Deep-Level Impurities: A Possible Guide to Prediction of Band-Edge Discontinuities in Semiconductor Heterojunctions

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Since transition-metal impurity levels are found to be aligned with respect to each other within a group of isovalent semiconductor compounds, as if a common *reference level* existed for them, we propose to use this fictitious level for the band alignment in semiconductor heterojunctions. This rule leads to a valence-band discontinuity in $Ga_{1-x}Al_xAs/GaAs$ heterojunction of $\Delta E_v = (0.34 \pm 0.05) x \Delta E_g$ (AlAs/GaAs) in agreement with the most recent measurements. Predictions of several III-V on III-V and II-VI on II-VI heterojunction band-edge discontinuities are also given.

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The band-edge discontinuity in semiconductor heterojunctions (HJ) is among the most important parameters characterizing such a structure. Both the experimental results and the predictions by different theoretical models scatter dramatically in spite of the great technological importance of these structures and the necessity of knowing a reasonably accurate value of the discontinuity for the purpose of device engineering. Recent reviews of the subject strongly reflect this situation.[1-3]

There is a clear indication that the band discontinuities are not only the result of the bulk properties of both constituents of the HJ, but may also depend on the way that the HJ is prepared. Among the most obvious of these variable parameters is the crystallographic orientation of the substrate, the possible reconstruction of the interface, a more or less graded transition from one constituent to the other, the formation of a dipole layer, and other technological factors as discussed by Bauer and Sang.[2] Therefore, two extreme approaches to the problem can be found.

(i) The existing universal approaches[4-7] are only of limited value in predicting band-edge discontinuities. The key argument is that they are based only on the bulk properties of the constituents. None of them nor the other more elaborate theoretical computations[8] takes into account the complete situation present in reality at the interface (see, e.g., the review by Bauer and Sang[2]).

(ii) In certain well-selected and well-prepared HJ's the discontinuity *can be* related to bulk properties alone. These restrictions would include, for instance, the formation of an abrupt junction, the absence of extra dipole layers and, therefore, electrically neutral surfaces [e.g., (110) in tetrahedrally coordinated compounds], and to some extent the choice of the constituents of the HJ from only one "class" of semiconductors, e.g., III-V or II-VI compounds. In this case the band-edge discontinuities are expected to fulfill the properties of "linearity and transitivity" as discussed by Kroemer.[1]

To separate the technology-dependent factors from the factors governed only by the bulk properties, it is necessary either to determine experimentally or to predict in a reasonably accurate way the latter contribution.

From the experimental side, the achievements of molecular-beam-epitaxy or metal-organic chemical-vapor-deposition growth techniques allow for preparation of almost ideal HJ's. However, because of the technological complexity as well as the difficulties of proper design and interpretation of the experimental determination of the discontinuity, only very few HJ combinations can be considered as test examples for the prediction of HJ discontinuities. The year-long dispute on the correct value of the discontinuity in what is one of the most extensively studied systems, $GaAs/Ga_{1-x}Al_xAs$,[1,2,9-15] should be taken as a warning.

The purpose of this Letter is to propose a new heuristic approach to the prediction of band-edge discontinuities between semiconductor pairs. It is based upon the assumption of the discontinuities of some *bulk reference level* which serves as a reference level for the alignment of the band edges of the constituents of the HJ. It seems that such a reference level exists at least for the transition-metal (TM) impurities in semiconductors.

This group of elements is known to form localized deep impurity states in semiconductors. One of the most surprising features of TM impurities in semiconductors is that they can possess several charge states separated even by a fraction of the host energy gap in contrast to the much larger difference in the atomic ionization potentials. With this in mind, conservation of both the ordering and the relative energy separation of the like-impurity ground levels for the whole series of transition metals in similar groups of compounds (e.g., III-V or II-VI semiconducting compounds) is even more puzzling. The evidence for such a trend, exemplified in Fig. 1, has been pointed out recently[16-18] but on a more limited data basis than that used

