Surface Science 168 (1986) 518–530
North-Holland, Amsterdam

# DEFECTIVE HETEROJUNCTION MODELS

J.L. FREEOUF and J.M. WOODALL

*IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598, USA*

Received 10 June 1985; accepted for publication 14 June 1985

Fermi-level pinning behavior has been observed at the free surface, oxide interface, metal interface, MBE grown surface, stop-regrown homojunction, and misfit-dislocation pinned heterojunction of GaAs. Theories of such behavior are numerous and disparate. Theories of ideal heterojunction band offsets are less diverse, but have still not converged to a single mechanism. Recent studies of heterojunctions suggest that the conduction-band offsets are relatively independent of interface Fermi-level position, including situations in which the interface Fermi-level appears to be strongly "pinned". In "ideal" heterojunctions, the conduction-band offsets and bulk doping determine interface Fermi-level location; among other results, this mechanism allows the two-dimensional electron gas at modulation-doped AlGaAs–GaAs heterojunctions. If "pinned" heterojunctions involve charge densities comparable to those inferred for Schottky barriers, then the pinning interface states should set up a dipole sufficient to alter the band offsets; the interfacial band alignment should then be dominated by the alignment of the pinning states, rather than that of the bulk bands. The experimentally suggested lack of sensitivity of band offsets to changes in pinning at heterojunction interfaces suggests that the mechanisms involved in band line-ups at "ideal" heterojunctions may be related to those mechanisms involved in Fermi-level "pinned" systems. A simple mechanism is that of work function matching, in which the transition to "pinned" behavior involves the generation of a new material at the interface; since the work function difference between heterojunction materials is unaffected, the band offset would likewise be unaffected. The effective work function model explains the pinning phenomenon on the basis of anion clusters, which have been observed at all classes of pinned interfaces involving III–V compounds. The application of other models to both pinned and unpinned interfaces is less clear; more information is required. Pinning models which involve interface state densities within each semiconductor must address the lack of sensitivity of band offset to different interface Fermi-level locations.

## 1. Introduction

Heterojunction-based device structures offer very intriguing possibilities [1,2]. The possibility of separately "biasing" electrons versus holes or of confining one or both classes of carriers without applied bias and separately from the source ions permits new device structures; implementing such structures in III–V materials to exploit greater mobilities and possible ballistic transport could permit the increased fabrication costs to be justified by improved device

0039-6028/86/$03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)



G. Margaritondo (ed.), *Electronic Structure of Semiconductor Heterojunctions*
© Editoriale Jaca Book spa, Milano 1988

performance. Furthermore, heterojunctions provide an ordered single-crystal interface between two well-characterized semiconductors; their fabrication is becoming increasingly controlled and routine via several techniques, thereby permitting extensive experimental characterization of the formation and electronic properties of these interfaces. Theoretical analysis of such interfaces faces few of the difficulties encountered in similar treatments of Schottky barriers; in at least some cases, the interfaces are known to be ordered and abrubt on an atomic scale, and the crystal structure and band structures of the two sides of the interface are quite similar. We regard these interfaces as the likely first candidates for "complete" understanding, at least at the level currently achieved for the cleaved free surface of III–V compound semiconductors.

However, the hoped-for understanding has not yet been achieved; in fact, there is little agreement on so fundamental an issue as the "correct" division of the total change in band gap (between the two semiconductors) between a valence-band offset and a conduction-band offset. The literature contains many studies asserting that the band offsets depend upon growth conditions, growth sequence [3–5], and crystallographic orientation. Such studies typically conclude that, since more than one band offset is possible, a simple prediction ignoring such complications is demonstrably false and unwarranted [3]; furthermore, authors still willing to rashly ascribe some validity to a simple "zeroth-order" approximation [1] often assert that a work function matching approach [6] is demonstrably less accurate than a "first-principles" bulk approximation.

