ELECTRONIC PROPERTIES OF INTERFACES

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Some fundamental microscopic electronic properties of vacuum-semiconductor, metal-semiconductor and semiconductor-semiconductor interfaces are discussed in connection with the question of their meaning for macroscopic transport properties of junction devices.

1. Introduction

Electronic properties of interfaces between a semiconductor and a metal or another semiconductor are subjects of very intensive fundamental and applied research. The primary incentive for many of the studies is the outstanding technological importance of these interfaces in Schottky barriers and heterojunctions. Schottky barriers are used in innumerable electronics devices and heterojunctions have their most important applications in photonic devices. The extremely useful properties of metal-semiconductor (m-s) and semiconductor-semiconductor (s-s) interfaces are described in great detail in the book by Sze [1] where the various phenomenological models for describing the macrofeatures of these interfaces are presented, as well. In these models the basic characteristics of m-s and s-s interface systems are monitored by a few key parameters like the Schottky barrier height or the heterojunction band edge discontinuities. These key quantities determine the transport properties of the devices to a large extent and are, therefore, of paramount importance. In spite of the usefulness and great success of the phenomenological models, a fully conclusive understanding of what determines the values of the key parameters on a microscopic level is still lacking.

Since m-s and s-s interfaces play such a vital role in modern semiconductor technology, there is a strong stimulus to understand their properties at a fundamental level and to possibly advance existing technology thereby. In consequence, the microscopic electronic properties of these systems have been studied in great detail in the past decade and a conclusive picture of electronic properties of well-ordered, well-characterized, stoichiometrically clean interfaces has emerged. Basic issues in this more fundamental research

have been (a) investigations of the existence, origin and nature of localized interface states, (b) investigations of the effects of bound interface states on macroscopic junction properties, i.e. on the barrier heights and the band edge discontinuities and more recently (c) studies of the initial stages of m-s and s-s interface formation. The progress in the various areas has been summarized in great detail in many recent review articles on Schottky barriers and on semiconductor heterojunctions [2-11]. (A full account of the vast literature on this field can be found in the reference lists of the cited review articles.) Here we only very briefly summarize the basic results related to the key questions in a fairly general way and point out some of the outstanding problems.

2. Schottky Barrier Height and Band Edge Discontinuities

From an applied point of view, the key parameters of m-s and s-s interfaces are the Schottky barrier height and the band edge discontinuities. They define the macroscopic, phenomenological energy-band models which have been used successfully for decades to adequately explain most transport properties of m-s and s-s junction devices [1]. Nevertheless, a fully quantitative, microscopic understanding of these parameters is still lacking. It is subject of very intensive experimental and theoretical research, currently. The problem is very easy to state and extraordinarily complicated to solve. Consider the schematic Fig. 1 which shows the available state density for electrons in semiconductors (homopolar and heteropolar covalent, shown separately) and in simple metals. Occupied states for intrinsic materials at T=0 are indicated by shadings. Semiconductors and metals are characterized by their respective bulk state densities, their Fermi levels, band edges, work functions and electron affinities, respectively. For a metal, the electron affinity is, of course, equivalent to the work function. Note that the Fermi levels and band edges of the separate materials are different, in general. As long as the materials are separate, it is sufficient to know the energy levels *relative* to e.g. the bottom of the respective bulk bands. But if a contact between two materials is established, a common *absolute* energy scale is needed, to which the properties of both materials can be referred.

