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Theoretical approaches of semiconductor interfaces and of their defects : recent developments

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Résumé. — Nous donnons ici une revue des diverses études théoriques sur les interfaces de semiconducteurs et leurs défauts. Divers aspects sont considérés : d'une part le problème délicat de l'approximation de la masse effective (utilisée très fréquemment) et de ses limitations ; d'autre part nous passons en revue les différentes approches possibles pour le calcul des discontinuités de bandes à l'hétérojonction ; une attention particulière est accordée aux modifications apportées par la présence d'une contrainte biaxiale (due à un désaccord de maille) ; enfin divers défauts localisés à l'interface, qui ont fait l'objet d'études récentes, sont pris en compte.

Abstract. — We describe recent developments of theoretical studies concerning semiconductor interfaces from different points of view : the widely used effective mass approximation and its limitations are considered ; different ways to calculate band offsets are described and compared ; the interesting problem of the effect of strains is discussed ; several interface defects that have been recently studied are also considered.

1. Introduction.

The aim of the present paper is to provide a general picture of the theoretical approaches of interfaces of tetrahedral semiconductors and of their defects.

In this framework it is very important to first consider the widely used effective mass approximation, and in particular the main problem raised by the boundary conditions at the interface. As a matter of fact, it appears that the widely used boundary conditions are quite inaccurate in some cases. This is the purpose of section 2.

Section 3 is devoted to a leading parameter of every heterojunction device, that is the band offset. The different calculations of band offsets do split into two types : empirical approaches where band offsets result from bulk properties of the two components of the heterojunction, and direct calculations, taking into account charge transfers across the interface.

In many heterojunctions, lattice mismatch induces some biaxial strain. This biaxial strain can have a very strong influence on the system, as some features specific to strained systems appear. This is discussed in section 4.

In section 5, we consider some defects localised near the interface that have been recently studied, and especially how these defects modify band offsets.

2. The effective mass approximation and boundary conditions.

The most commonly and widely used method for determining electronic states in bulk semiconductors is the effective-mass approximation (EMA). In the EMA, the total wave function is written as the product of the Bloch function (which varies rapidly within each unit cell) times a slowly varying envelope function. The Bloch function describes the perfect material for energies closed to a band extremum, and the envelope appears in a Schrödinger-like equation involving the effective masses [1]. The conventional EMA is not directly applicable to heterostructures, because the potential varies strongly within the distance of the lattice constant at the heterojunctions. Effects of such hetero-interfaces can be incorporated only in the form of *boundary conditions for envelope functions*. The choice of these boundary conditions is very important. Several theoretical works [2-14] have dealt with this point, and some of them have shown that the use of inaccurate boundary conditions can lead, in some special cases, to misleading conclusions. These works are recalled just below.

The EMA is widely used because it has advantages compared to direct tight-binding or empirical pseudopotential calculations. It leads to much simpler calculations and can easily be applied to self consistent descriptions of band bending due to charge redistribution [15, 16]. It is very practical for describing impurities or excitons, magnetic as well as the effect of electric fields. For transport properties and device simulations, EMA is practically the single available tool.

In the effective mass approximation, allowed energies are solutions of Schrödinger's equation written as follows :

$$\left[-\frac{\hbar^2}{2m^*} \Delta + V(r) \right] F_n(r) = (E - E_n^0) F_n(r) \quad (1)$$

where E_n^0 is the allowed energy of the perfect crystal, V the perturbation potential, and $F_n(r)$ is not the total wave function, but only its envelope function. The first term of the left hand side describes the effect of the band structure, for energies near a single non degenerate extremum, it is given by the effective mass m^* ; in the vicinity of a degenerate band (like the top of valence band) it has to be replaced by a matrix operator [1]. As V has to be slowly varying, equation (1) is applied on each side of the heterojunction, and then one has to match the solutions from both sides of the interface.

The most widely used conventional boundary conditions, first proposed by Ben Daniel and Duke [2], consist to impose the continuity of the envelope function and of $1/m^*$ times its first derivative, assuming that this is equivalent to continuity of the wave function and conservation of the current probability across the interface. But, as shown by Kroemer and Zhu, these conditions are very often invalid. However these approximate conditions frequently give results in good agreement with experiment. More recently Burt [6] has derived the exact equations. They allow one to identify the terms that are implicitly omitted in the standard envelope function approximation and give valuable insight into the reasons of its success. These omitted terms correspond to the rapidly varying part of the wave function (that is the Bloch function), so the conventional envelope function approximation is quite justified whenever the bulk Bloch functions are practically similar on both sides of the heterojunction. On the other hand, it becomes inappropriate for systems where the bulk structures are different, as for example for systems including one direct gap material and one indirect gap material, or strained systems. Quite recently Ando and his coworkers [13, 14]

have clearly demonstrated the failure of conventional boundary conditions in a direct/indirect gap system ($\text{Ga}_x\text{Al}_{1-x}\text{As}/\text{Ga}_y\text{Al}_{1-y}\text{As}$). In [13] they propose, using the interface matrix formalism [12], a way to derive accurate boundary conditions: the interface matrix (that relates envelope functions and their first derivative in both sides of the interface) is determined with an « exact » calculation (either tight-binding or empirical pseudopotentials plus the use of the $\mathbf{k} \cdot \mathbf{p}$ formalism) and then can be used in an envelope function description. It appears that, depending on which band extrema are close to each other in energy, the interface matrix is either equal to :

$$T_{AB} = \begin{vmatrix} 1 & 0 \\ 0 & m_B/m_A \end{vmatrix} \quad (2)$$

that corresponds to the conventional boundary conditions, or it can be strongly different, as in the InAs/GaSb system :

$$T(\text{InAs} \leftarrow \text{GaSb}) = \begin{vmatrix} 0.033 & 2.113 \\ 0.268 & 0.033 \end{vmatrix}. \quad (3)$$