In this paper, we wish to suggest that simple models are both useful and valid – both as initial guides in device design and in terms of addressing theoretical aspects of interfaces. Furthermore, we assert that at present a work function matching scheme of heterojunction band offsets is the "simple model" of choice; it is at least as consistent with current acceptable data as any competitor, and it describes a wider range of experimental conditions than do alternatives. In support of this suggestion, we shall first briefly describe our modified work function matching scheme for "pinned" compound semiconductor surfaces and interfaces – and explain why we feel these modifications are justified. Next, we shall discuss why this model is also consistent with band offsets as currently measured. We shall exclude some interfaces from current attack by our model; we add that such an exclusion should also be the current approach of theorists wishing to achieve a first-principles full understanding of these interfaces. Finally, we shall point out that the interfaces in which a range of band offsets have been observed may well not be of any interest to device designers, since the electrical properties of such interfaces are unknown. In fact, the alteration of band offsets (at least under most current models) would appear to require a charged dipole and/or graded, mixed, disordered and/or roughened interface; all of these pos-

sibilities offer reasons for concern to a device designer, at least for specific classes of devices.

## 2. Work function matching

Conceptually the most straightforward mechanism for understanding of the bands of two dissimilar materials is to seek some means of aligning them both with respect to the same reference. If we make this reference the vacuum level, then we are invoking a work function matching scheme. Advantages of such a choice include thermodynamic validity and observability. A detailed treatment of the thermodynamic basis for work functions has been available for many years, as have many caveats which we shall discuss shortly [7]. The observability of work functions by many techniques has been exploited for an even longer time; the fruits of such labor are the availability of data concerning the work functions of many materials under many conditions as measured by many techniques. For many materials, the work function of specific, ordered surfaces are known to two or three decimal places, without debate. Objections to the application of such data to schemes matching two work functions may be divided into three classes:

(1) They don't work [3].

(2) The difference of two large numbers to derive a small number is risky [1].

(3) The surface/interface dipole invalidates the thermodynamic treatment [8].

We shall present data suggesting that such schemes do work fairly well, if one properly allows for interface metallurgical effects. We agree that the limited precision in defining the difference in two large ($\approx 5$ V) numbers to infer a small ($\leq 1$ V) number limits the utility of the method; however, this is a practical question, not one of basic concepts [9]. The primary conceptual objection to this scheme is one of surface and interface dipoles and their effect upon both measured work functions and actual interface band alignments. This question is difficult to address experimentally, since separation of "bulk" work functions from surface dipole effects is basically not possible [7,10]; the magnitude of variation of work functions from one crystal surface to another suggest possible dipole-induced errors of $\approx 1$ V [11] suggesting that this effect could dominate the desired answer in a fashion that cannot be addressed by simple techniques. Theoretically, the answer is "maybe": some recent models describing band line-ups of either metals or semiconductors on semiconductors have ascribed the *entire* observed band line-ups to interface dipole-driven effects [12,13]; another recent calculation suggests that interface dipoles deviate from surface dipoles by $\leq 0.1$ V [14], suggesting that the *intrinsic* error to the concept may be only comparable to the present measurement precision.

## 3. Effective work function model

The question of why the model "doesn't work" despite these conclusions must now be addressed; in point of fact, we believe that the model [15] does work! We first discuss metal contacts on compound semiconductors, in which purported disagreement is larger. We note that in-situ surface-sensitive studies of the formation of such interfaces have often observed metallurgical disruption of the semiconductor [16], giving rise to several "explanations" of Fermi-level pinning based upon such disruption [15,17]. The effective work function (EWF) model assumes such disruption occurs, leading to mixed phase interfaces. On chemical grounds, the interface between most III–V compounds and oxygen or Au should lead to cation compounds and/or alloys with the overlayer, along with free excess anion. The work function of this postulated anion corresponds to the work function observed for the barrier height.