When we bring a metal and a semiconductor into contact, they set up a common electrochemical potential, i.e. they equilibrate their Fermi levels, thereby establishing a barrier for electron movement from the metal
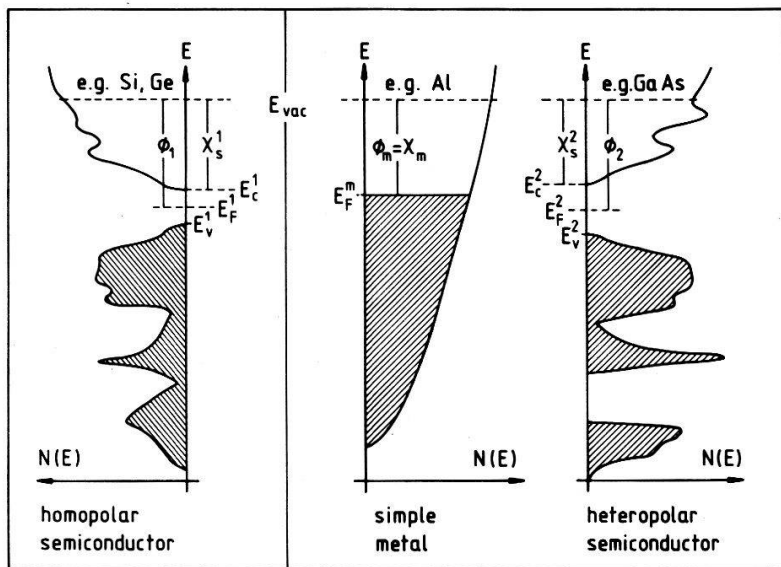
Fig.1 Schematic comparison of the bulk DOS of typical constituents of Schottky barriers or heterojunctions (for details see text).

to the semiconductor. According to Schottky, the barrier height of an ideal barrier is given by

$$\phi_B = \phi_m - \chi_s \equiv \chi_m - \chi_s \tag{1}$$

where ϕ_m is the metal work function and $\chi_{m,s}$ are the electron affinities of the metal and the semiconductor, respectively. (It should be noted, that χ_s and χ_m can experimentally be determined only in surface measurements and they are found to depend on the surface orientation.) For a given semiconductor, the barrier height is thus expected to vary linearly with ϕ_m, when different metals are put on the semiconductor surface. Very often, however, this simple behaviour is not observed and a much weaker dependence of ϕ_B on ϕ_m is found. For homopolar and heteropolar covalent semiconductors like Si, Ge or GaAs, ϕ_B was even found to be essentially independant of the metal contact; e.g. for GaAs(110)-metal junctions the Fermi level turns out to be "pinned" at roughly mid-gap no matter which metal is put on the surface [3]. In particular, it is observed that pinning is complete already for metal coverages far below monolayer coverage [see e.g. 2,3].

When two dissimilar semiconductors are brought into contact their respective conduction and valence band edges do not necessarily match. Again a common electrochemical potential is set up, the Fermi levels equilibrate and the band edge discontinuities ΔE_c and ΔE_v are established. The sum of the discontinuities is obviously given by the difference in gap energies ΔE_g of the two components of the junction. According to Anderson [12], the conduction

band discontinuity is given by (in complete analogy to equation (1))

$$\Delta E_c = \chi_s^1 - \chi_s^2 \qquad (2)$$

where $\chi_s^{1,2}$ are the electron affinities of the two semiconductors, respectively
This is the so called electron affinity rule. Like equation (1) for the
Schottky barriers, equation (2) for heterojunctions often fails to quanti-
tatively predict the measured ΔE_c. From figure 1 it is obvious, that these
simple equations do nothing but relate the characteristic energies of two bulk
materials to one another without taking into account any effect of the inter-
face formation. In consequence the shortcommings of the above relations are
due to the neglect of all the specific microscopic characteristics of the
interfaces in question. It is well-established, by now, that the interface key
parameters depend on the junction growth procedure and mechanism, on interface
interdiffusion, on chemical reactions at the interface, on interface imper-
fections, on annealing temperature, initial surface treatment and on surface
reconstruction [see e.g. Refs. 1-3,8,9,11,14]. The latter effect causes e.g.
that ΔE_c for Ge-Zn Se junctions depends on the order of deposition [15]. Many
different ways of improving the phenomenological relations (1) and (2), in
order to take into account some of the above mentioned effects, have been
suggested with varying degree of success. The interested reader is referred
to Refs. 2,5 and 4,7 for ϕ_B and ΔE_c, respectively.

