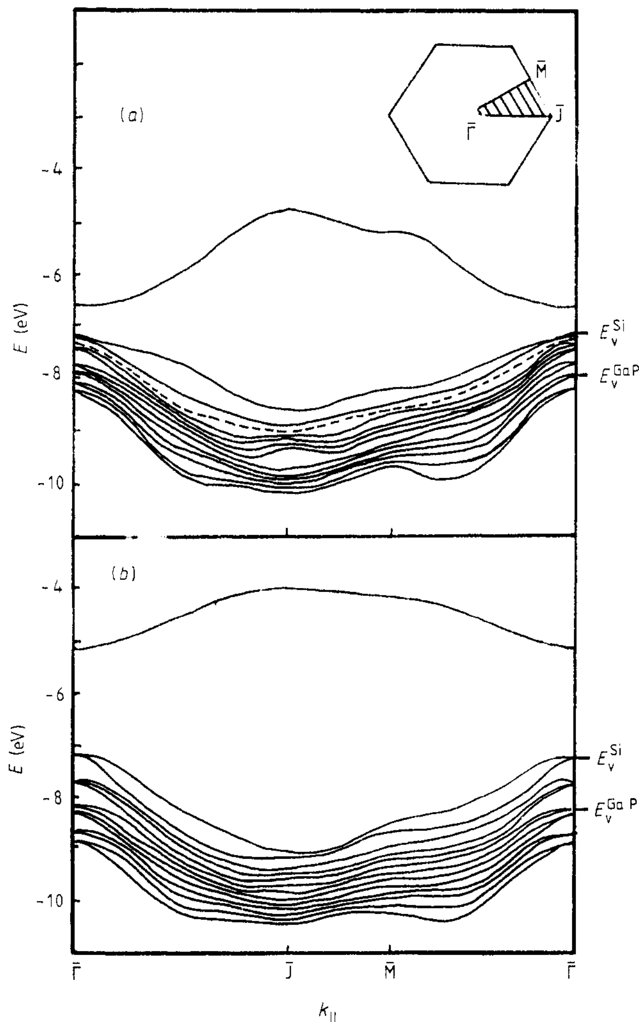

Figure 2. Two-dimensional projected energy band structures of (*a*) Si/GaP(111) and (*b*) Si/GaP($\bar{1}\bar{1}\bar{1}$). The energies refer to the zero ionisation potential. The inset shows the two-dimensional reduced Brillouin zone.

charge transfer leads to a reduction in the ionisation potentials of both Si and Ga atoms at the Si/GaP(111) interface, whereas, at the Si/GaP($\bar{1}\bar{1}\bar{1}$) interface, the ionisation potential becomes smaller for P atoms but larger for Si atoms. Although the TDOS for these interface systems could be derived from the calculation, it is difficult to designate the positions of valence band maxima (VBMs) for Si and GaP from the calculated electronic states since the clusters are too small.

Therefore, we must turn to the slab model as described in figure 1(*a*). The slab possesses two-dimensional periodicity parallel to the interface. The unit cell used in the calculation contains 12 real atoms and two pseudo-atoms. The two-dimensional Brillouin zone is shown as the inset to figure 2. In the EHT calculations, all the K-parameters and ionisation potentials used were derived from the previous EHT cluster results. The ionisation potentials for the atoms at the interface, i.e. the Si atom in layer 1 and the Ga (or P) atom in layer 2, were obtained from the self-consistent results of an interface cluster, whereas for other atomic layers the parameters derived from the self-consistent calculations of the bulk Si cluster and GaP cluster were chosen. The TDOS and the local density of states (LDOS) for each atomic layer in the system were calculated by taking into account 66 k-points in a one-twelfth reduced Brillouin zone (shown as the shaded part in figure 2). For comparison, the calculations on a slab containing only six layers of Si and a slab containing six alternately stacked Ga and P layers saturated with corresponding pseudo-atoms were also included.