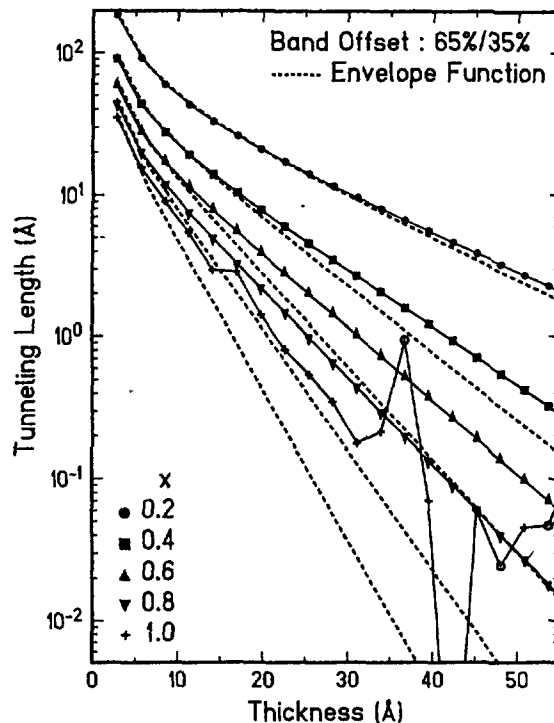


Fig. 1. — Calculated tunneling length (proportional to the tunneling probability) as a function of the thickness of the barrier $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layer for different x 's. For high potential barriers the envelope-function approximation underestimates the tunneling probability considerably. (For $x = 1$, the tunneling length exhibits nonsmooth dependence on the barrier thickness and can also be negative (open circles) due to resonances and antiresonances with virtual bound states associated with the X valley.) (From Ref. [14].)

Moreover the interface matrix depends on whether the interface consists of Ga-As or Sb-In atoms. In [14], application to tunnelling across a barrier clearly shows the failure of the standard envelope function approximation : for $\text{Ga}_x\text{Al}_{1-x}\text{As}$ barriers in GaAs, figure 1 points out the strong deviation of the tunneling length from classical EFA results. Interface matrix formalism allows to take into account the important point of mixing of Γ and X valleys that occurs very clearly in $(\text{Ga}_{0.32}\text{Al}_{0.68}\text{As}/\text{Ga}_{0.5}\text{Al}_{0.5}\text{As})$ system as illustrated in figure 2. One can note that deviations from the standard envelope function approximation pointed out in [14] appear when bulk Bloch functions are strongly different from one side to another. Similar behavior could happen in strained systems, but this has not yet been studied.