The very weak dependence of ϕ_B on ϕ_m for Schottky barriers with
Si and Ge led Bardeen [13] already in 1947 to the conjecture that trapped
charge at the m-s interface is responsible for the difference between ob-
served and predicted (1) barrier heights. Likewise, the deviations between
measured and predicted (2) band edge discontinuities are related to micros-
copic electronic interface features which can trap charge at the s-s inter-
face. The basic question then is: "What is the nature of these charge trap-
ping states at interfaces?" Bardeen suggested semiconductor surface states.
As further promising candidates m-s and s-s interface states have been con-
sidered in great detail [2-11]. In the next Section we, therefore, briefly
discuss characteristic microscopic electronic properties of semiconductor
surfaces and m-s as well as s-s interfaces.

3. Electronic Structure of Interfaces

From a fundamental point of view, the existence, origin and nature of local-
ized states at vacuum-semiconductor, metal-semiconductor and semiconductor-

semiconductor interfaces are of primary interest. Most studies, therefore, concentrate on investigations of the spectral changes of the available electronic bulk states (see Fig. 1) when an interface is formed. New states in the gap energy region are of particular importance in context with the above discussed Fermi level pinning.

In order to evaluate the electronic structure of surfaces and interfaces one has basically to cope with two problems which are related to the new boundary conditions imposed by v-s, m-s and s-s interfaces. One is the lack of periodicity perpendicular to the interface and the other is the lack of an exact knowledge of all atomic positions near the interface. The former problem is purely mathematical in nature. It has been solved in the 1970's for almost all practical purposes [see e.g. Refs. 4-6]. The latter is the basic physical problem in surface and interface electronic structure theory since the electronic structure is intimately related to the atomic structure. The structure determination has become, e.g. in the case of surfaces, an extremely fruitful joint experimental and theoretical effort during the past decade (for a few examples see Ref. 16 and the references therein). Very impressive progress has been made in the identification and understanding of characteristic surface reconstructions and relaxations. The m-s and s-s interface studies have mostly been based on junction geometries which use "bulk-like" lattices matched ideally at the interface.

Detailed electronic structure calculations for the currently accepted *semiconductor surface* geometries have been carried out leading to results that agree very well with high-resolution surface spectroscopy data. In general, one finds that surfaces of homopolar semiconductors show strong reconstructions and give rise to gap surface states. We mention only a few very recent publications on Si(111)-2x1 [17] and Si(100)-2x1 [18,19]. The natural cleavage faces of heteropolar covalent materials, like GaAs(110), show a charge transfer relaxation [16,20] which moves anion- and cation derived dangling bond states, that were present at the ideal surface, out of the gap. The resulting electronic structure is in good agreement with experiment [16,20, 21]. The polar faces of III-V materials, like e.g. GaAs(001)-2x4, show strong reconstructions and give rise to gap surface states [22]. Ionic materials, finally, like ZnO, do not show any gap states at all [23,24]. Thus we note, that e.g. Si(100)-2x1 and GaAs(110) behave very different, as far as gap surface states are concerned. Nevertheless, both materials show Fermi level pinn-
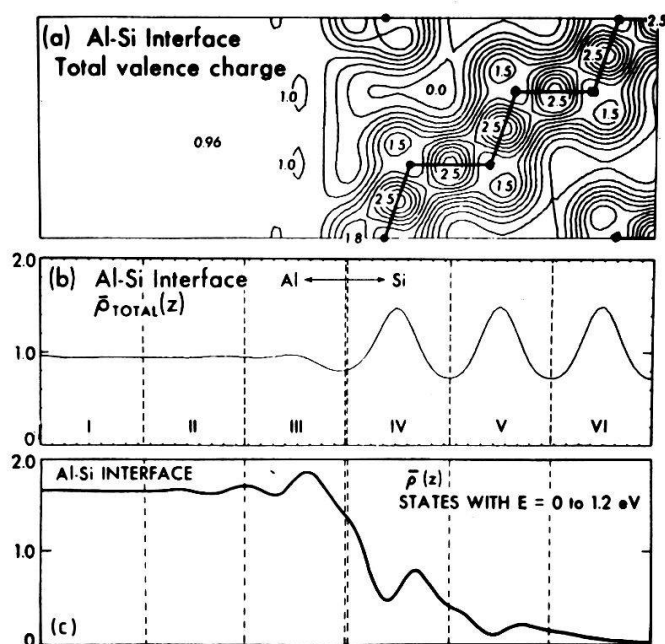
Fig.2 Valence charge density
near an Al-Si junction; details
see text (from Ref. 26).

ing when they are contacted to metals. Thus intrinsic surface states are cer-
tainly not the cause of Fermi level pinning, in contrast to Bardeen's suggest-
ion.