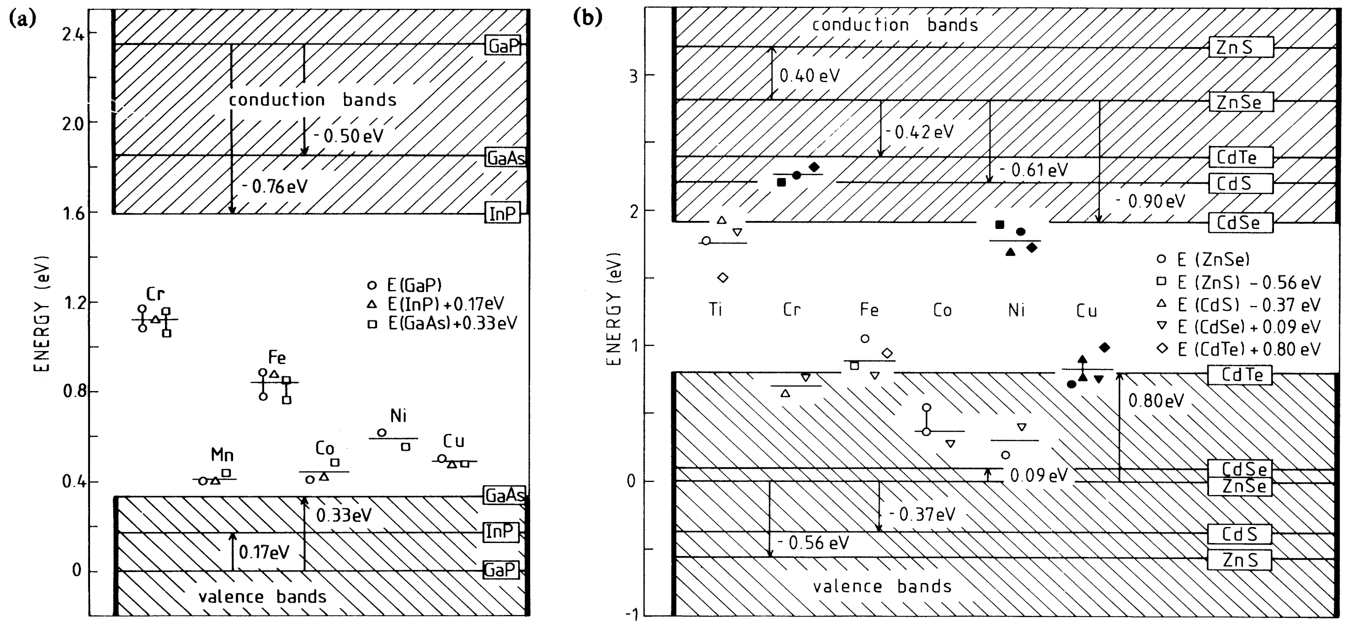

FIG. 1. (a) Average energy levels of TM acceptors (−/0) in GaP, InP, and GaAs relative to the top of the valence band of GaP. They were determined by the appropriate vertical shift of the experimental (Refs. 16–21) TM energy pattern in all three compounds so as to minimize the overall mean square deviations. The resulting shifts give the relative positions of the top of the valence-band edges of InP and GaAs relative to the GaP valence-band edge. The relative positions of the conduction bands were then obtained from the low-temperature energy gaps (see Ref. 19). It should be noted that the so-obtained GaAs/GaP valence-band shift equal to 0.33 eV is in excellent agreement with that value obtained from the composition dependence of the ionization energy of several TM acceptors in $GaAs_{1-x}P_x$ compounds ($dE/dx = 0.35$ eV; see Ref. 21). (b) The average energy levels of TM donors (0/+) (open symbols) and acceptors (−/0) (filled symbols) in II-VI compounds obtained in the same way as in (a). All band-edge shifts are relative to the ZnSe band edges. The impurity ionization energies were taken from Refs. 17, 19, and 22.

by us. This indicates that TM impurities are not pinned to either of the nearby band edges. The observed alignment suggests the existence of a common *bulk reference level* for them in isovalent semiconductor compounds. Its connection with the vacuum level as proposed by several authors[16–18] is not necessary for our purposes. Having established the existence of such a level for two classes of materials (III-V and II-VI compounds) we postulate that the same reference level can be used for the band alignment for a pair of isovalent compounds (i.e., III-V on III-V or II-VI on II-VI). *A valence-band-edge discontinuity in HJ is then given by just the difference in the energy-level positions of a TM impurity in the two compounds forming the HJ.*

To test the above proposal the existence of reliable data on HJ band-edge discontinuities as well as the complete set of energies of TM impurities in both constituents of the HJ are necessary. Unfortunately, the only system for which data are available is GaAlAs/GaAs. Even for this pair the discussion on the value of the band-edge discontinuity is still progressing. The most recent data[9–15] indicate that the band-edge discontinuity ratio $\Delta E_c{:}\Delta E_v$ in the direct-band-gap region of GaAlAs is approximately 0.6:0.4 in contrast to the older ratio 0.85:0.15 inferred from the IR absorption of multiple-quantum-well structures by Dingle *et al.*[23] Both the experimental technique and the progress in the HJ preparation favor the most recent findings, which should then be used as the test for any band-edge–discontinuity predictions.

