**Invited**

# Band Offsets at II-VI Heterojunctions

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Heterojunctions could become particularly useful for II VI compounds in which pn junctions are not obtainable, though better understanding of their properties will be needed. The standard Harrison theory is discussed vis a vis alternative possibilities in the empirical common anion rule. Experimentally important factors are the apparent process dependence of band offsets, and the abruptness attainable by various processes, particularly within the past two years. The merits of HgTe/CdTe in terms of theory, advantageous processing, and possible applications are cited.

In III V compounds, heterojunctions substantially extend the capabilities of p-n homojunctions, e.g. in various quantum-well devices. In II VI compounds, while such sophistication may eventually develop, the more immediate use for heterojunctions is to substitute for pn junctions which are not usually obtainable. Photovoltaic technology already does this and one hopes electroluminescence will in the future.

Fig. 1 sketches some ways in which band offsets occur at the interface of two semiconductors. Fig. 1 (a) shows both offsets, $\Delta E_c$ and $\Delta E_v$, contributing in a positive way to make up the bandgap difference, $E_{g1} - E_{g2}$. This is the carrier confinement structure so widely used in III Vs. Fig. 1 (b) shows one offset, $\Delta E_v$, making up for more than $E_{g1} - E_{g2}$, so that the other offset, $\Delta E_c$, will be called negative. This type of structure is favored for solar cells, e.g. InP/CdS, where one does not want to block both carrier flows. A rather special case is shown in Fig. 1 (c), where both an offset and a bandgap are zero. It is similar to a Schottky barrier, should provide substantial minority carrier injection, and will be discussed later as a special example.

A Theory and an Empirical Rule.

How band offsets arise from the physics and chemistry of the interface is a long-standing question. In Swanks[1] 1967 study of II VI photo-
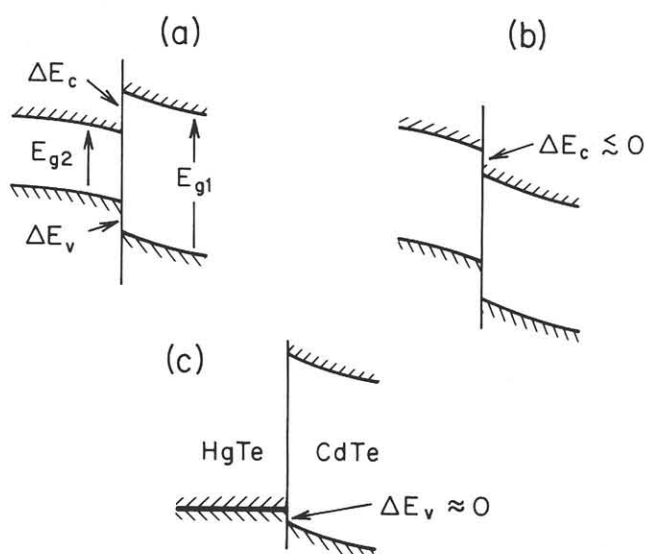


Fig. 1 Energy band lineups at heterojunctions.
(a) Smaller bandgap, nested within a larger one.
(b) Staggered lineup.
(c) Lineup proposed for HgTe/CdTe.

