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Abstract. We have carried out a theoretical investigation of the surface electronic structure of the relaxed GaP(110) surface and of a monolayer of Sb on GaP(110) by a self-consistent tight-binding method. These calculations, yielding band structure and local densities of states, show some marked differences from other calculations. In addition we have been able to determine the amount of charge transferred between the Sb overlayer and the substrate.

1. Introduction

Over recent years there has been much work done on investigating the atomic and electronic structure of adatoms on semiconductor surfaces. The motivation for such work is a desire to understand both the structural and the electronic properties of semiconductor interfaces, which provide the basis of very-large-scale integration (VSLI) technology. Thus the electrical transport across interfaces is determined by the barriers (band offsets or Schottky barrier heights), which in turn depend on the amount of charge transfer across the interface and the presence of interface states. The optical properties also depend on these interface states and in particular on their position relative to the band edges. Many of the properties of the interface are established by the first monolayer deposited on a surface and as surface structures are more accessible to experimental investigation, it is not surprising that much effort has been directed towards surface studies.

Although many III–V semiconductor surfaces have been studied theoretically, these calculations have either been ones in which charge transfer has not been included [1, 2] or where density functional theory (DFT) in the local density approximation has been utilized [3–5]. In neglecting charge transfer effects on the band structure, calculations of the former type must necessarily give an incorrect description of systems in which these effects are important. Adatoms on surfaces naturally fall into this category and so investigations of such systems should be carried out using techniques which take into account changes in the electron potential due to charge rearrangement. Calculations using norm conserving non-local pseudopotentials and other *ab initio* methods such as the linear muffin tin orbital approach use DFT, which is only predicted to give the correct ground state (or occupied) density. Unoccupied states need not be correctly described and indeed the band gap in bulk semiconductors is usually underestimated. However, the consequences of this approximation are not restricted to the unoccupied states; the energies of surface states, which depend on the coupling of valence and conduction band states, also need to be shifted to agree with experimental measurements.

The tight-binding method in the extended Huckel approximation (TBEHA) is a self-consistent approach that has been shown to give results in excellent agreement with experiment for occupied and unoccupied electron states of semiconductor surfaces, with and without adatoms. It has also been used to study the band alignment at metal–semiconductor interfaces and semiconductor heterojunctions. We have therefore applied this method to make a fresh study of the Sb/Ga(110) surface. The system we have chosen has been investigated theoretically by both empirical tight-binding and pseudopotential methods and so is one in which it is possible to make a direct comparison of the different approaches. In the next section we give a brief outline of the TBEHA method and how it has been used to perform the surface electronic structure calculations. This is followed by the results, which are discussed in relation to other theoretical and experimental findings for similar adatom/III–V systems.

2. The TBEHA method

Tight-binding methods are increasingly being used to investigate various problems in condensed matter physics. This is no doubt due to the local description of the problem which is physically appealing and in addition gives deep insight about the nature of the chemical bonds at or near the surface. The extended Huckel method has been used to study the electronic structures of bulk transition metal silicides, investigate chemisorption sites and determine the influence of defects on the electronic structure of bulk materials. The self-consistency built into the model allows it to be used in the study of systems where charge transfer is an important factor. Thus it has proved to give an excellent description of the band alignment at metal–semiconductor interfaces (the Schottky barrier height) even to the extent of determining the pressure dependence of this alignment [6]. The success in describing these different systems gives confidence in the suitability of the approach to study adatoms on semiconductor surfaces.

In the tight-binding formalism, the Bloch functions are taken to be linear combinations of atomic orbitals labelled α centred on sites R_{li}

$$\Phi_{\alpha i}(k, r) = \frac{1}{\sqrt{N}} \sum_l \exp(ik \cdot R_{li}) \phi_\alpha (r - R_{li}) \tag{1}$$

where the summation is over all lattice vectors, N being the number of unit cells in the crystal and i the basis atom index. The energy eigenfunctions can then be written in the form

$$\Psi_n(k, r) = \frac{1}{\sqrt{B_n(k)}} \sum_{\alpha i} C_{\alpha i}(k, n) \Phi_{\alpha i}(k, r) \tag{2}$$

where n is the band index and $B_n(k)$ is a normalization factor. Substituting for Ψ in the one-electron Schrodinger equation leads to the secular equation

$$\det|H_{\alpha\beta}^{ij}(k) - E_n(k) S_{\alpha\beta}^{ij}(k)| = 0 \tag{3}$$

where H and S are the matrix elements of the effective Hamiltonian and the overlap matrix between the energy eigenfunctions.