To summarize, the EWF model assumes that, at pinned interfaces, the interface Fermi-level location is determined by the work function of the anion released from the substrate by the processes used to generate the interface. A major implication of this model is that the Fermi-level position is relatively independent of the bulk metallurgy, since the anion at the interface is the determing factor. Another implication is that the observed pinning position should have a work function ($\phi = \chi + \phi_{bn}$) equal to that of the anion. This prediction is compared with experiment in fig. 1 for some materials; note that

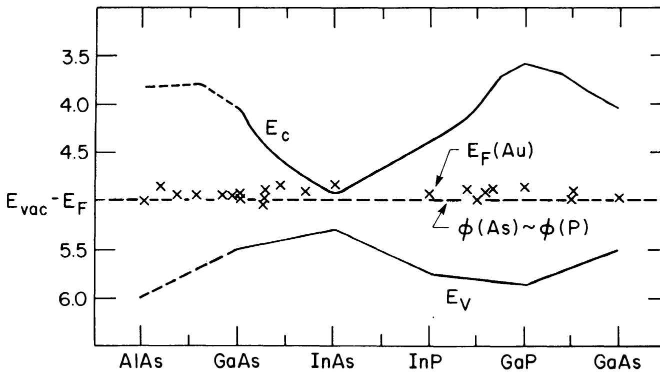


Fig. 1. Interface Fermi-level location for (mostly) Au contacts on various compounds and alloys. Except AlAs affinity, the electron affinities, band gaps, and barrier heights for compounds from references in ref. [15]; AlAs electron affinity derived by *assuming* the EA model for heterojunction band alignments. All alloys *assume* that the valence bands vary linearly with composition between the end-point compounds; the barrier heights for alloys are from ref. [39] (GaAsP), ref. [40] (InGaAs), ref. [41] (InGaP) and ref. [42] (AlGaAs).

$\phi_P \approx \phi_{As}$, so the model predicts a constant work function in this series, as is observed. In ref. [15] we compare the predictions with experiment for other materials. Pinning behavior has been observed on free surfaces and at III–V interfaces with oxides, metals, and misfit dislocations [17]; anion clusters or excesses have been observed on free surfaces [18], metal interfaces [19], oxide interfaces [20], and at dislocations [21]. We believe the correlation of measured barrier heights to this simple model, which is based upon effects that have actually been observed to occur in at least some instances, is highly suggestive. We further note that the mixed phase assumption embedded in our model provides a natural explanation for the discrepancies between different measurement "definitions" for a single barrier height, since different techniques will average via *different weighting functions* over the mixed phase interface. However, we add that valid questions concerning the model include:

(1) The work function of small anion clusters, and in fact the size distribution of such clusters.

(2) The persistence of these "pinning" positions under conditions where surface probes suggest depletion of the anion.

(3) The manifold parameters available to vary alloy and/or compound distribution to "explain" deviations from our modified "anion rule".

Further, all models based upon metallurgical interactions must assume a "universality" of such interactions; given the small degree of disruption necessary for such a model to "explain" experimental results ($\approx 10^{12}$ $cm^{-2}$ for chemisorbed surfaces and $\approx 10^{14}$ $cm^{-2}$ for metal–semiconductor interfaces), the exclusion of such effects at any interface may not be possible with current techniques. While we are uncomfortable invoking a "Maxwell's demon", we advocate use of the model for its practical utility, its chemical intuition, and the *observation* of our proposed demon in the same classes of interfaces that are pinned.

We note that the defect model [17] also must assume "universality", has a large number of defect parameters, assumes "demons" never observed at these interfaces, and must further assume that interface defects are not subject to the metal screening demonstrated by Heine [22] to apply to surface states at metal–semiconductor interfaces. Finally, the defects must be stable under very substantial fields – of order $\approx 2 \times 10^7$ V $cm^{-1}$ [23]. Furthermore, the calculations for such levels [24] demonstrate that the energies are a strong function of whether the defects are at the surface or in the bulk; this suggests that pinning positions should differ between chemisorbed surfaces and stop-regrow interfaces.