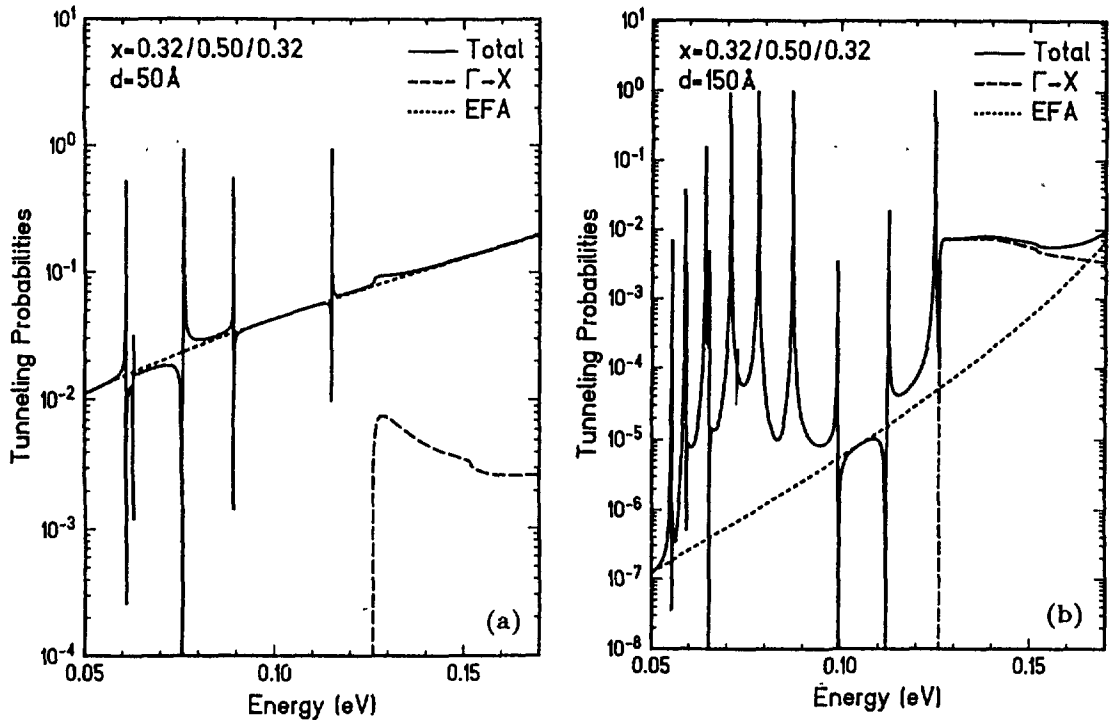


Fig. 2. — Calculated tunneling probabilities as a function of energy across a single-barrier structure consisting of $\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$, $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$, and $\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$. Electrons are incident from the left-hand side in the Γ valley. When the barrier thickness d is small [(a) $d = 50 \text{ \AA}$] and the tunneling within the Γ valley is dominant, the presence of virtual bound states in the X valley in the barrier layer gives rise to small constructive and destructive interferences with waves in the Γ valley. With the increase of the barrier thickness [(b) $d = 150 \text{ \AA}$], the tunneling through Γ -X- Γ channels becomes dominant (from Ref. [14]).

In this section, we have reported different works dealing with the description of heterojunctions within the effective-mass approximation. All these works tell the reader to use it very cautiously for heterojunction treatments. Let us now focus our attention to band offsets.

3. Theoretical determinations of band offsets.

The crucial parameters which determine the electronic behavior of the heterojunction interface are the valence and conduction band-edge discontinuities. These discontinuities play a role analogous to the p- and n-type Schottky barrier heights at metal-semiconductor

interfaces, in that they determine the barrier for hole or electron transport across the interface, and act as boundary conditions in calculations of band bending and interface electrostatics. This section attempts to give an overview of the theoretical understanding of heterojunction band lineups (a more detailed discussion of all these theories is given in [17]). One can distinguish two types of calculations in this field : (i) full selfconsistent calculations, taking into account charge transfers across the interface (these calculations are described in Sect. 3.2) ; (ii) simpler approaches in which band offsets are related to bulk quantities (these are reviewed in Sect. 3.1).

3.1 « BULK » APPROACHES FOR BAND OFFSETS. — The earliest experimental determinations of band offsets have been interpreted by means of theories which refer bulk band structures of semiconductors to an absolute reference level. The most famous of these theories is certainly the *Anderson's electron affinity rule* [18]. In this theory, the reference level is assumed to be the surface vacuum energy level. Thus the conduction band discontinuity becomes equal to the difference of electron affinities. The main failure of this rule is due to the fact that the ionization potential is not a bulk property, but depends on the surface, and is affected by surface reconstructions and relaxations which may be entirely irrelevant to the structure of the heterojunction interface.

An other approach based on reference surfaces is due to Harrison [19]. He uses a tight-binding description which takes as starting point the free atom term values plus interatomic matrix elements. This approach is reasonably successful in predicting band lineups ; as shown in reference [17], the typical errors are found to be about 0.2-0.4 eV.

Among all the bulk approaches for determining band offsets, the most successful attempt was provided by the concept of « charge neutrality level » [20, 21]. For the semiconductor this level E_B plays the same role as the Fermi level for a metal. Thus the Schottky barrier height is simply obtained by aligning the metal Fermi level E_F and the semiconductor neutrality level E_B . In a similar way, the heterojunction band offset is obtained by aligning E_B on both sides. Several solutions for determining E_B were then proposed : Harrison and Tersoff [22] have shown that it could be related to the average sp^3 energy level of anion and cation ; other groups [23, 24] have assimilated it to the cation vacancy level ; our group [25] has proposed to relate it to the average dangling bond energy. At both types of interfaces, dangling bonds are strongly coupled either to metal atoms or to other dangling bonds and one could believe that the « concept » of dangling bond is no more interesting. This is not so however since they play at least the role of a reference level. The argument at the metal semiconductor interface is that the interaction between the surface dangling bond and the metallic continuum leads to a half filled resonance centered on the average dangling bond energy. If the resonance has symmetrical shape the direct conclusion is that the Fermi level is at the average dangling bond energy E_{db} . One is thus led to identify E_{db} with the neutrality level E_B . This is confirmed for heterojunctions where one can show [25] that the condition of local neutrality on each side of the interface corresponds to the alignment of E_{db} on each side. Finally, as emphasized in figure 3, numerical calculations of E_{db} still give more credit to this identification.

An interesting question in this field has been the empirical correlation which has been shown to exist between transition metal impurity levels, Schottky barrier heights and heterojunction band offsets. Thus an other empirical approach, offering surprising accuracy in the prediction of band offsets has been proposed [26, 27]. This approach, is based upon the assumption that a reference level, which seems to exist for transition metal (TM) impurities in semiconductors, may be used for determining band offsets. It has been observed that the relative ordering of the ionization energies for the whole series of TM's is preserved when the isovalent host is changed. It is therefore possible, by a shift in the valence band edges of two isovalent semiconductors, to align the respective TM ionization levels. Several explanations

