Proposal of a new visible light emitting structure: *n*-AlSb/*p*-ZnTe heterojunctions

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From considerations of dopability, band offset, and lattice match, we find that of the various heterojunctions containing II–VI compounds, the *n*-AlSb/*p*-ZnTe heterojunction has the most promising properties for fabricating visible light emitters. The materials lattice match to 0.5%. Experimental evidence and theoretical predictions for the band offset blocking minority carrier injection indicate a range from zero to 0.3 eV maximum. This range of values is the lowest for heterojunctions involving *wide-gap* II–VI's. Substantial electron injection into the *p*-ZnTe should be possible. Control of doping may suffice to suppress undesired hole current originating in the ZnTe.

The wider band gap II–VI semiconductors, though potentially attractive for electroluminescent devices, have been severely limited by the difficulty, if not impossibility, of producing *pn* junctions in these materials. One potential solution to this problem is to join an *n*-type II–VI to a *p*-type II–VI forming a heterojunction (HJ). The HJ approach has been tried for over 20 years, particularly in the system ZnSe/ZnTe.[1] Success has been limited, however, with much of the difficulty ascribed to problems with abruptness and perfection of the HJ. Recent advances in epitaxial growth technologies, particularly molecular-beam epitaxy (MBE) and chemical vapor deposition (CVD), have greatly improved both these aspects of HJ, however.

Another problem for the HJ approach arises from the sizes of band offsets. This problem has been the less discussed, probably due to the large uncertainties about offset sizes. These uncertainties have been reduced in recent years, however, with the appearance of over a dozen papers presenting "linear" predictions of offset size. Thus now is an opportune time to consider the various HJ containing wide gap II–VI's to determine which systems will present the small offset needed for electroluminescent devices.

In this paper we propose a new HJ that shows considerable promise for fabricating visible light emitters. We find the *n*-AlSb/*p*-ZnTe HJ to be a very attractive system for this application. In particular this system offers a small enough offset that the *pn* HJ should inject minority carriers and thus electroluminescence may be obtained in the same simple way as in conventional III–V electroluminescent devices.

ZnTe has been involved in many of the efforts to overcome the above-mentioned problems. Serious studies were made in the 1960s to extend the readily obtainable *p*-ZnTe to include *n*-type material, for example in the experiments of Fischer *et al.*[2] At about the same time studies were begun of the ZnTe–ZnSe system, involving alloys as well as HJ,[3] which continue until the present day. Electroluminescence has been obtained in ZnTe by metal/semiconductor[4] and metal/insulator/semiconductor[5] structures, which appear to involve complex injection mechanisms. Quantum efficiencies up to 10^{-3} photons/electron at 300 K have been reported when isoelectronic oxygen centers are used.[6]

We turn now to the relevant energies for the proposed HJ sketched in Fig. 1. ZnTe shown on the left has the larger band gap, 2.25 eV,[7] compared to 1.615 eV for AlSb.[8] The difference in the two band gaps is distributed between a conduction band offset, labeled ΔE_c in the figure, and a similar offset ΔE_v in the valence band. If the offset ΔE_c is zero or negative, as implied by some calculations and experiments to be discussed later, then no essential barrier to the desired electron injection current exists. In this favorable case, injection efficiency depends only on the relative doping of the two semiconductors, as in the well-known case of a *pn* homojunction. If $\Delta E_c > 0$, however, two potentially serious problems arise in obtaining reasonably efficient minority carrier injection into the ZnTe.