## 4. Electron affinity rule

The original "rule" for ascertaining heterojunction band alignments was due to Anderson [6]; this rule is simply work function matching, and is typically called the Anderson rule or the electron affinity rule (EA). Despite the compelling nature of the thermodynamic argument in favor of such a description, the electron affinity rule has come under strong attack for the same reasons as the work function matching scheme for metal–semiconductor contacts. Further objections specific to the heterojunction literature refer to various observed "non-linear" results [3–5]; this term is used to refer to aspects of interfaces not addressable by any model that defers treatment of interface dipoles, grading, etc. The magnitude of such effects seems to be large; in favorable cases heterojunction band offsets have been observed to vary by $\approx 0.3$ V depending upon which semiconductor is deposited upon the other [3]. It is clear that the electron affinity rule cannot predict such behavior; it is less clear that predicting such behavior is a desirable aspect of even a first-order theory.

At present, one cannot exclude the possibility that such effects are extrinsic, and not related to abrupt ideal heterojunctions at all. These effects have been reported for heterojunctions involving Ge with some compound semiconductors; such interfaces are experimentally attractive because germanium is easy to deposit "stoichiometrically". Problems with comparing such experiments with any theory include:
(1) The theoretical "certainty" of atomic rearrangement/intermixing at most such interfaces [25].
(2) The uncertain growth morphology on the (110) growth plane less susceptible to the above effect [26].
(3) The absence of electrical characterizations of such heterojunctions grown in the same systems under the same conditions as were the interfaces for which a band offset was measured.
The experimental situation becomes even more uncertain given the current status of the device world's favorite heterojunction, AlGaAs/GaAs. The "best guess" value for that band offset has recently been revised by of order 0.3 V [27]. The revision of the band offset in this case is largely due to the application of new techniques for determining the offset, coupled with reevaluation of the theoretical basis for the original technique. Although such revisions should not have impacted the surface studies, the only previous surface study of that interface was consistent with the old "right" answer [4]. We feel that this result reflects the quality of those samples, which unfortunately were not of state-of-the-art caliber even for that time. Those results were obtained for growth in the (110) orientation, an orientation notoriously difficult to grow well [26], at an unusually low growth temperature; a year after those measurements, segregation or spinodal decomposition of AlGaAs

alloys grown in that orientation at that growth temperature was reported by another group [28].

However, we must work with what we have; in fig. 2 we compare the electron affinity model to the selected heterojunction band offset values presented by Kroemer in a recent critical review [29], with the AlAs value altered to reflect the current understanding. In fig. 3 we present the same comparison after exclusion of the homopolar/heteropolar interfaces for which we have strong questions. For comparison, we include the Harrison atomic orbital model (HAO) [30], and an empirical model of Katnani and Margaritondo (KM) [31]. In fig. 3 we have added a point with question marks; AlSb/GaSb appeared a possibly useful device interface [2], and the HAO model disagrees with the EA model. Current data are intermediate, but place only a lower bound on the discrepancy [32] with the HAO model; the data are not yet sufficiently complete to warrant strong conclusions, however. Based on the new AlAs/GaAs, and possibly the AlSb/GaSb, values, we suggest that the EA model fits the data at least as well as the HAO model; we suggest that the HAO model incorporate modifications to deal with the potential of aluminum compounds differently. We further note that the empirical model of Katnani and Margaritondo seems in error for InAs/GaSb, CdS/InP, and (possibly) GaAs/InAs. The EA model shows errors only for Si/Ge and for ZnSe/GaAs; while the former interface was found to be inde-

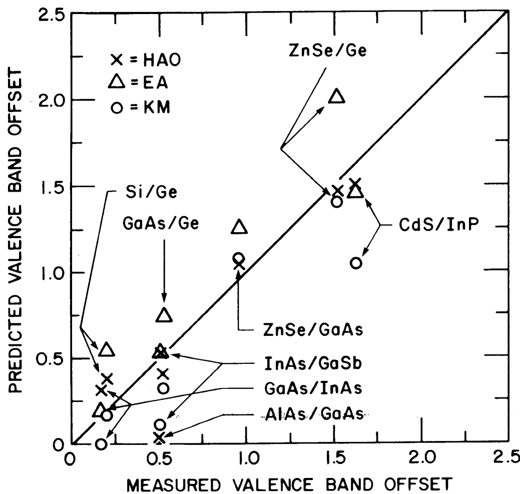


Fig. 2. Heterojunction band offsets as predicted by refs. [6, 31, 30] compared with "critically selected" values of ref. [8]. Electron affinities for compounds from references cited in ref. [15]; those for sillicon and germanium from ref. [43].