Heine [25] questioned already in 1965 the existence of free, intrin-
sic surface states at a *metal-semiconductor interface*. He suggested the exis-
tence of bulk-like metal states which tail over some ten Å into the semicon-
ductor occuring energetically within the semiconductor band gap. This
suggestion has been confirmed by the beautiful results of selfconsistent
pseudopotential calculations by Louie and Cohen [26]. They studied m-s junc-
tions between Al and Si, GaAs, ZnSe and ZnS using the supercell technique
[see e.g. Ref. 4]. Five Si layers in the supercell were described in terms of
bulk Si pseudopotentials and five Al layers were monitored by jellium of appro-
priate electron density. The total valence charge density for an Al-Si junc-
tion is shown in Fig. 2 (top panel). The left half corresponds to the Al and
the right half to the Si layers in the supercell. The middle panel shows the
corresponding total valence charge density integrated over the plane parallel
to the interface. In this integral picture only very little effect of the
interface is to be noted. If, however, the charge density is only calculated
for states between 0 and 1.2eV, i.e. states in the gap energy region, a very
interesting result is obtained (lower panel of Fig. 2). The constant charge
density on the Al side starts to oscillate around its average value when
approaching the interface (very much like a Friedel oscillation) and decays
on the semiconductor side within 4 to 5 Å. The decay is not purely exponen-

tial but shows structure due to the underlying Si lattice. Louie and Cohen observed, as well, that with increasing semiconductor gap energy the decay length decreases to roughly 3Å, 2Å and 1Å for GaAs, ZnSe and ZnS, respectively [4]. These states, which are fairly bulk-like on the metal side and which tail into the semiconductor were labelled MIGS, i.e. metal-induced gap states by Louie and Cohen. They are specific interface semiresonances in nature. From the calculated layer densities of states (see Refs. 4 or 26) it is obvious that the MIGS span the entire gap energy region. Thus they can act as charge trapping states at the m-s interface. Consequently, they were related to the Fermi level pinning in Schottky barriers in Refs. 4 and 26. Further calculations [27,28] in which both Al and Si were described by bulk pseudopotentials confirmed all the basic results of the jellium-Si calculations. Again the intrinsic Si surface states were found to disappear upon interface formation and MIGS were found. Although all of these calculations produce electronic features which may account for Schottky barrier formation, many recent experimental results provide a strong counter argument against an interpretation of the Fermi level pinning by MIGS. It is found, e.g. for barriers utilizing the (110) face of III-V semiconductors, that pinning is complete already after adsorption of metals far below monolayer coverage [2,3,9]. Therefore, bulk-like metal states tailing into the semiconductor obviously cannot be the primary cause of the pinning.

The disappearance of intrinsic surface states upon interface formation is observed for lattice-matched *semiconductor heterojunctions,* as well. Characteristic differences in semiconductor surface and interface features for e.g. Ge-GaAs(110) are shown in Fig. 3. Note that the interface yields no pronounced electronic structures in the fundamental gap, as compared to the strong dangling bonds, exhibited by the corresponding surfaces. This result is different, as well from the result for m-s interfaces. At m-s interfaces, there exist metal states "opposite" to the entire semiconductor gap energy region that can tail into the semiconductor (see Fig.1). At the s-s interface, on both sides of the junction, fundamental gaps exist and only the states at the gap edges of the semiconductor with the smaller gap can tail into the other semiconductor. These states are shaded in Fig. 3 and they occur near the valence band edge on the GaAs side of the junction. Semiresonances, like the MIGS at m-s interfaces, nevertheless, occur in homopolar-heteropolar heterojunctions. For the latter systems they are, however, found deeper in
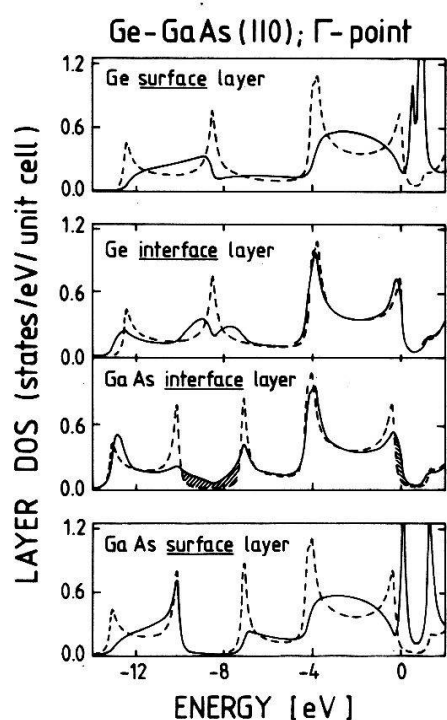
Ge-GaAs(110); Γ-point