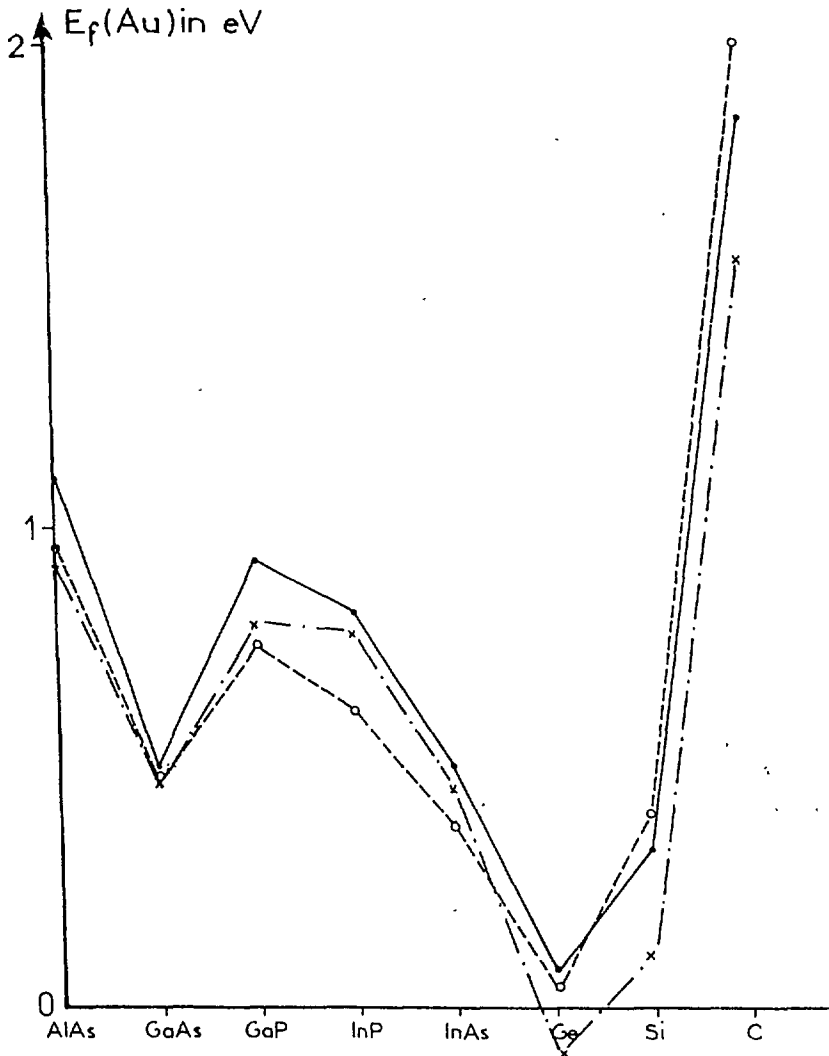


Fig. 3. — Surface Fermi energy for Au on different semiconductors. Comparison between the experimental value (solid line) and the average dangling bond energy obtained with two different sets of tight-binding parameters (given in Ref. [25]). The differences between the two sets of results (dotted and dashed dotted line) are only indicative of the error bars inherent to empirical tight-binding theory (from Ref. [25]).

for this have been proposed. First Zunger [28] identified the reference level with the vacuum level. Thus differences between reference levels should be equal to differences between electronic affinities. This is not the case within the range of 100 meV. Tersoff and Harrison [29] have concluded, on the basis of a defect molecule model previously introduced by Picoli *et al.* [30], that the TM impurity levels are pinned to the bulk cation vacancy level. Following what had been shown for band offsets, Delerue *et al.* [31] identified the reference level with the average self energy of dangling bonds. They performed a self consistent charge dependent tight-binding calculation. This showed that, because of strong Coulomb interactions, the TM impurity level is pinned to a bulk level, the latter being related to the average dangling bond

energy and not just to the cation vacancy level because of long range effects (delocalisation, screening).

Here we have emphasized the role of dangling bonds in band alignment at heterojunctions ; for more detailed reviews on this subject see [30] and [31], entirely devoted to these topics.

3.2 FULL SELFCONSISTENT CALCULATIONS. — Here we consider microscopic theories based on direct solution of the Schrödinger equation. These are based on the calculation of charge transfers across the interface, which provides the mechanism of band alignments. In this field, one has to separate *a priori* and empirical calculations.

The calculations based on first principles use either the pseudopotential technique (this has been done by Martin and Van de Walle [34]) or the Linear-Muffin-Tin-Orbital method (applied to band offsets calculations by Christensen and Cardona [35, 36]). These calculations, which are a bit heavy and require the use of powerful computers, should, in principle, provide quite accurate results. Nevertheless they contain a few approximations, the crudest being the use of the local-density approximation (LDA) for correlation and exchange. LDA, indeed, is known to give large errors in the calculated band gaps. If the band gap values are wrong, there must be a corresponding error in the band-edge discontinuities. It is usually assumed that the calculated discontinuity is more reliable for the valence band than for the conduction band, and the conduction band discontinuity is related to the valence band discontinuity *via* the experimental band gaps difference. However Carlsson has shown [37] that the error in the LDA band gaps comes from errors in both valence and conduction bands, with the valence band error in fact being the larger of the two (typically 0.5 eV). Of course the LDA errors in the two semiconductors could cancel each other. But Zhang *et al.* [38] have shown that the LDA errors on valence band offset discontinuity are typically 0.12 eV. This explains why first principles determinations of band offsets give results not so close to experimental values, as indicated in table I (where we have reported, in order to allow comparison, calculated valence band offsets for several lattice matched heterojunctions).