electric threshold, $\Phi$ = vacuum energy $- E_v$, he observed that $\Phi$ was ". . . . determined primarily by the chalcogen . . . .". Combining his own II VI and earlier III V data of others, he further found a linear relation between $\Phi$ and Pauling electronegativity of the anion. In 1976 McCaldin, McGill, and Mead[2] using a different method for determining $E_v$ analyzed Schottky barrier height, $\phi_p$, for holes at semiconductor/ Au interfaces obtaining results *qualitatively*
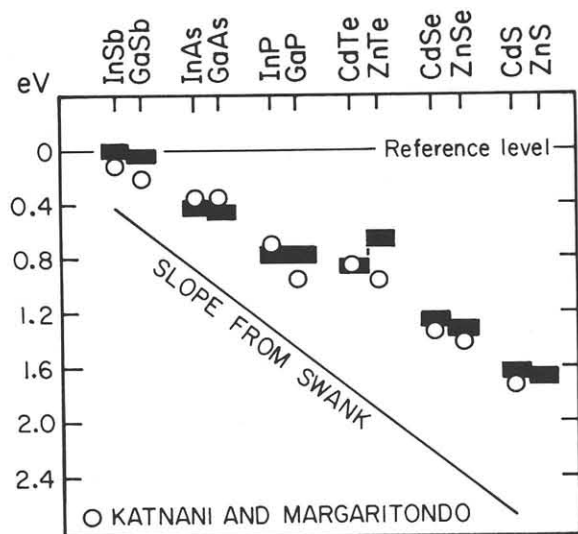
Fig. 2   $E_V$ for III V and II VI compounds.
■ data from common anion rule with Au $E_F$ as
reference. O data sets Ge $E_V$ as zero.   For
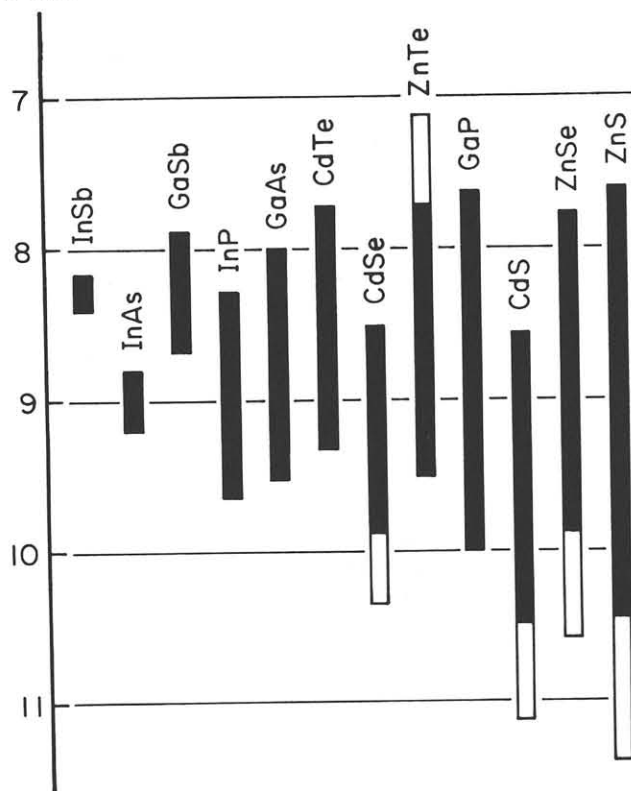detail on Swank data, see ref. 3, Fig. 6



Fig. 3   Relative positions of bandgaps according
to Harrison model (voltage measured from vacuum
level).   Solid black bars represent bandgaps at
0°K of compounds which can be made highly con-
ducting n-type or p-type.   Where one conductivity
type is not accessible (at high conductivity), the
appropriate end of the bar is left unshaded, e.g.
n-type regime in ZnTe.   Semiconductors are
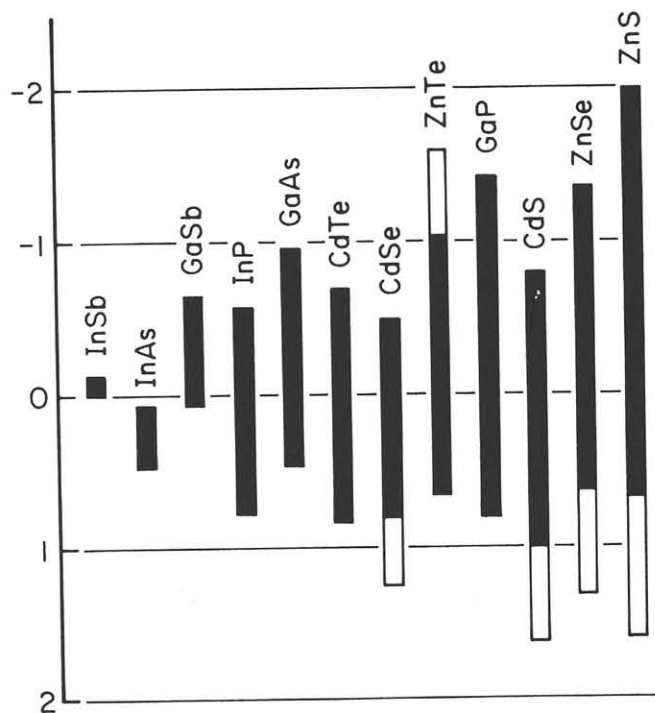arranged in order of increasing bandgap from left
to right.