LAYER DOS (states/eV/unit cell)

Ge surface layer

Ge interface layer

GaAs interface layer

GaAs surface layer

ENERGY [eV]

Fig.3 Layer densities of states at the
Γ-point for a Ge or GaAs(110) surface
layer (top and bottom panel) in com-
parison with the LDOS's at a Ge-GaAs(110)
interface. The corresponding bulk LDOS's
are shown by dashed lines (from Ref. 6).

the valence bands [7,29]. They typically occur in the heteropolar gap energy
region between -7 and -10eV for Ge-GaAs junctions (see the shadings in Fig.3).
They are bulk-like on the Ge side and decay within a few layers on the GaAs
side of the junction [29]. These Ge-induced states in the GaAs heteropolar
gap are equivalent to the above discussed MIGS.

The theoretical treatment and the characteristic electronic proper-
ties of heterojunction interfaces have been described in great detail in Refs.
4,5,6 and 7. By now the theory of electronic properties of lattice-matched
heterojunctions seems to be a mature field and the basic properties of these
systems are well-understood. Two main formal approaches have been employed;
one is the supercell method [4] and the other is the tight-binding scattering
theoretical method [6,29]. The supercell method makes use of a superlattice
geometry and pseudopotential Hamiltonians are employed in the selfconsistent
calculations. Both the band edge discontinuities ΔE_c, ΔE_v and the interface
band structure result from these calculations. The tight-binding scattering
theoretical method uses two semiinfinite crytals in contact at the interface
and empirical tight binding Hamiltonians are employed. The calculations make
use of Green's functions. They yield the interface band structure and wave-
vector-resolved layer densities of states (see e.g. Fig.3) but need the dis-
continuities as an input. Both approaches yield interface bandstructures in
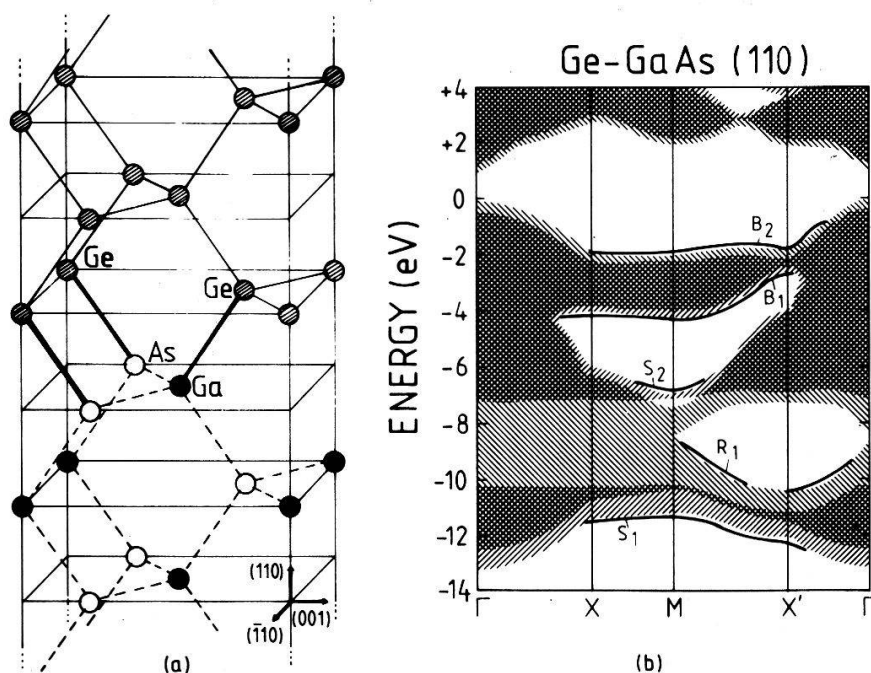
Fig.4 Ge-GaAs(110) interface band-structure (b) and small lattice section near the interface (a) (from Ref. 7)