The semi-empirical descriptions of heterojunctions use either pseudopotentials, or the

Table I. — *Experiment and theoretical results for valence-band discontinuities, in eV, for lattice matched interfaces from various approaches : a) selfconsistent a priori pseudopotentials [34] ; b) empirical pseudopotentials [39] ; c) selfconsistent LMTO 7 + 7 superlattice [35] ; d) « LMTO dielectric midpoint energy model », [36] ; e) selfconsistent tight-binding [42]. Results for which the discrepancy with experiment is lower than 100 meV are underlined ; if the agreement is better than 50 meV, the result is doubly underlined.*

System	Exp.	a	b	c	d	e
AlAs/GaAs	0.45, 0.55	<u>0.37</u>	0.25	<u>0.53</u>	<u>0.43</u>	<u>0.50</u>
InAs/GaSb	0.51	0.38		<u>0.46</u>	<u>0.55</u>	
ZnSe/GaAs	1.10	1.59	2.0	<u>1.07</u>	0.99	
ZnSe/Ge	1.52	2.17	2.0	<u>1.58</u>	<u>1.46</u>	
GaAs/Ge	0.53	<u>0.63</u>	0.35	<u>0.46</u>	<u>0.51</u>	
AlAs/Ge	0.95	<u>1.05</u>		<u>1.03</u>	<u>0.87</u>	
AlSb/GaSb	0.45	<u>0.38</u>		<u>0.45</u>	<u>0.34</u>	<u>0.45</u>
CdTe/HgTe	0.35			<u>0.22</u>	0.64	<u>0.39</u>
AIP/Si		1.03			0.92	
GaP/Si	0.80	0.61		0.27	0.53	
GaP/AIP		0.36			0.38	

tight-binding formalism. Their main interest is that they consider realistic bulk band structures. The earliest band offset calculations of that type have been performed by Pickett *et al.* [39], using empirical forms for the pseudopotentials. The results present strong discrepancies with experiment, as can be shown in table I. This is probably the reason why empirical pseudopotential have no longer be used for band discontinuities calculations, but rather for band structure determinations as recently done by Friedel *et al.* [40] for the strained Si-Ge interface. The way of calculating band offsets within the tight-binding approximation has been set up jointly by Flores' group [41], and our group [42]. As dielectric constants in the studied materials are of the order of 10, a *numerical* accuracy of 10 meV requires a knowledge of the charge modifications induced by the presence of the interface with precision better than at 0.001 electron. This accuracy is not trivial, and has been reached only with the use of a decimation technique. As can be seen in table I, the band discontinuities calculated in this way agree fairly well with experimental data (we have estimated the error bound to the empirical tight-binding description to about 100 meV). This is due to the fact that the starting point is realistic bulk band structures, and that we have set up, for the self-consistent treatment, an accurate description of charge screenings and transfers. The last column of table I, corresponding to the tight-binding treatment, presents only 3 results because, up to now, interactions crossing the interface are well defined only when the system presents a common cation or anion, the other cases requiring a more elaborate study (we have recently started such a study, and we hope this will allow to be free of the «common atom limitation »).

Table I indicates that, at this time, several theoretical models are available, which can predict band offsets with an accuracy of about 100 meV. Up to now, we have not considered lattice mismatched systems, this being done in the next section.

4. Lattice mismatched heterojunctions.

These systems are of great interest, at least because they provide a large range of systems, with the possibility of « tailoring » band discontinuities for device applications (they are widely considered for optoelectronic applications). The development of epitaxial growth has provided high quality lattice mismatched superlattices or quantum well systems. Whenever the lattice mismatch is weak enough (lower than 10 %) and strained layer thicknesses are small enough (the critical thickness is related to the strain, as established by Matthews and Blakeslee [43]), the mismatch is entirely taken up by elastic strains, and misfit dislocations generation is avoided. Substrate imposes the in-plane lattice parameter (in the layers planes), which determines the biaxial stress. The latter can be decomposed as the sum of a purely hydrostatic part, plus a uniaxial part. The stress components of these two parts are simply related to the lattice parameters and elastic constants :

$$\left. \begin{aligned} \frac{a_{\perp}}{a_{\parallel}} &= \left(1 + 2 \frac{C_{12}}{C_{11}} \right) \frac{a_0}{a_{\parallel}} - 2 \frac{C_{12}}{C_{11}} \\ \varepsilon^{zz} &= \frac{1 - \frac{a_{\perp}}{a_{\parallel}}}{1 + \frac{a_{\perp}}{a_{\parallel}} + \frac{C_{11}}{C_{12}}} \\ \varepsilon^{xx} &= - \left(\frac{C_{11} + C_{12}}{C_{12}} \right) \varepsilon^{zz} \\ \varepsilon_h &= \frac{a_{\parallel}}{a_0} \left(\frac{1}{1 + \varepsilon^{zz}} \right) - 1 \end{aligned} \right\} \quad (4)$$

where a_{\parallel} is in-plane parameter (given by the substrate), a_0 is the unstrained lattice parameter, C_{11} and C_{12} are the elastic constants and ϵ_h and $(\epsilon^{xx}, \epsilon^{yy} = \epsilon^{zz})$ the hydrostatic and uniaxial stress components.

The first effect of strain is to alter the atomic positions, thus to modify charge distributions, and then charges transfers at the heterojunctions. Therefore band discontinuities are modified.