similar to Swanks, often alluded to as the "common
anion" rule.   However, their measurements of $E_V$
showed a significantly *smaller* dependence on
electronegativity than Swanks, as depicted in
Fig. 2 and shown more explicitly in ref. 3.   In
1977 Harrison[4] proposed a LCAO theory of hetero-
junctions, which has since become the standard in
the field and which agrees with many recent band
offset measurements to about ± 0.2 eV.   It also
agrees reasonably well with the Swank data,
especially in the overall sense that $E_V$ is pre-
dicted to decrease ∿ 2.7 eV in going from the
antimonides to the sulfides.

Recently Katnani and Margaritondo[5], using
photoemission measurements, obtained $E_V$ values
more consistent with McCaldin, McGill, and Mead
than with Swank, and hence Harrison.   Their $E_V$
values are also plotted in Fig. 2, where it should
be noted that reference levels are arbitrary.   In
going from antimonides to sulfides, Katnani and
Margaritondo, as well as McCaldin, McGill, and
Mead, find that $E_V$ changes only about 1.7 eV.

These comparisons can be seen in greater
detail in Figs. 3 and 4, in which Ev appears as



Fig. 4   Plot similar to Fig. 3, except using
data from ref. 3 (common anion rule).   Zero is
Au $E_F$.   Bandgaps at 300°K.

the bottom of a bar representing bandgap. Overall the Harrison $E_v$ values in Fig. 3 decline more steeply than those in Fig. 4. Also a few near-neighbor heterojunctions, e.g. GaAs/CdTe, differ substantially in the two figures.

How do experimental band offsets compare to Figs. 3 and 4? As mentioned earlier, Fig. 3 gives remarkably good agreement with some rather well-characterized heterojunctions. For example, the n-CdS/p-InP solar cell is predicted to have $\Delta E_c =$ -0.29 eV by the Harrison model, which is almost halfway between the two reported experimental values, -0.56 eV[6] and -0.112 eV[7]. On the other hand, Fig. 4 predicts $\Delta E_c = +0.23$ eV, in rather poorer agreement.

There are reasons, however, that experimentalists, especially those working with II VIs, should consider Fig. 4, besides checking against the standard Harrison theory. Of course, the Katnani-Margaritondo results suggest such a check. Also qualitative information on II VIs such as the well-known difficulty in making ohmic contact to ZnS, or intercomparisons of ZnSe and ZnS, suggest Fig. 4 may be relevant.

Lastly it is interesting to note that band offsets for several heterojunctions are roughly the same in the two figures. For example, $\Delta E_v$ for GaP/ZnSe is 0.58 eV in Fig. 3 and 0.51 eV in Fig. 4. This heterojunction, which has recently been formed at relatively low temperature[8,9], $\sim$ 300°C, could, in principle, provide significant hole injection into ZnSe, since the difference in bandgap is only $\sim$ 0.4 eV and the modest $\Delta E_v$ is no serious obstacle.

Experimental Considerations.

Treatments of band offsets just discussed are said to be "linear" because the only independent variables are parameters of each individual semiconductor. No terms for a specific interface, e.g. describing the specific bonds at the interface or the specific orientation of the interface, are included. Thus some variability is expected from specific interface to interface.