First, ΔE_c must not be too large. As indicated in Fig. 1, the barrier tending to block the desired electron current i_n contains some terms adjustable by doping and bias voltage, plus ΔE_c, which is fixed by the HJ materials. The total barrier, and therefore ΔE_c, should not be $> \approx 0.4$ eV, at which value Richardson's equation[9] indicates a 300 K current of the order of 1 A/cm^2. A barrier height of 0.5 eV would represent

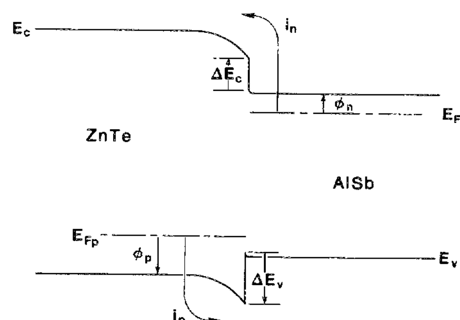

FIG. 1. Thermionic emission currents at a forward-biased heterojunction between *p*-ZnTe and *n*-AlSb. Sketch assumes HJ to be type I and there is no intermediate blocking layer. Offset component appears in the barrier against the desired current i_n, but not against the current i_p to be suppressed.

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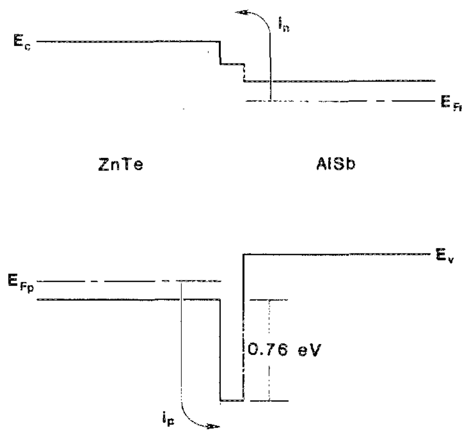

FIG. 2. Same as sketch in Fig. 1, but with intermediate blocking layer. Layer presents an offset barrier, 0.76 eV in this example, to the current i_p, but no additional barrier to the desired current i_n. Bias shown increased to flat-band to maximize i_n.

an upper limit for practical electroluminescent devices.

Second, the barrier blocking the desired current i_n should be no higher than the barrier blocking the hole current i_p, so that reasonable injection efficiency is obtained. Comparing the two barriers in Fig. 1, the amount by which the first barrier exceeds the second is

$$\textit{excess barrier height} = \Delta E_c + (\phi_n - \phi_p) + BB_{\rm AlSb} \leqslant 0 ,$$

where ϕ_n and ϕ_p are Fermi potentials, i.e., the difference in energy between the respective band edge and the quasi-Fermi energy E_{Fn} or E_{Fp}, and $BB_{\rm AlSb}$ is the band bending within the AlSb. The latter term will be small compared to the $BB_{\rm ZnTe}$, when the AlSb is relatively heavily doped, and will not be considered further. Thus the offset ΔE_c is to be balanced by $(\phi_n - \phi_p)$, i.e., by doping the ZnTe more lightly than the AlSb. Since the heaviest doping reported[10] in the limited literature for AlSb to date appears to be $\approx 10^{16}/\text{cm}^3$, this could be difficult unless ΔE_c is quite small, e.g., <0.2 eV.

If ΔE_c is too large to permit the second criterion to be satisfied by doping, it may still be possible to block the undesired hole current with an intermediate layer as sketched in Fig. 2. For this illustration, a layer of MnTe is assumed with the band offset predicted by Tersoff.[11] While such an offset would strongly block the undesired hole current, and indeed Mn centers could possibly assist in photoemission (at ≈ 2.1 eV, near the ZnTe band gap), the MnTe layer would introduce complications related to its crystal structure and lattice mismatch. The alternative of increasing the carrier concentration in AlSb may be more attractive.