But an important point that one has to keep in mind is that strains also change bulk band structures of strained materials : bands are shifted and distorted (for example, at the top of the valence band the degeneracy is removed as shown in Fig. 4). Provided the stress is kept small enough, strain induced shifts of band edges are related to a and b deformation potentials [44, 45] and the stress components as given by [46] :

$$\left. \begin{aligned} \Delta(E_c - E_v^{av}) &= 3 a \epsilon_h + a (\epsilon_u^{xx} + 2 \epsilon_u^{zz}) \\ E_{v2} - E_v^{av} &= \frac{1}{3} \Delta_0 - b (\epsilon_u^{xx} - \epsilon_u^{zz}) \\ E_{v1} - E_v^{av} &= -\frac{1}{6} \Delta_0 + \frac{1}{2} b (\epsilon_u^{xx} - \epsilon_u^{zz}) + \frac{1}{2} \sqrt{\Delta_0^2 + 2 \Delta_0 b (\epsilon_u^{xx} - \epsilon_u^{zz}) + 9 b^2 (\epsilon_u^{xx} - \epsilon_u^{zz})^2} \\ E_{v3} - E_v^{av} &= -\frac{1}{6} \Delta_0 + \frac{1}{2} b (\epsilon_u^{xx} - \epsilon_u^{zz}) - \frac{1}{2} \sqrt{\Delta_0^2 + 2 \Delta_0 b (\epsilon_u^{xx} - \epsilon_u^{zz}) + 9 b^2 (\epsilon_u^{xx} - \epsilon_u^{zz})^2} \end{aligned} \right\} \quad (5)$$

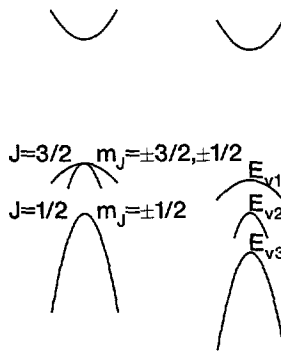


Fig. 4. — The left hand side shows the valence band and lowest conduction band in an unstrained direct gap zinc-blende compound near $k = 0$. The right hand side shows the effect of compressive stress on the bands.

E_c is the bottom of conduction band (here we consider direct gap semiconductors), E_v^{av} is the average top of the valence band (split into three bands : v_1 corresponds to light holes (LH), v_2 to heavy holes (HH) and v_3 to the spin-orbit split-off band (SO).

Using equation (5) and (4), as the b deformation potential is negative, it is straightforward to show that, under a compressive stress ($a_{\parallel} < a_0$), the HH level is shifted upwards and the LH level is shifted downwards, and this is the contrary for an extensive stress ($a_{\parallel} > a_0$). This result is in fact partly misleading : the strains do not shift bands quite rigidly indeed, but also modify band shapes, and consequently effective masses. So the HH band does no longer correspond to a heavy hole mass in all the directions. At the opposite of a hydrostatic strain, the biaxial strain induces a strong coupling between HH, LH, and SO bands and a strong anisotropy. This is why the « heavy hole » band corresponds to a heavy mass in the growth

direction and to a light mass in the layer planes. This is the « mass crossover » phenomenon [47, 48]. In this field, theoretical calculations are rather rare [45-50], the attention being focused on band edge energies rather than on masses. We have recently studied the problem of stress dependent conduction and electron masses within the tight-binding approximation [51]. From this study the crossover of the « heavy » hole band clearly appears. The behavior of the « light » hole band is not so clear. This result has to be supported by a pseudopotential description of the semiconductor under biaxial stress and also a more analytical treatment using the $\mathbf{k} \cdot \mathbf{p}$ formalism (both these studies are currently in progress). If this feature is confirmed, this would be of great importance for devices using extensively strained materials.

An other point has to be clarified : in the studies using Luttinger's Hamiltonian [1], the strain induced modifications are often confined to a diagonal additional terms which describes band edge shifts. In principle off-diagonal Luttinger matrix elements are modified by the symmetry break but nobody knows how they are modified and what consequences would follow for the band structure.

As indicated above, the strains modify band offsets [52, 53]. In mismatched interface, the concept of ratio E_c/E_v^{3v} is no longer so useful as, for a given system (e.g. GaAs/InAs), it strongly varies with the strain (from 87/13 for a GaAs substrate to 63/37 for an InAs substrate). Whether light and heavy holes are localised in one material or in the other also depends on strain [53].

X-ray photoemission spectroscopy is used to measure valence band offsets. The principle of the measurement is illustrated by figure 5. The difference between core levels on both sides of the interface is measured, and the valence band offset is deduced, with the introduction of energetic distances between core levels and the top of the valence band in the bulk material. Application of this technique to strained systems provides an « unstrained valence band offset » [54] that has to be related to the real valence band offset. Thus, the question is : how does the strain modify the difference between the top of the valence band and core levels ? The problem of the top of the valence band has been discussed earlier, but the strain induced core level shift is still unknown. This point is quite controversial at this time : in both theoretical and experimental work of Schwartz *et al.* [55], core levels are implicitly shifted by the strain ; an experimental study of Waldrop *et al.* [54] shows that core level differences remain unchanged when strain varies ; from this they deduce that core levels are unaltered by strains. The same group has produced quite recently (PCSI 90) additional experimental proofs of this [56]. A calculation, by Staub *et al.* [57] confirms this hypothesis. On the other hand, Williams *et al.* (also in PCSI 90) have observed that In_{4d} , in InAs follows the top of the

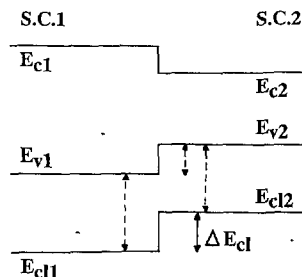


Fig. 5. — Schematic energy band diagram near an heterojunction valence band discontinuity as deduced from core levels difference.

valence band, which indicates that it varies by a few tens of meV [58]. To elucidate this question, study of cation-anion core level differences would give some help. Strain indeed will not modify equally both these levels and a modification of this difference would clearly indicate that strain shifts core levels. Quite recently, Hollinger *et al.* [59] measured this quantity and showed it does not move by more than 50 meV. We have also tried to calculate this shift, and found that it probably moves, but by no more than a few tens of meV. At the present time, the «state of the art» of both theory and experience do not allow a more precise conclusion.