good agreement with one another. Many different prime heterojunction pairs with lattice-mismatch of less than 1% have been investigated theoretically [see 4-7]. It is found that the electronic properties for the various studied junctions are very similar. As a characteristic example, we show the interface bandstructure of the prototype heterojunction Ge-GaAs(110) in Fig. 4 together with a small section of the lattice near the interface. The shaded regions are areas where either Ge or GaAs bulk states exist (the so-called joint projected bulk bandstructure) and the full lines depict the energies of bound interface states. The states S_1 and B_1 are related to the Ge-As interface bonds while S_2 and B_2 stem from the Ge-Ga interface bonds. The most important result in our context is the fact, that there occur no gap interface states. This is a very general finding, typical for many heterojunction interfaces. First, it means that most of the ideal, lattice-matched heterojunction interfaces do not give rise to localized states in the gap energy region which could trap charge near the interface. Second, it expresses the important fact that semiconductors which match structurally do match electronically "on the average", as well.

4. Overlayer Systems

So far, we have pointed out, that neither intrinsic semiconductor surface states nor metal-induced gap states nor intrinsic heterojunction inter-

face states can conclusively explain charge trapping at interfaces which seems to be the primary cause for deviations of measured values for ϕ_B and ΔE_c from the expected values according to relations (1) and (2), respectively. Currently, interface states due to chemical reactions at the interface [2,11] or due to interface imperfections [3,8,9] are intensively discussed as origins of Fermi level pinning. For shortness sake we could not even touch upon these subjects.

In order to better understand the microscopic properties of *real* interfaces the initial stages of interface formation are currently investigated in great detail both experimentally and theoretically using *overlayer systems* as samples. Theoretical results, e.g. on Ge-GaAs(110) overlayer systems are discussed in Ref. 30 and recent experimental data are presented and discussed in Refs. 8,9 and 31-33. Theoretical studies of the formation of m-s interfaces with Al-GaAs(110) as the prototype example have been undertaken by Zunger [10,34] and by Ihm and Joannopoulos [35]. The latter authors investigated by a very impressive total energy calculation favourable adsorption sites for the submonolayer, half-monolayer and full monolayer adsorption regimes. The Al-Ga and Al-As bond lengths of 2.49Å and 2.38Å, respectively, resulting in this study for the very low coverage limit are in sharp contrast to Zungers results [34] which yield a much longer bond length of 3.1Å and a correspondingly weaker Al-GaAs bonding. Ihm and Joannopoulos identified most favourable adsorption sites for the various coverage regimes and Al clustering as well as Al-Ga exchange reactions were found to be most probable for specific coverages and temperatures. Al clustering and surface exchange reactions are considered in Ref. 34, as well. A comprehensive discussion of these more recent theoretical m-s overlayer studies in connection with the question of Fermi level pinning in Schottky barriers may be found in Refs. 2,5 and 10.

5. *Summary*

We have briefly summarized some fundamental properties of well-ordered, well-characterized and stoichiometrically clean v-s, m-s and s-s interfaces in the context of the question of *how* the key parameters of macroscopic, phenomenological models for junction devices are related to microscopic properties of interfaces. The whole field is a very active area in interface research and it would be very premature to try to give conclusive answers. This paper is

rather meant to be a guide to the many review articles published during the last several years describing our current knowledge in the field in great depth.

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