In the extended Huckel approximation, we assume that the diagonal matrix elements of the Hamiltonian are given by the negative of the valence orbital ionization potential $I_{\alpha i}$ of

the αth orbital of the ith basis atom. The off-diagonal elements are obtained by relating them to the overlap matrix elements, viz.

$$H_{\alpha\beta}^{ij} = -0.5 K_{\alpha\beta}\left(I_{\alpha i} + I_{\beta j}\right) S_{\alpha\beta}^{ij} \tag{4}$$

where the $K_{\alpha\beta}$ are treated as constant parameters. For off-diagonal matrix elements involving two different atomic species, i and j, K was taken to be the arithmetic average of those of the two elements, viz. $\frac{1}{2}(K_{\alpha\beta}^{i} + K_{\alpha\beta}^{j})$.

The ionization potentials do of course depend on the charge on the atom and on its electron configuration and this can be put in the form

$$I_{\alpha i}(\Delta q) = P_{\alpha i} + Q_{\alpha i}\,\Delta q_i + \sum_j R_{ij}\,\Delta q_j \tag{5}$$

where Δq_i is the charge excess on atom i. $Q_{\alpha i}$ is the change in the orbital energy of atom i due to the deviation from charge neutrality and R_{ij} is the Coulomb repulsion integral between the charges on the different atoms. The constants P, Q and R were obtained from spectroscopic tables for the ionization potentials for neutral and ionized atoms. In the latter instance, the term energies need to be averaged over all multiplet configurations.

3. Calculational procedure

To calculate the overlap matrix and hence the Hamiltonian, the atomic functions were taken to be Slater type orbitals multiplied by an appropriate spherical harmonic term. The radial components were approximated by single or double zeta functions depending on the type of orbital. In general, the lower orbitals of the light elements required only single zeta functions whereas the higher-energy orbitals of heavy elements require at least double zeta functions. The overlap matrices S were calculated exactly for interatomic distances up to 7 Å as this was found to be sufficient for the bulk Si system. Beyond this range, the overlaps were negligibly small. For this particular system, this meant that each atom in the basis was allowed to interact with approximately 60 of its closest neighbours. The exponents of the zeta functions, and the constants K appearing in the tight-binding matrix elements in equation (4), were treated as parameters to be determined by ensuring that the appropriate bulk band structures are well produced.

Table 1. Parameters used in the calculations. ζ refers to the zeta function exponents appearing in the radial wavefunction.

	Ga	P	Sb
$\zeta(s)$	1.815	1.915	2.439
$\zeta(p)$	1.4	1.38	1.999
K_{ss}	1.3	1.4	2.0
K_{sp}	1.2	1.3	1.78
K_{pp}	1.3	1.4	1.52
P_s	9.44	11.15	10.45
P_p	7.33	8.99	7.6
Q_s	12.61	18.76	14.52
Q_p	6.5	10.15	8.44

The parameters for Ga and P were obtained by fitting the bulk GaP band structure to the results of the pseudopotential calculations of Chelikowsky and Cohen [7]. The parameters for Sb were obtained by fitting the band structure to that reported by Falicov and Lin [8]. These parameters (shown in table 1) were used in the surface calculations. To determine the electronic structure of clean GaP(110) and Sb/GaP(110), the systems were modelled as periodic structures made up of GaP slabs (including Sb where required) separated by a few 'layers' of vacuum. The width of the vacuum region was such that there was no interaction between the surfaces.

4. Results

4.1. The clean GaP(110) surface

For the clean Gap surface, the unit cell was taken to be orthorhombic in structure with the z axis perpendicular to the (110) plane. The length of the cell along the z axis was taken to be three times the bulk lattice constant. Two separate calculations were performed, one to simulate an unrelaxed clean surface and the other taking the known relaxation into account. The GaP slab comprised 11 GaP layers making 22 atoms in the unit cell. The odd number of layers is necessary to make the top and bottom layers of the slab equivalent and nullify any spurious results which might arise from a breaking of symmetry. For the relaxed structure the positions of the atoms in the top (and bottom) layer were taken from the results of Mailhiot *et al* [2] whereas the atoms in the other nine layers were assumed to occupy bulk positions.

