Strain and the Interpretation of Band-Lineup Measurements

In a recent Letter, Duc, Hsu, and Faurie[1] (hereafter DHF) reported band-lineup determinations for several Te-based heterojunctions, obtained from core-level measurements. In this Comment, we wish to clarify the interpretation of such measurements for the case of strained-layer heterojunctions, such as ZnTe-CdTe and ZnTe-HgTe.

DHF measured the core-level energy differences ΔE_{cl} across their heterojunctions. They then inferred the valence-band discontinuities ΔE_v across the interfaces from measurements of the relative positions $E_v - E_{\mathrm{cl}}$ in the respective *bulk* materials. This procedure involves no approximations in principle for lattice-matched semiconductors. However, to obtain the *true* valence-band discontinuity in a *strained* heterojunction, i.e., the barrier for transport of holes across the interface, the measurements of $E_v - E_{\mathrm{cl}}$ must be performed on crystals in the *same state of strain* as the respective semiconductors in the heterojunction.

The resulting valence-band discontinuities ΔE_v depend both on the degree of strain (presence or absence of misfit dislocations), and on the choice of substrate (which determines how the strain is apportioned between the two semiconductors). For strained-layer heterojunctions, ΔE_v will in general exhibit neither linearity nor commutativity,[2] contrary to the conclusion of Ref. 1. Moreover, even a direct measurement of ΔE_v would be useless without precise knowledge of the state of strain in the heterojunction. This is about all one can say with complete rigor.

However, core-level measurements such as those of DHF may *under certain assumptions* be *more* valuable than measurements of the true valence-band discontinuity ΔE_v. Unlike ΔE_v, the core-level energy differences measured by DHF *do* apparently exhibit linearity, commutativity, and transitivity, at least in this case, and to within the accuracy of the experiment. Then the remaining issue is how to relate ΔE_v to the core-level measurement in the presence of strain.

Van de Walle and Martin[2] showed that a primary effect of strain was simply to split the three states at the top of the valence band. If we denote the average energy of the three highest occupied states at Γ as $E_{v,\mathrm{av}}$, then the discontinuity $\Delta E_{v,\mathrm{av}}$ was found (at least in the cases studied) to be virtually independent of how strain was apportioned between the two semiconductors.

The interpretation of experiments such as that of DHF becomes straightforward if we make a reasonable assumption, motivated by the results of Ref. 2. Specifically, if we *assume* that the difference $E_{v,\mathrm{av}} - E_{\mathrm{cl}}$ is independent of the crystal strain, then the core-level measurement, analyzed as in Ref. 1, provides essentially a direct measure of $\Delta E_{v,\mathrm{av}}$. That assumption also implies that $\Delta E_{v,\mathrm{av}}$, like ΔE_{cl}, will exhibit linearity, transitivity, and commutativity. (Though we stress core-level measurements here, valence-band photoemission is usually insensitive to splitting of the actual band edge, and so also tends to measure $E_{v,\mathrm{av}}$ rather than E_v).

It is worth stressing that the assumption above is certainly not exactly correct. In particular, the presence of strain implies a net hydrostatic pressure, which will shift E_v relative to E_{cl}. A rough estimate, based on the "model solid" approach,[3] suggests that even $\Delta E_{v,\mathrm{av}}$ could vary by 0.15 eV for ZnTe-CdTe, depending on whether or not the strain is relieved by misfit dislocations. The mere possibility of such an effect makes clear the importance of determining and reporting the strain in the semiconductors, for cases such as ZnTe-CdTe and ZnTe-HgTe where the lattice mismatch is severe.

For certain purposes, such as device design, it is necessary to know the true valence-band discontinuity ΔE_v. However, with the assumptions above, ΔE_v can be inferred directly from $\Delta E_{v,\mathrm{av}}$ by use of the appropriate deformation potential,[2] if the state of strain in the interface is known. For example, using the analysis of Ref. 2 and deformation-potential parameters from the literature,[4] one can infer the noncommutativity of ΔE_v for ZnTe-CdTe in the absence of dislocations. For a ZnTe substrate (all strain in the CdTe layers), assuming $\Delta E_{v,\mathrm{av}} = 0.10$ eV,[1] one obtains $\Delta E_v = -0.80$ eV. For a CdTe substrate, the result is $\Delta E_v = 0.32$ eV. Thus there is a huge noncommutativity, 0.4 eV, for the true valence-band discontinuity. This fact may prove to be exceedingly important for providing flexibility in device design.

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