The band offsets needed to construct figures like the one just discussed are rather well defined for the most used HJ, e.g., AlGaAs/GaAs. For the larger number of relatively unstudied HJ, recourse can be made to so-called linear predictions, as was done recently for the ZnSe/ZnTe HJ.[12] These prescribe an energy for a band edge, usually E_v, of each semiconductor, so that the offset ΔE_v for a given HJ is then the difference between the two prescribed values of E_v. In Fig. 3 we show predicted values of E_v and E_c for semiconductors closely lattice matched to ZnTe, according to Harrison and Tersoff.[13] In this view a GaSb contact to ZnTe would have a moderate ΔE_c, 0.27 eV, whereas an AlSb contact would have a negative offset, i.e., would form a type II HJ. The latter prediction may be too optimistic, however, as it derives from the close proximity of E_v (AlSb) to E_v (GaSb), in the spirit of the common anion rule. This rule is known, however, not to apply to the Al pnictides.[14]

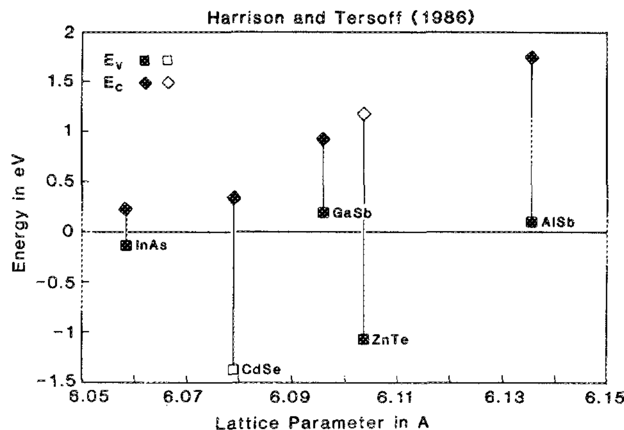

FIG. 3. Energy relationships for the band edges, E_v and E_c, of some semiconductors with good lattice match to ZnTe, according to Harrison and Tersoff, Ref. 13. Mismatch between AlSb and ZnTe is seen to be about 0.5%. Filled-in symbols represent materials that can be strongly doped. Material that conventionally cannot be made usefully p-type or n-type is denoted by the appropriate open symbol. Vertical solid lines represent band gaps. The zero of energy is arbitrarily set at E_v (GaAs).

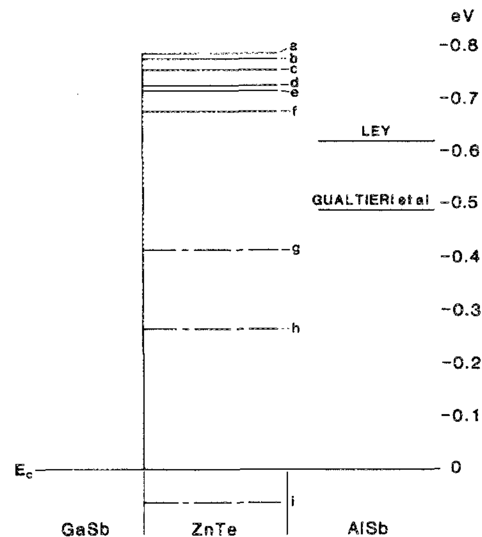

FIG. 4. Indirect predictions from which ΔE_c for ZnTe/AlSb may be inferred. The zero of energy is arbitrarily set at E_c of GaSb. E_c (AlSb), shown on the right, comes from Ref. 22 and further references cited therein. E_c (ZnTe), shown in the middle, comes from many sources: (a) Ref. 15; (b) Ref. 16; (c) Ref. 11; (d) Ref. 17; (e) Ref. 18; (f) Ref. 19; (g) Ref. 20; (h) Ref. 13; and (i) Ref. 21. E_c (ZnTe) predictions, (a) through (f), which appear to give a positive offset for the AlSb/ZnTe HJ are indicated by a solid line; those predictions, (g) through (i), giving a negative AlSb/ZnTe offset are indicated by a broken line.