The calculated electron energy band structure along symmetry directions for the *relaxed* structure is shown in figure 1 along with the total density of states (DOS) for the slab. The main differences between the unrelaxed and relaxed surfaces are the numbers and positions of the states in the bulk GaP band gap. Whereas the unrelaxed surface shows four states right across the gap, the relaxed surface displays only three states, one unoccupied state (C4) in the upper half of the band gap and two occupied states (A3 and A4) near the valence band edge. However, A3 is always below the valence band maximum (VBM). Total and local DOSs are shown in figure 1(*b*). These show that the unoccupied surface state is derived from the Ga atom in the surface layer and the occupied surface states from the surface P atom. These states correspond to the dangling bond states found by both Alves *et al* [5] and Manghi *et al* [3]. Whereas the latter find all three states pushed out of the bandgap, the former find two states in the gap, one unoccupied cation state and one occupied anion state; however these states are closer to the band edges than the ones observed in our calculation. The mean energy of C4 is in good agreement with the experimental position of unoccupied surface states at ~ 1 eV below E_c observed in 'partial yield' spectroscopy [9].

4.2. The Sb/GaP(110) surface

The electronic structure of Sb monolayers on GaP(110) was calculated in a manner similar to that used for the clean surface. The geometric structure was assumed to be the same as that predicted by a total energy calculation [1] in which the Sb overlayer atoms saturate the dangling bonds of both the Ga and P atoms. The slab was taken to consist of nine layers of GaP (nine Ga atoms plus nine P atoms) with one layer of Sb at the top (two atoms) and at the bottom. Thus the total number of atoms in both calculations was the same and the size of the unit cell was also taken to be the same as for the clean surface computation.

The electronic band structure of Sb/GaP(110) is shown in figure 2. The occupied (S8) and unoccupied (S9) surface states are both outside the fundamental band gap. In figure 3
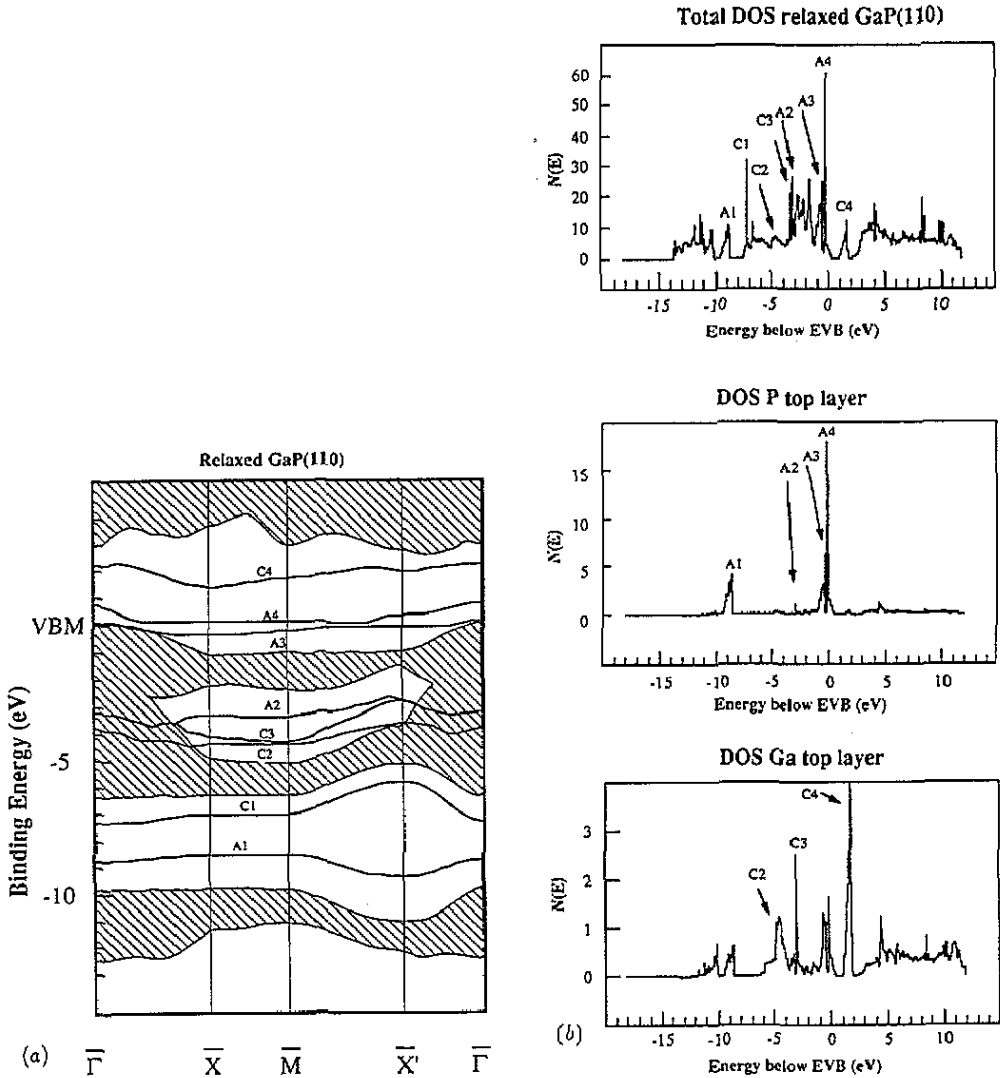
Total DOS relaxed GaP(110)