The ground-level position of an Fe impurity as well as of several other defects has been determined in $Ga_{1-x}Al_xAs$ by Lang, Logan, and Kimerling[24] by the technique of deep-level transient spectroscopy. Using these data, we therefore predict the valence-band-edge discontinuity between GaAs and $Ga_{1-x}Al_xAs$ for $x = 0.2$ to be equal to $\Delta E_v = (0.42 \pm 0.06 \text{ eV})x$. Therefore, the extrapolated valence-band discontinuity between GaAs and AlAs predicted by our method would be $\Delta E_v = (0.34 \pm 0.05)\Delta E_g$. This value is in excellent agreement with the recent data.[9–15] The agreement is best visualized in a band-edge evolution diagram, based upon the prediction of our proposal, in which the most recent data[9–14] are included (Fig. 2). It is intriguing that the theoretical predictions of the GaAs/AlAs discontinuity suggest a much smaller

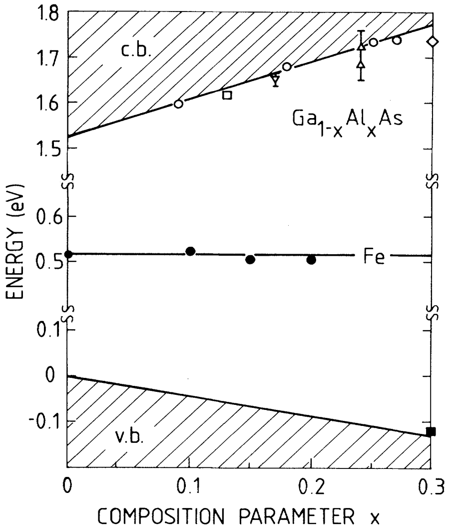

FIG. 2. $Ga_{1-x}Al_xAs$ band-edge energies measured relative to the Fe acceptor level (Ref. 24), which was taken as a reference level independent of x. The band-edge–discontinuity data of GaAs/$Ga_{1-x}Al_xAs$ heterostructures were taken from Refs. 9 (open circle), 10 (inverted triangle), 11 (open square), 12 (triangle), 13 (lozenge), and 14 (filled square).

value of the valence-band-edge discontinuity (0.04 eV by Harrison,[5] 0 by Frensley and Kroemer,[6] 0.35 eV by Tersoff,[7] and 0.25 eV by Picket, Louie, and Cohen[8]). It is worth pointing out, however, that inclusion of the charge-transfer dipole by Frensley and Kroemer[6] in their model calculation increases the value of ΔE_v from 0 to as much as 0.69 eV.

The success of our proposal in prediction of the HJ band-edge discontinuity for GaAlAs/GaAs allows us to predict the discontinuities for the other systems. They can be obtained directly from the relative positions of the band edges given in Fig. 1. Our approach is limited to only the isovalent HJ (III-V on III-V and II-VI on II-VI). If we had, however, one reliable matching point between the two isovalent classes of compounds (like GaAs/ZnSe HJ) it could also yield predictions for a much larger class of HJ. Our approach assumes explicitly the "linearity" as well as the "transitivity" of the HJ band-edge lineup as the other universal approaches[4-7] do. It also does not take into account any additional factors which may arise in practice, e.g., the orientation dependence and the existence of the charge-transfer dipole layer. The principal value of our empirical method is that it relies only upon the bulk semiconductor data and not on the much less accurate and less obvious procedure employing the semiconductor electron-affinity data (see Kroemer's recent reviews[1] for a discussion of the conditions when the use of the semiconductor affinities for predicting the HJ band structure is valid). It requires, however, a determination of the TM impurity levels by the same technique and the same fitting procedure for both constituents of the HJ. Furthermore, it would be most accurate for determination of level position in the mixed compounds consisting of both constituents of the HJ, like in the GaAlAs case discussed here. It is tempting to extend our proposal to the other deep-level impurities. The available experimental data on their ionization energies[21,25] as well as the theoretical arguments[26] make, however, such a procedure neither reliable nor justified.