The observed experimental variability, however, appears to include additional effects. When the epitaxial growth of semiconductor A onto B is reversed (i.e. B grown onto A), band offsets

change, in one instance by 0.5 eV. Examples of this growth-sequence dependence, recently compiled by Bauer et al.[10], mostly are complicated by strong interdiffusion/doping effects. One example[11], however, GaAs/AlAs versus AlAs/GaAs, which exhibits 0.25 eV change in offsets on reversing the growth sequence, is particularly worrisome. Two possible explanations[12] in this system are presently being considered: dependency of C incorporation or of Al/Ga interchange on growth sequence. Thus, even in this seemingly simple system, it may be a lack of the ideal compositional abruptness assumed in the simple interface models that causes the variability. Incidentally, the at-present poorly understood variability could become useful to obtain desired offsets for device purposes.

Experimentally the abruptness achievable has been improved substantially in recent years by use of lower growth temperatures. Growth of ZnSe and ZnS, usually on III V substrates, is now performed at $\sim$ 300°C to 400°C by both MBE and CVD (usually metalorganic), a considerable achievement. Whether the abruptness obtained is sufficient to avoid some of the variabilities mentioned is an interesting question.

Lattice strain is also clearly a factor in junction quality, whether due to lattice mismatch or differences in thermal expansion. Also, deliberately grown-in lattice strain sufficient to change a bandgap substantially[13] is now achieved in III V systems.

HgTe/CdTe.

This particular system may be quite timely to help answer some of the questions just mentioned, one has reason to hope. In any case, the present discussion may benefit by focusing on a specific case for illustration.

From various guiding ideas, one expects the small offset, $\Delta E_v$, sketched in Fig. 1 (c). The common anion rule, of course, predicts $\Delta E_v = 0$, since Te is common to both sides of the junction. The older Anderson electron-affinity rule[14], applied to the data of Shevchik et al.[15], gives a modest offset, $\Delta E_v = 0.3$ eV. Harrison's tabulated values of $E_c$ and $E_v$, sketched in Fig. 3, do not include the Hg chalcogenides, possibly because of certain difficulties with the

conduction band on one side of the junction overlapping the valence band on the other side, as discussed in the appendix to his paper[4]. However, if one neglects this difficulty, the formulations in his paper indicate $\Delta E_v < 0.1$ eV, as has been pointed out[16].

Experimentally this heterojunction is favored by a modest lattice mismatch, $\sim 0.3\%$, which, however, is still appreciably larger than for the selenide and sulfide analogs. Because of the substantial current interest in HgCdTe detectors, substrate material of good quality is often obtainable and considerable data on physical properties is being published. Probably the most important consideration, however, is processing temperature. Recent diffusion measurements[17,18] now enable good estimates of the concentration profiles to be expected at different temperatures.

The lowest reported junction formation temperature comes from MBE studies[19]. Although even lower temperatures were investigated, most growths were made near 200°C. Extrapolating from 340°C – 280°C diffusivity measurements[17], $D \approx 10^{-17}$ cm$^2$s$^{-1}$ can be estimated so intermixing layer thicknesses near 20 Å or so are probable. From optical absorption measurements, an offset of $\Delta E = 0.04$ eV was deduced[19].

Temperatures near 350°C have been reported[20] for CVD growth. Expected[17,18] diffusivity is $\approx 10^{-13}$ or $10^{-12}$ cm$^2$s$^{-1}$, so that intermixing layer should be $\sim 100$x thicker than for MBE growth. Schottky barrier heights up to 0.92 eV were measured[16], which is 0.58 eV short of the band-gap. The 0.58 eV difference arises from several factors, including the inversion layer effects originally discussed[16] and, in retrospect, from intermixing.

LPE, widely used in making HgCdTe structures, is generally practiced at even higher temperatures. However, lower temperatures should be feasible in Hg-rich solutions, because Hg is such a good solvent for many elements, including chalcogens[21]. Using Te-saturated Hg solutions, growth of HgTe onto CdTe substrates has been obtained at MBE-type temperatures, i.e. 200°C and lower[22].

If small $\Delta E_v$ values are confirmed for HgTe/CdTe, the proposed superlattice[23] becomes an especially interesting goal. Furthermore, small $\Delta E_v$ values imply substantial hole injection can be obtained in this heterojunction. Because of the long-standing interest in II VI electrolumin-escence, whether from electrolyte[24] or solid-state injection, the selenide and sulfide analogs should then be investigated.

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