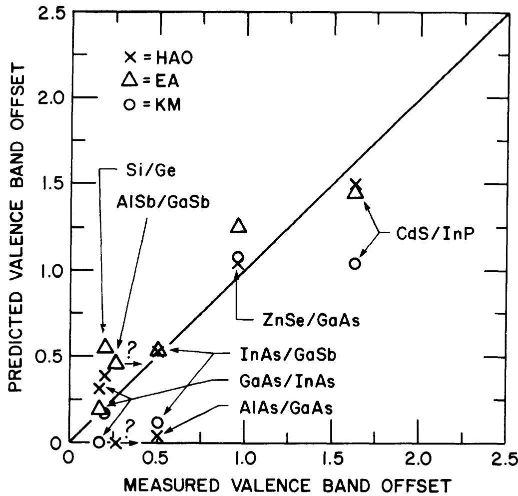


Fig. 3. Same as fig. 2, without the homopolar/heteropolar heterojunctions.

pendent of deposition order (the latter was not studied in the inverse order), there are insufficient data to establish the electrical perfection and abruptness of these interfaces. We note that the experimental [31] offset plotted implies that the band gap of Ge is entirely contained within that of Si ("normal offset") and that $\Delta_v \leq \Delta_c$. Some strained layer superlattice studies suggest [33] that $\Delta_v \gg \Delta_c$. Further, preliminary data on strained layer SiGe/Si superlattices suggest a "staggered" configuration [34], as the EA model predicts, but of unknown magnitude; further, we do not know whether this staggering would be observed in the absence of strain, which is the configuration being predicted by all the models. From fig. 2 we could infer a general failure of the EA model to explain heterojunction offsets involving germanium; should this failure persist in "perfect" heterojunctions, perhaps a calculation of expected "dipole changes" for this indirect small band-gap semiconductor might be appropriate.

In general, however, we believe that current "best data" on "best ordered" and understood heterojunctions permit the EA rule to be applied with at least the confidence due other first-order theories. We feel that a large discrepancy between the EA rule and experiment or theory should stimulate study to ascertain the cause of the discrepancy. We do not feel the EA rule will always be the state of the art heterojunction band offset theory; in fact, we encourage theorists to attack this problem on systems currently under experimental control (AlAs/GaAs, GaSb/InAs) where interfaces of near ideal abruptness and order appear feasible. We note, however, that since the band-gap discon-

tinuity and its allocation between the valence and conduction bands are a crucial aspect of the issue, theories which properly obtain the band gaps (including subsidiary minima at L and X) would be highly desirable.

## 5. Pinned heterojunctions

A work function matching picture appropriate to both pinned and unpinned heterojunctions is clearly possible; the pinned heterojunction is assumed to have some metallurgical interactions giving rise to the excess anion postulated by the effective work function model. Such an interface will have band bending in both semiconductors permitting the interface Fermi level to coincide with the work function of the postulated anion. For an interface between materials using different anions, such as InAs/GaSb, one would presumably have some form of alloy of the two anions, with a possibly different work function. However, unless there are two *layers* of anions each contacting only the other and the semiconductor (i.e. InAs/As/Sb/GaSb) there should be a single interface work function; both semiconductors should line up with respect to this single work function by standard work function matching arguments, and the *difference* between the two semiconductor band alignments should again correspond to the difference in their electron affinities, so the band offset should be independent of pinning or interface Fermi level location. For this argument to apply, we need not even assume the pinning is due to excess anion; *any* single work function interface layer leads to this conclusion. This does assume that the interface disruption does not lead to graded or intermixed interfaces leading to unusual dipoles.