Figures 2(*a*) and 2(*b*) show the calculated two-dimensional projected energy bands of Si/GaP(111) and Si/GaP($\bar{1}\bar{1}\bar{1}$) respectively. When the electronic population in the valence band is taken into account, it is shown that all the valence levels are fully occupied up to the highest-lying valence state. The problem of the appearance of unoccupied valence band states for the polar unreconstructed interfaces as pointed out in previous papers (Baraff *et al* 1977a, b) does not happen here. The characteristic of the wavefunction of the highest-lying valence energy state possesses predominantly the bulk properties of Si; so we can designate the maximum energy of this state at $\bar{\Gamma}$ point as the VBM on the Si side. Similarly, the VBM on the GaP side could also be assigned by identifying the valence energy state which possesses basically the bulk properties of GaP. The VBMs are indicated in figure 2 by E_v^{Si} and E_v^{GaP}. The valence band discontinuities given by the

Table 1. Calculated and measured ΔE_v for a GaP/Si heterojunction: EAR, electron affinity rule; LCAO, linear combination of atomic orbitals.

Method	ΔE_v (eV)	Reference
EAR prediction	0.33	Anderson (1962)
Harrison LCAO	0.50	Harrison (1977)
Frensley–Kroemer	0.96	Frensley and Kroemer (1977)
Adam–Nussbaum	0.58	Adam and Nussbaum (1979)
Von Ross	1.15	Von Ross (1980)
Tersoff	0.45	Tersoff (1984)
Harrison–Tersoff	0.86	Harrison and Tersoff (1986)
SCIP	0.61	Van de Walle and Martin (1987)
Experiment	0.8	Perfetti *et al* (1984)
Present work	0.88 (111)	
	0.97 ($\bar{1}\bar{1}\bar{1}$)	
	0.87 (110)	

difference between E_v^{Si} and E_v^{GaP} could be derived as $\Delta E_v = 0.88$ eV and 0.97 eV for Si/GaP(111) and Si/GaP($\bar{1}\bar{1}\bar{1}$), respectively. The valence band offset for a Si/GaP(110) system calculated by using a similar Si/GaP slab and the same approach was almost the same as that of Si/GaP(111) interface (0.87 eV). As a comparison, we list in table 1 various values of ΔE_v obtained by previous theoretical predictions as well as the experimental result on the Si/GaP(110) system. It is quite encouraging that our result is in better agreement with the observation than most of the previous theories.

Although the difference between ΔE_v for the three crystal orientations is not very large, the distribution of interface states and their effect on the band structure are significantly different. In figure 2(*a*), the broken curve is identified as an interface-related electronic state, the wavefunction of which arises mainly from the Si and Ga atoms at the interface. In contrast, for Si/GaP($\bar{1}\bar{1}\bar{1}$) the interface states lie dispersively within the valence band and are mixed with the bulk states, such that one could not distinguish a branch of dispersion curve solely contributed by the interface states in figure 2(*b*). However, from the LDOS at the interface which is different from that in the bulk in our calculations, we can derive the energy distribution of interface states even for the Si/GaP($\bar{1}\bar{1}\bar{1}$) system. Figure 3(*a*) and 3(*b*) and figure 3(*c*) and 3(*d*) show the LDOSs at each atomic layer for the Si/GaP(111) and Si/GaP($\bar{1}\bar{1}\bar{1}$) slabs, respectively. On the Si side, the LDOSs of the fourth and fifth layers are quite similar to each other and are comparable with the TDOS of a bulk Si crystal as shown by the broken curves in figures 3(*a*) and 3(*c*)