Relaxed GaP(110)

DOS P top layer

DOS Ga top layer

Figure 1. (*a*) The electronic band structure of the clean relaxed GaP(110) surface. The surface states are shown as full curves against the projection of the bulk band structure. C*i* refer to the cation derived states and A*i* refer to anion derived states. (*b*) The total DOS and local (surface Ga and P) DOS for the clean surface. The energies are all taken with respect to the valence band maximum in bulk GaP.

the total DOS for this system are shown and the local DOS contributions at Ga and P just below the surface as well as that of the Sb layer. This top-layer contribution is further separated into those from the Sb atoms bonded to the Ga atoms (Sb1) and those bonded to the P atoms (Sb2). The lowest surface state labelled S1 can be seen in the Sb1 and P LDOS suggesting an Sb–P bond state. The next prominent features are the S2 and S3 states. While the former is derived mainly from the two Sb atoms and P, the latter has a large contribution from the Ga atom. There are three states in the stomach gap (S4, S5 and S6) and they appear to be derived largely from the P and Sb atoms. At the valence band edge, the states S7 and S8 are from the Sb1 and P atoms. The states at the conduction band
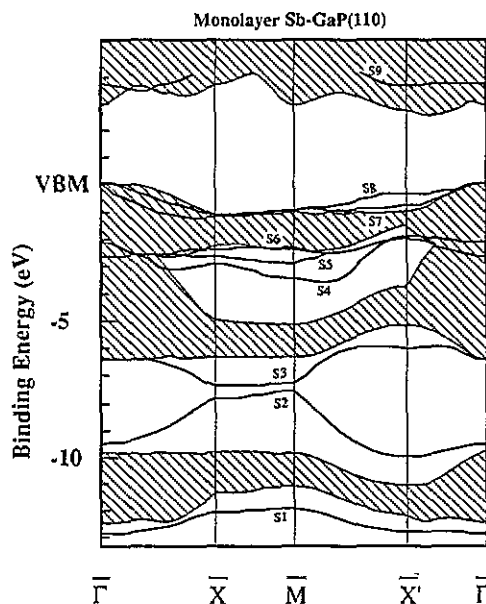
Figure 2. The electronic band structure for the Sb/GaP(110) system.

edge (S9) are clearly Sb–Sb and Sb–Ga antibonding states corresponding to the S2 and S3 bonding states.

We have also been able to determine the amount of charge transfer between the overlayer and the substrate by performing a Mulliken charge analysis on the wavefunctions. The excess (positive) valence charges for the atoms in one half of the slab are shown in table 2. It can be seen quite clearly that Ga atoms in the layer beneath the Sb atoms are less positively charged than Ga atoms in the bulk.

Table 2. Excess positive charge Δq on each atom in the slab starting from the surface and ending in the middle of the bulk.

Atom (layer)	Δq
Sb1(1)	0.05
Sb2(1)	−0.06
Ga(2)	0.10
P(2)	−0.14
Ga(3)	0.12
P(3)	−0.21
Ga(4)	0.16
P(4)	−0.13
Ga(5)	0.17
P(5)	−0.12
Ga(6)	0.17
P(6)	−0.12