Such an argument leads to the conclusion that heterojunction band offsets should be independent of interface Fermi level location; this argument applies to both pinned and unpinned heterojunctions. Many heterojunction band offset models assume that interface Fermi level position has no effect upon band alignment, but it is not clear to us that this is true for all such models. The model of Tersoff discusses band alignments in terms of dipole formation at the interface; this dipole involves states tunneling from one material into the other. The "neutrality level" of this theory is somewhere in mid gap, and the imaginary states (and their decay length) used to derive a dipole are related to this point; we would expect their occupation to be dependent upon Fermi level position, especially as the Fermi level moves across the band gap, as it can do in an ideal heterojunction interface such as the AlAs/GaAs case, where both electron and hole two-dimensional gases have been observed. Further, we do not understand why the band offset for Ge/GaAs appears independent of Fermi level location when the interface Fermi level is varied from well within the fundamental band gaps to the case where the Ge is apparently degenerate n-type even at the interface [34]. A final problem with

the model of Tersoff [13] is that it apparently assumes that dielectric screening affects both electrostatic *and chemical* potential changes [10]; we are unable to reconcile band offsets depending upon, e.g., growth sequence, by $\approx 0.3$ V [3] with such screening affecting all possible sources of chemical potential shifts.

We believe that these arguments also have some relevance to other models of Fermi-level pinning; a standard current model for Fermi-level pinning is that of metallurgical interaction-induced defects [17]. Within this model, both the pinning position [17] and the sign of the charge induced in these defects is a function of the bulk doping [35]. Defect densities adequate to pin Schottky barriers would also strongly alter band offsets [35] and align pinned Fermi levels rather than bulk bands [36]; we would predict that a pinned n–p heterojunction should exhibit a different band offset than would a pinned p–n heterojunction grown under the same conditions and the same order. Both values should be different from that of an unpinned heterojunction. With some effort, one should be able to perform the same band offset tuning for pinned homo-junctions! We suggest that some effort in realizing this intriguing possibility is warranted; aside from intrinsic interest in interface state densities arising solely from band offsets and totally independent of material and band structure changes (since there are none!), such studies should be directly relevant to an important device issue: namely, that of stop-regrow epitaxial growth techniques. Performing such studies on GaAs(100) surfaces and interfaces should strongly impact both device technology and our understanding of pinning mechanisms. We note that this raises the possibility of experimentally performing the gedanken experiment discussed by Tersoff of fabricating a heterojunction between two semiconductors of identical band structure but containing a band offset [13]. However, we must note that this inferred offset arises from an *electrostatic* potential shift; unlike chemical potential shifts [10], the screening discussed by Tersoff [13] should apply to such abrupt potential shifts, possibly reducing the magnitude by a factor of the dielectric constant of the semiconductor. Furthermore, the postulated existence of such strong fields at the interface could well destabilize the pinning centers; this suggests that stop-regrow interfaces without Fermi-level pinning may prove simpler to achieve at n–p junctions than at n–n or p–p junctions!

We have performed some preliminary measurement on misfit-dislocation pinned heterojunctions [37]. These measurements are fully consistent with the band offset being independent of the existence of interface pinning; the observed rectification can be modelled semiquantitatively (including its temperature dependence) in terms of pinning at the dislocation and screening of this potential along the interface away from the dislocation. The point is that there is no indication of a dependence of band offsets upon Fermi-level position within the interface. We have not yet attempted to repeat this study for p–p, or the p–n and n–p possibilities, so we cannot rule out the occurrence of

these intriguing possibilities of band-offset tuning.