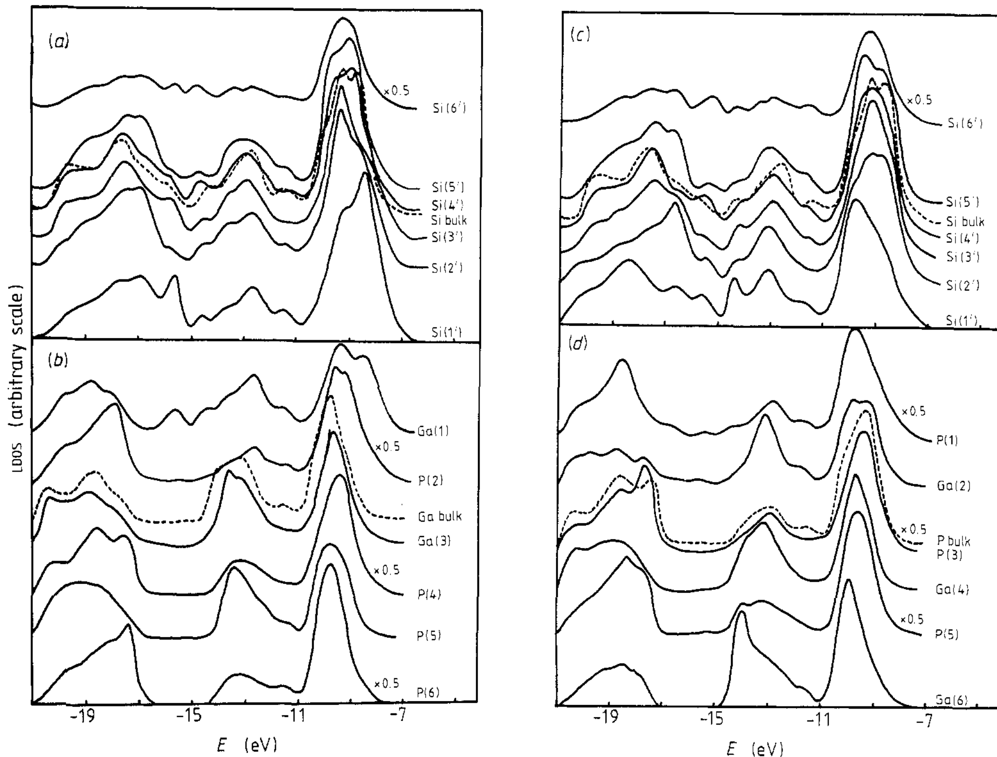

Figure 3. The LDOS of each atomic layer for (*a*), (*b*) a Si/GaP(111) slab and (*c*), (*d*) a Si/GaP($\bar{1}\bar{1}\bar{1}$) slab: ---, calculated LDOSs of a six-Si-layer slab (labelled Si bulk), and alternately stacked Ga–P–Ga–P–Ga–P slabs (labelled P bulk and Ga bulk).

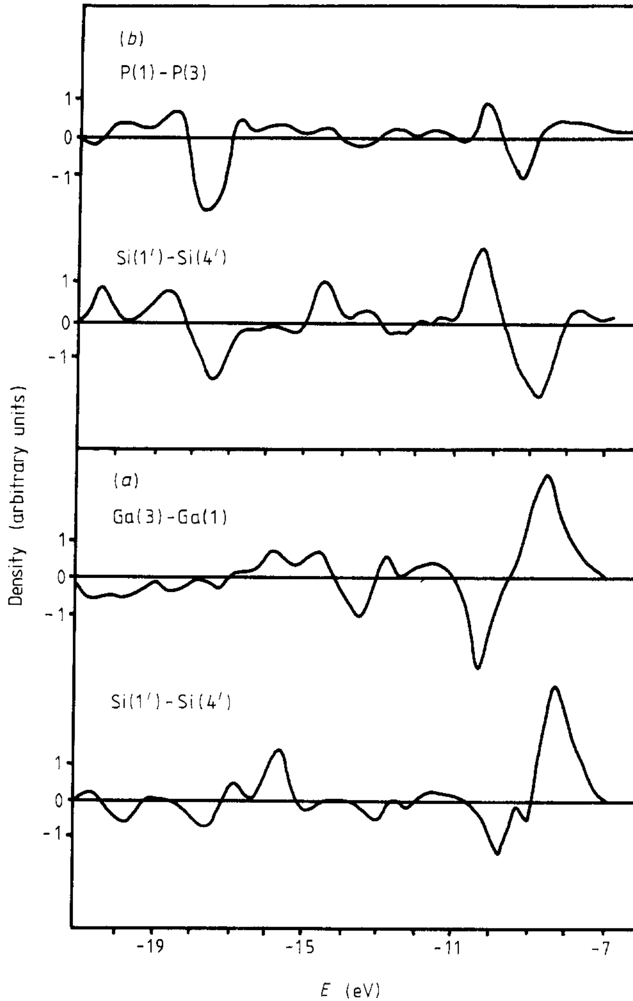

Figure 4. The densities of interface states obtained by the difference spectra of curves Ga(3)–Ga(1), P(3)–P(1) and Si(4')–Si(1'): (*a*) Si/GaP(111) interface; (*b*) Si/GaP($\bar{1}\bar{1}\bar{1}$) interface.