5. Conclusions

We have performed self-consistent electronic structure calculations using a method which has been proven to give good descriptions of surface states and wavefunctions for other
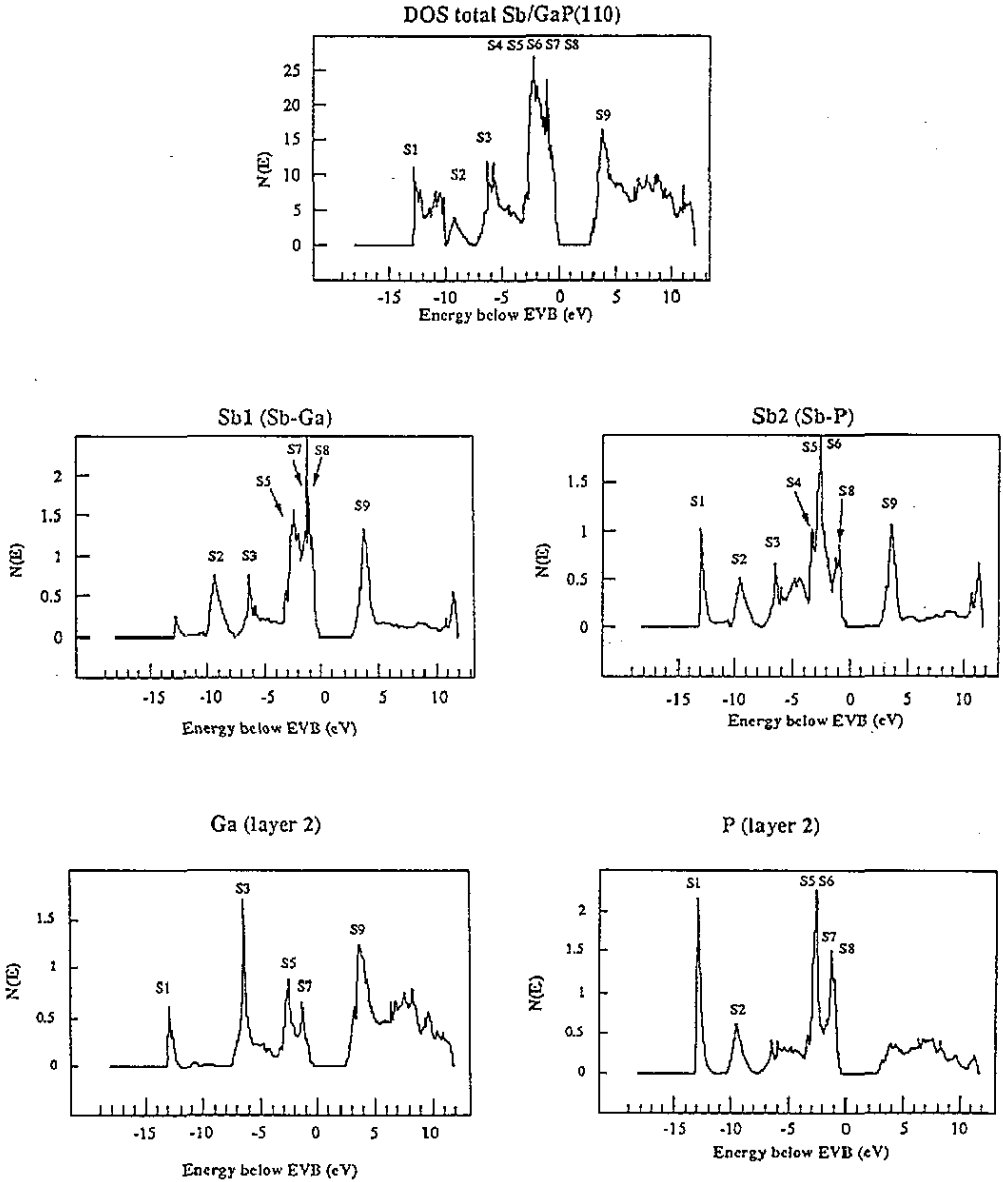
Figure 3. The total DOS for the Sb/GaP cell and local DOS at the surface Sb atoms and at the Ga and P atoms one layer below.

semiconductor surfaces. The results for the clean GaP surface and the Sb/GaP surface are different from two other calculations using the same geometry but different approaches. The pseudopotential calculation of Manghi *et al* [3, 4], although self-consistent, suffers from a possible non-convergence in the energy eigenvalues due to an insufficient number of plane waves. The tight-binding results of Mailhiot *et al* [1, 2] are not self-consistent and so are open to doubt. The new features arising from our work can be summarized as follows:

(1) The clean relaxed GaP(110) surface does have states in the band gap. The location of the unoccupied (Ga) state agrees with 'partial yield' data [9].

(2) An Sb overlayer on GaP(110) results in a complete passivation of the surface due to a mopping up of the bonds.

(3) The location of the occupied state S8 at Γ for the Sb/GaP(110) interface agrees with photoemission measurements [10].

(4) The Ga–Sb bonding states (S3) lie toward the bottom of the valence band and the antibonding states (S9) are found at the conduction band edge.

(5) Sb also bonds with P but this is a much weaker bond, so bonding and antibonding states (S4–S8) are close to the valence band edge and are filled. Also there is incomplete bonding as can be deduced from the presence of the P derived state below the bottom of the valence band.

(6) Although the charge on the P atom in the layer beneath the Sb is close to that in the bulk region, the Ga atom in the same layer is less positively charged, showing the difference in the Ga–Sb and P–Sb bonding strengths.

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