A further relationship between Fermi-level pinning and heterojunction band offsets has been noted by Katnani and Margaritondo [31]; this is that, if one "lines up" the pinned Fermi-level positions on two semiconductors, the resultant band offsets are in reasonably good agreement with experiment. This relationship between Schottky barrier heights and heterojunction band offsets follows naturally from the work of Tersoff [13], leading to answers presumably similar to those of ref. [31]. We note that the effective work function model, coupled to the EA model, requires such behavior for cases in which the pinning material (usually the anion) for the two materials has similar work functions. For anions having different work functions, our model would predict a discrepancy between Schottky barrier heights and heterojunction band offsets; this error is ≈ 0.1–0.3 V for GaSb/InAs, and nearly 0.75 V for CdS/InP, the two discrepancies between the KM model and experiment noted earlier in this paper.

## 6. Conclusion

In this paper we have demonstrated the ability of work function matching schemes to organize and predict experimental band alignments at Schottky barriers and at both pinned and unpinned heterojunctions. We have raised some questions as to the ability of alternative first-order models of such interfaces to account for some general aspects of these interfaces. Further, we have suggested several classes of experiments that appear likely to elucidate the role of at least some classes of pinning theories.

We note that no current model, including the work function models espoused herein, is truly sufficient for device design needs. A convincing, first-principles treatment of the underlying band structure is likely required to fully understand the manifold details of carrier confinement and transport both parallel and perpendicular to these very ordered interfaces. We strongly suggest that theorists address some specific interfaces where interface structure appears simple and well defined, and data appear likely to be both reproducible and available. However, we also point out that theories without an adequate description of band gaps are unlikely to provide convincing first-principles allocation of band offsets, let alone a detailed description of transport, tunneling, and carrier confinement.

## Acknowledgement

We gratefully acknowledge helpful discussions with S. Iyer, T. Jackson, W. Wang, S. Wright, and J. Van Vechten.

## References


[1] See, e.g., H. Kroemer, Surface Sci. 132 (1983) 132, for an excellent overview.
[2] F. Capasso, J. Vacuum Sci. Technol. B1 (1983) 457.
[3] R.S. Bauer, P. Zurcher and W. Sang, Jr., Appl. Phys. Letters 43 (1983) 663.
[4] J.R. Waldrop, S.P. Kowalczyk, R.W. Grant, E.A. Kraut and D.L. Miller, J. Vacuum Sci. Technol. 19 (1981) 573.
[5] S.P. Kowalczyk, E.A. Kraut, J.R. Waldrop and R.W. Grant, J. Vacuum Sci Technol. 21 (1982) 482.
[6] R.L. Anderson, Solid State Electron. 5 (1962) 341.
[7] C. Herring and M.H. Nichols, Rev. Mod. Phys. 21 (1949) 185.
[8] H. Kroemer, CRC Critical Rev. Solid State Sci. 5 (1975) 555.
[9] Note that one of the "best" current measurements of band offsets, used in refs. [3–5], obtains the band offset from a difference between two numbers typically 5 times larger than the work function.
[10] J.A. Van Vechten, presented at the 12th Ann. Conf. on the Physics and Chemistry of Semiconductor Interfaces (PCSI-12), Tempe, AZ, January 29–31, 1985, J. Vacuum Sci. Technol., to be published.
[11] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
[12] C. Tejedor, F. Flores and E. Louis, J. Phys. C10 (1977) 2163;
C. Tejedor and F. Flores, J. Phys. C11 (1978) L19.
[13] J. Tersoff, Phys. Rev. Letters 52 (1984) 465; Phys. Rev. B30 (1984) 4874.
[14] C. Mailhot and C.B. Duke, presented at the 12th Ann. Conf. on the Physics and Chemistry of Semiconductor Interfaces (PCSI-12), Tempe, AZ, January 29–31, 1985, J. Vacuum Sci. Technol. to be published.
[15] J.L Freeouf and J.M. Woodall, Appl. Phys. Letters 39 (1981) 727.
[16] I. Lindau, P.W. Chye, C.M. Garner, P. Pianetta, C.Y. Su and W.E. Spicer, J. Vacuum Sci. Technol. 15 (1978) 1332.
[17] W.E. Spicer, I. Lindau, P. Skeath and C.Y. Su, J. Vacuum Sci. Technol. 17 (1980) 1019.
[18] F. Bartels, H.J. Clemens and W. Mönch, Physica 117/118B (1983) 801.
[19] F.A Ponce and S.J. Eglash, Thin Solid Films 104 (1983) 317.
[20] R.L. Farrow, R.K. Chang, S. Mroczkowski and F.H. Pollak, Appl. Phys. Letters 31 (1977) 768.
[21] A.G. Cullis, P.D. Augustus and D.J. Stirland, J. Appl. Phys. 51 (1981) 2556.
[22] V. Heine, Phys. Rev. 138 (1965) A1689.
[23] A. Zur, T.C. McGill and D.L. Smith, Surface Sci. 132 (1983) 456.
[24] R.E. Allen and J.D. Dow, Solid State Commun. 45 (1983) 379.
[25] W.A. Harrison, E.A. Kraut, J.R. Waldrop and R.W. Grant, Phys. Rev. B18 (1978) 4402.
[26] W.I. Wang, J. Vacuum Sci. Technol. B1 (1983) 630.
[27] See, e.g., W.I. Wang and F. Stern, presented at the 12th Ann. Conf. on the Physics and Chemistry of Semiconductor Interfaces (PCSI-12), Tempe, AZ, January 29–31, 1985, J. Vacuum Sci. Technol., to be published.
[28] P.M. Petroff, A.Y. Cho, F.K. Reinhart, A.C. Gossard and W. Wiegemann, Phys. Rev. Letters 48 (1982) 170.
[30] H. Kroemer, J. Vacuum Sci. Technol. B2 (1984) 433.
[30] W.A. Harrison, J. Vacuum Sci. Technol. 14 (1977) 1016.
[31] A.D. Katnani and G. Margaritondo, Phys. Rev. B28 (1983) 1944.
[32] C. Tejedor, J.M. Calleja, F. Meseguer, E.L. Mendez, C.A. Chang and L. Esaki, presented at the 17th Intern. Conf. on the Physics of Semiconductors, San Francisco, Sept. 1984, to be published.