which was calculated by a slab containing only six layers of Si and two terminal layers of pseudo-atoms. On the GaP side, the LDOS of the third layer also coincides basically with the LDOS of a Ga layer or a P layer in bulk GaP (broken curves in figures 3(*b*) and 3(*d*)). The LDOS at the interface have different features from that of the bulk. This is attributed to the contribution of interface states. The difference spectra between Si(1') and Si(4') or Ga(1) or between P(1) and Ga(3) or P(3) represent the distribution of interface states as shown in figure 4. For Si/GaP(111), the major interface peak is located near the VBM of GaP, which coincides with the broken curve in figure 2(*a*). However, for Si/GaP($\bar{1}\bar{1}\bar{1}$), the major interface state peak is weaker and lower lying but its presence is definitive.

One point which is very important and should be mentioned, we believe, is that, although the values of ΔE_v are slightly different for different orientations, the electronic structures within the energy range of band discontinuity are dramatically deformed by

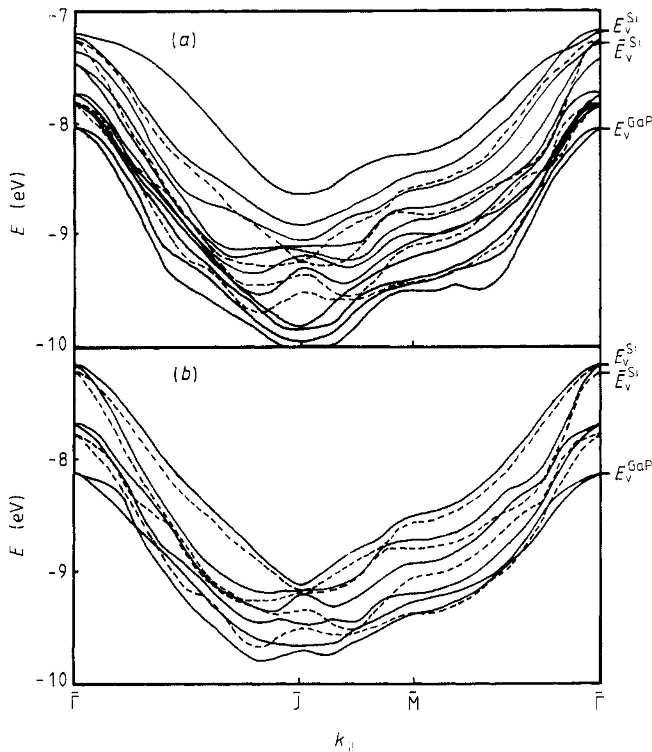

Figure 5. The higher-lying valence band structures: (*a*) bulk Si (---) and Si/GaAs(111) (——); (*b*) bulk Si (---) and Si/GaAs(111)(——). E_v^{Si} and E_v^{GaP} represent the VBMs of Si and GaP in Si/GaP; $\bar{E}_v^{Si}$ represents the VBM of bulk Si.

the influence of the interface. Figure 5 shows the band structures of figure 2 plotted on a larger scale near the energy interval of ΔE_v to show the deformation. This must be seriously considered in the optical and transport properties of the heterojunction, since these properties are closely related to the details of the band structure (effective mass, joint density of states, etc).

Here we treated only the discontinuity of valence band; since in the EHT, which is based on the LCAO method, only the valence orbitals of the atoms are involved, it is expected that satisfactory results could be derived only for the valence band but not the conduction band. In this method, only a set of parameters K_{ij} are adjustable; all the overlap integrals are non-parametric and are obtained from calculation. In principle, there will be no additional difficulties in applying this method for calculations on other heterojunction systems including lattice-mismatched systems. To confirm the effectiveness of this simple method as a general approach in calculating band offsets, further work is needed.

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