Our proposal bears a certain similarity with a recent band-structure calculation by Tersoff[7] of Schottky barrier heights and HJ band discontinuities. According to Tersoff, band structures at the HJ match at the reference level E_B, the energy of a semiconductor at which "the gap states cross over from primarily valence to conduction character." The same type of fictitious level is expected to serve as the reference level for TM impurities because of their peculiar structure. A clear advantage of our approach is, however, that it relies only on the experimentally determined impurity levels, while Tersoff's approach requires heavy computational work with an accuracy of 0.1–0.2 eV at best, typical for current band-structure calculations.

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[1] H. Kroemer, Surf. Sci. **132**, 543 (1983), and in *Proceedings of the NATO Advanced Study Institute on Molecular Beam Epitaxy and Heterostructures, Erice, Sicily, 1983,* edited by L. L. Chang and K. Ploog (Martinus Nijhoff, The Netherlands, 1984), p. 331, and J. Vac. Sci. Technol. B **2**, 433 (1984).

[2] R. S. Bauer and H. W. Sang, Jr., Surf. Sci. **132**, 479 (1983).

[3] G. Margaritondo, Surf. Sci. **132**, 469 (1983).

[4] R. L. Anderson, Solid State Electron. **5**, 341 (1962).

[5] W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977).

[6] N. R. Frensley and H. Kroemer, Phys. Rev. B **16**, 2642 (1977).

[7] J. Tersoff, Phys. Rev. B **30**, 4874 (1984).

[8] W. E. Pickett, S. G. Louie, and M. L. Cohen, Phys. Rev. B **17**, 815 (1978).

[9] H. Okumura, S. Misawa, S. Yoshida, and S. Gonda, Appl. Phys. Lett. **46**, 377 (1985).

[10] O. J. Glembocki, B. V. Shanabrook, N. Bottka, W. T.

Beard, and J. Comas, Appl. Phys. Lett. **46**, 970 (1985).

[11] M. H. Meynadier, C. Delalande, G. Bastard, M. Voos, F. Alexandre, and J. L. Liévin, Phys. Rev. B **31**, 5539 (1985).

[12] J. Batey, S. L. Wright, and D. J. DiMaria, J. Appl. Phys. **57**, 484 (1985).

[13] E. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984).

[14] D. Arnold, A. Ketterson, T. Henderson, J. Klem, and H. Morkoç, J. Appl. Phys. **57**, 2880 (1985).

[15] T. W. Hickmott, P. Solomon, R. Fisher, and H. Morkoç, J. Appl. Phys. **57**, 2844 (1985).

[16] L. A. Ledebo and B. K. Ridley, J. Phys. C **15**, L961 (1982).

[17] P. Vogl and J. M. Baranowski, Acta Phys. Pol. **A67**, 133 (1985), and to be published.

[18] M. J. Caldas, A. Fazzio, and A. Zunger, Appl. Phys. Lett. **45**, 671 (1984).

[19] *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Techology,* edited by O. Madelung (Springer-Verlag, Berlin, 1982), Group 3, Vol. 17, Parts a and b.

[20] D. C. Look, Semicond. Semimetals **19**, 76 (1983); G. Neumark and K. Kosai, Semicond. Semimetals **19**, 1 (1983); B. Clerjaud, J. Phys. C **18**, 3615 (1985); A. G. Milnes, Adv. Electron. Electron. Phys. **61**, 63 (1983).

[21] L. Samuelson, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors, Coronado, California, 1984,* edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of AIME, Warrendale, Pa., 1985), p. 101.

[22] A. Fazzio, M. J. Caldas, and A. Zunger, Phys. Rev. B **30**, 3430 (1984); W. Jantsch and G. Brunthaler, Appl. Phys. Lett. **46**, 666 (1985); K. Lischka, G. Brunthaler, and W. Jantsch, in Proceedings of the Second International Conference on II-VI Compounds, Aussois, France, 1985, J. Cryst. Growth (to be published).

[23] R. D. Dingle, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **34**, 1327 (1975); see also, R. Dingle, in *Festkörperprobleme,* edited by H. J. Queisser (Vieweg, Braunschweig, 1975), Vol. 15, p. 21.

[24] D. V. Lang, R. A. Logan, and L. C. Kimerling, in *Physics of Semiconductors, Proceedings of the Thirteenth International Conference, Rome, 1976,* edited by F. G. Fumi (Tipografia, Marves, Rome, 1976), p. 615.

[25] P. Vogl, in *Festkörperprobleme,* edited by J. Treusch (Vieweg, Braunschweig, 1981), Vol. 21, p. 191, and Adv. Electron. Electron Phys. **62**, 101 (1984).

[26] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).