In this section, we have seen that strains are capable of inducing interesting modifications of band alignment and band structure of heterojunctions. Defects are also good candidates for such modifications. These we consider now.

5. Interface defects.

Several models use interface defects to explain some features of heterojunction systems. Let us notice that we have, on the one hand, interface states which occur even at perfect heterojunctions, and, on the other hand, interface defects such as vacancies, antisites or interstitials. The latter defects appear in Spicer's unified model [60] and have localised states at given energies. At an opposite point of view, in Hasegawa and Flietner's models [61, 62], interface states are due to the disorder near the heterojunctions which induces an «interface disorder continuum». At this point it is important to remember that, as shown in section 3, vacancy levels can play a role even when there is no vacancy near the interface.

Interface defects can strongly alter devices, and reduce their performances, for example they induce aging problems in MIS structures. A detailed review on defects induced breakdown of devices behavior and on the passivation is given in [63].

A phenomenon that can be considered as a deviation from perfect interface corresponds to a junction in formation. Recently the formation of Schottky barriers has been studied experimentally at different temperatures [64, 65]. Figure 6 shows that the evolution of the surface Fermi level *versus* coverage is very different between 300 K and 80 K and between n and p type materials. This difference has been attributed to the fact that, at room

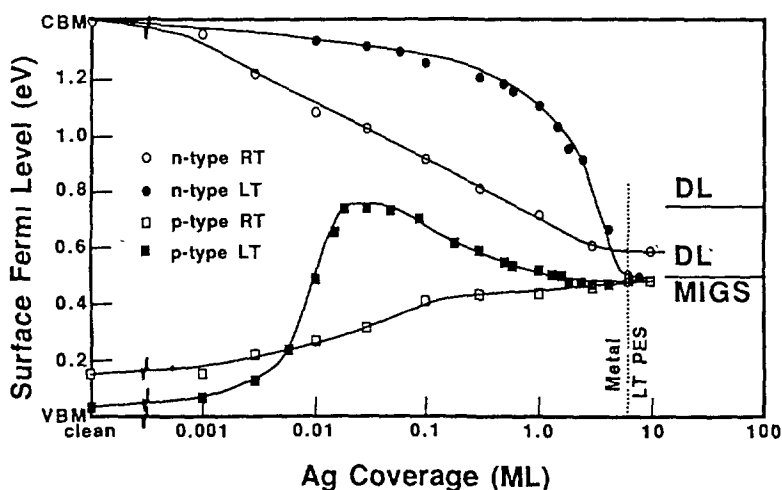


Fig. 6. — Surface Fermi level position at the RT and LT Ag/GaAs(110) interfaces. Strong temperature dependence is observed (from Ref. [65]).

temperature, surface diffusion can occur, leading to the formation of islands of adatoms. In the low temperature case this phenomenon would not occur leading, at low coverage, to a distribution of individual adatom-semiconductor bonds.

This idea can be checked theoretically by using a molecular model in which one adatom is coupled for instance to one dangling bond. This was done independently in references [66] and [67]. As shown in detail in reference [66] the corresponding tight-binding parameters can be determined from well-defined rules and the calculations can be made selfconsistent, which represents an essential step of the treatment. The theoretical results are given in figure 7 for Cs and Ag and it is clear that they explain the main experimental features except for a dip which is not seen experimentally (possible explanations for this are given in [66]). The main conclusions of this study are that the plateau on p type materials corresponds to the position of the adatom-Ga bonding state which only acts as a donor and the final pinning position is given by the average dangling bond energy.

An interface defect that probably occurs frequently corresponds to interdiffusion localised near the heterojunction. First interdiffusion was a candidate for band offsets engineering. In fact the candidate appeared to be very bad : we have compared calculated band offsets of abrupt and interdiffused heterojunction [68]. From this we deduced that, of course, interdiffusion modifies the potential shape near the interface, but it absolutely does not alter the step amplitude. Baroni *et al.* [69] have got the same conclusion. Quite recently, Hybertsen [70] published a quite amazing calculation about the lattice-matched In(Ga)As/InP system. In the ideal system, as $d_{\text{In-As}} > d_{\text{In-P}}$, a large (6%) interface strain is localised at the interface. Chemical intermixing (a plane of AsP) is shown to reduce the interface strain. But the band offset is sensitive to strain. Hybertsen performed a very elaborated calculation whose result is