[33] R. People, J.C. Bean, D.V. Lang, A.M. Sergent, H.L. Störmer, K.W. Wecht, R.T. Lynch and K. Baldwin, Appl. Phys. Letters 45 (1984) 1231.
[34] H. Jorke and H.-J. Herzog, presented at the 167th Meeting of the Electrochemical Society, Toronto, Ontario, May 12–17, 1985, extended abstracts, p. 211.
[35] A.D. Katnani, P. Chiaradia, H.W. Sang, Jr. and R.S. Bauer, J. Electron. Mater. 14 (1985) 25.
[36] A. Zur and T.C. McGill, J. Vacuum Sci. Technol. B2 (1984) 440.
[37] Please note that the difference between p–n and n–p junctions derives from the dependence of pinning position upon doping type. For a pinning position independent of doping type, there should be no effect in a homojunction; the effect in a pinned heterojunction would depend upon the difference between pinned Fermi-level alignment and unpinned band alignments, as discussed later in this manuscript in relating band offsets and Schottky barrier heights, and would be independent of doping types.
[38] J.M. Woodall, G.D. Pettit, T.N. Jackson, C. Lanza, K.L. Kavanagh and J.W. Mayer, Phys. Rev. Letters 51 (1983) 1783.
[39] D.A. Neamen and W.W. Grannemann, Solid State Electron. 14 (1971) 1319.
[40] H.H. Wieder, Appl. Phys. Letters 38 (1981) 170;
K. Kajiyama, Y. Mizushima and S. Sakata, Appl. Phys. Letters 23 (1973) 458.
[41] T.F. Kuech and J.O. McCaldin, J. Vacuum Sci Technol. 17 (1980) 891.
[42] J.S. Best, Appl. Phys. Letters 34 (1979) 522.
[43] C.A. Sébenne, Il Nuovo Cimento 39B (1977) 768.