Many other linear predictions[15–21] have been made for GaSb/ZnTe and these are shown on the left-hand side of Fig. 4. The Harrison and Tersoff value just discussed appears as (h) in this plot, which covers values from nearly 0.8 eV to a negative value for ΔE_c. Most of these predictions do not favor GaSb contacts to ZnTe. However, E_c (AlSb) has been measured[22] to be $\approx$0.5 eV or so higher than E_c (GaSb), as shown to the right of Fig. 4. While the two experimental values shown for AlSb differ by 0.13 eV, both are encouraging for AlSb contacts. Clearly the first criterion, i.e., $\Delta E_c \leqslant 0.4$ eV, is easily met in spite of the wide range of linear predictions and experimental values. The second criterion, i.e., $\Delta E_c < 0.2$ eV so that injection efficiency can be obtained by doping alone, may be possible, depending on how the uncertainties in the figure are eventually resolved.

A more direct estimate of ΔE_c (AlSb/ZnTe) can be had from linear predictions that include both these materials. Figure 5 shows the direct prediction of Tersoff,[11] labeled (j); it differs only modestly from the value that could be inferred from Fig. 4, where Tersoff's prediction is labeled (c). Two other linear predictions, including that of Harrison and Tersoff, would give negative offsets, indicated by the arrow at the bottom of Fig. 5, and are considered too optimistic for the reason discussed earlier.

Finally, for completeness, we include estimates from the well-known "electron affinity rule." This rule has been substantially criticized by Milnes[23] and Bauer, Zurcher, and Sang.[24] Electron affinity predictions from data of Milnes and Feucht,[25] labeled (k) and Freeouf and Woodall,[26] labeled (l), appear in the figure and are seen to lie near the midrange of the linear HJ predictions, nevertheless.

Some practical considerations should be mentioned. The Al pnictides are well known to present oxidation problems. One way to deal with this would be to use a GaSb "guard ring" surrounding the AlSb to prevent contact between AlSb and air. The only current that the GaSb guard ring should draw would be an i_p similar to that shown in the lower portion of Fig. 1 for AlSb. The rather ideal MnTe offset illustrated in Fig. 2 remains to be confirmed, since a recent measurement[27] suggests a substantially smaller offset than that predicted by Tersoff. While low resistance Ohmic contact is readily achieved to p-ZnTe, contact to n-AlSb is much less studied. It should be noted, however, that early experiments[10] on resistivity and Hall coefficient in AlSb with n as low as 10^{15} cm^3 did not require special contacting procedures. Temperatures for epitaxial growth of these materials, particularly AlSb, have not been extensively studied and remain relatively high. At such relatively high temperatures, the abrupt HJ assumed here becomes more difficult to obtain. While very abrupt HJ have been obtained in AlGaAs/GaAs and at much lower temperatures in HgCdTe systems, the extension to the proposed HJ is untested and HJ between a III–V and a II–VI have been reported to encounter more interdiffusion problems.[28]

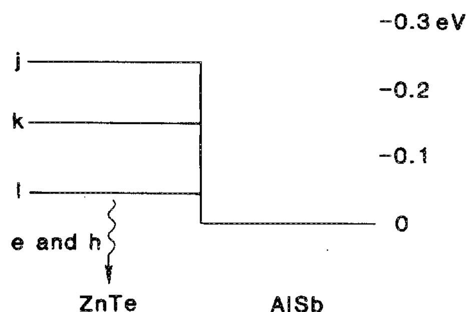

FIG. 5. Direct predictions for ΔE_c of ZnTe/AlSb. (j) Ref. 11; (k) Ref. 25; and (l) Ref. 26. Two other predictions, indicating a much lower barrier, (e) Ref. 18 and (h) Ref. 13, are discussed in the text.

In summary, the predicted values available for the offset ΔE_c (AlSb/ZnTe) have been intercompared. Many predictions indicate a value near 0.1 eV. Even the largest prediction $\Delta E_c \approx 0.3$ eV, should permit a substantial electron current to be injected into p-ZnTe producing electroluminescence. The undesired hole current into the n-AlSb may be suppressed by suitable doping or possibly by a blocking layer at the interface. Due to the small offset between this wide-gap II–VI and the proposed minority carrier injecting contact, this HJ is the most favorable for visible II–VI electroluminescence of the lattice-matched cases covered by present predictions and/or measurements.

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