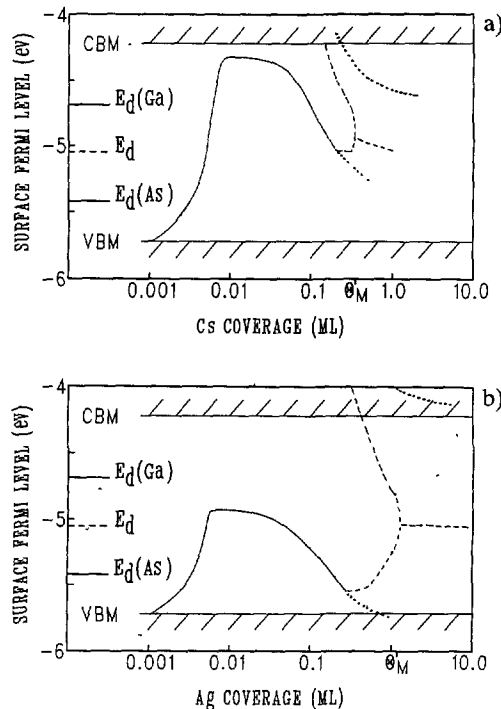


Fig. 7. — Theoretical curve of the surface Fermi level versus coverage : a) for Cs, b) for Ag (from Ref. [66]).

that these two phenomenon exactly balance and thus the calculated valence-band offset is independent of intermixing. This is illustrated in figure 8.

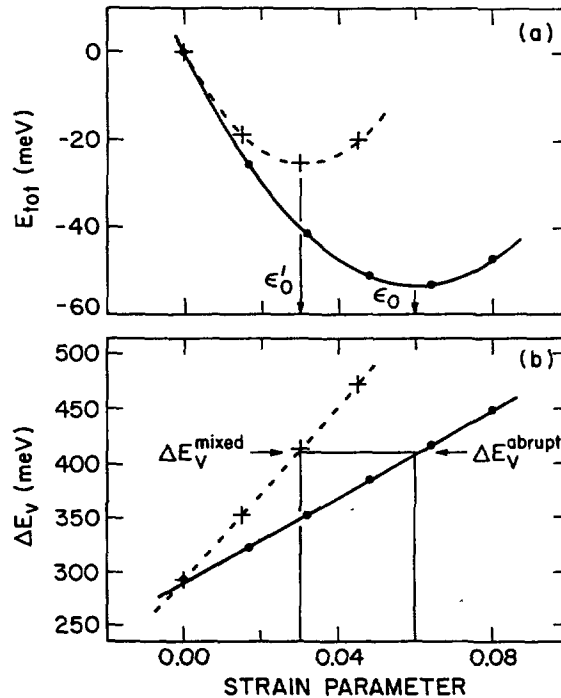


Fig. 8. — a) Superlattice total energy as a function of the local interface strain parameter. b) Calculated valence-band offset as a function of local strain parameter. Solid line: abrupt case; dashed line: chemically intermixed case (from Ref. [70]).

An other interface defect consists of an intentionally introduced ultrathin interlayer at the interface. If the offset is shown to be sensitive to the inserted interlayer, then there is a deviation from the transitivity rule established by many theoretical and experimental works. This has been studied by Christensen and Brey [71]. They consider GaAs/AlAs (110) with several interface layers (Ge, Si, GaSb, ZnSe, CuBr). Only CuBr appeared to break the transitivity rule.

Finally, after transitivity, one can consider commutativity: is the band offset sensitive to the growth sequence? Waldrop *et al.* [72] reported some experiment on GaAs/AlAs where such an effect has been observed. Recently, Horn *et al.* [73] have investigated the ZnTe/CdS system from this point of view. They found a difference between ZnTe/CdS and CdS/ZnTe band offsets of about 100 meV, but as the experimental error bar was 50 meV, they could not conclude. From a theoretical point of view, whereas, in GaAs/AlAs, the failure of the commutativity rule can only be explained by the presence of different defects at both interfaces; for ZnTe/CdS, the difference between the Zn-S and the Te-Cd interface could induce a difference in band offsets.

6. Summary and conclusions.

Theoretical studies of semiconductor interfaces and of their defects are a very broad investigation field. Here we have considered different aspects of this field. The important points coming out can be summarized as follows :

The very powerful effective mass approximation and its conventional boundary conditions cannot be used in all systems. Sometimes new boundary conditions are an absolute necessity.

At the present time, band offsets can be calculated to about 100 meV by the use of different techniques.

In lattice mismatched heterojunctions, the effect of strains is considerable, especially band structures near the band edges are strongly modified, and some conventional notions (such as the concept of heavy or light holes) have to be abandoned.

This field remains an open field (the recent controversies [38, 27-31, 54-58] give evidence of this). Even if the state of knowledge has advanced in the 80's, further investigations are required for a better knowledge of heterojunctions physics.

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Note added in proofs :

After this paper has been written for the « journées de microélectronique et d'optoélectronique III-V », some papers related to this review became available. Related to section 2, one can note a paper J-B Xia (*Phys. Rev. B* **41** (1990) 3117). Related to section 3, one can note some work by Segall and Lambrecht (*Phys. Rev. B* **41** (1990) 2813 and 2832), which calculate band offsets of several unstrained isovalent heterojunctions using selfconsistent LMTO calculations. One can also mention Tafener and Allen's work (« March Meeting » of the APS Anaheim, CA (1990)) providing tight-binding calculations of heterojunction band offsets, using local charge neutrality, but the results do not seem to be accurate and only (110) systems seem to be considered. Related to section 4, one can note a work by Wang *et al.* (*J. Appl. Phys.* **67** (1990) 344), an other by Bahder (« March Meeting » of the APS Anaheim, CA (1990)), and also a work by People *et al.* (*Phys. Rev. B* **41** (1990) 8431).

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