Empirical fit to band discontinuities and barrier heights in III–V alloy systems

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(Received 16 October 1991; accepted for publication 13 November 1991)

We present a figure summarizing the variation of conduction band discontinuity, valence band discontinuity, and gold Schottky barrier height for binary and ternary III–V semiconductors. This figure, which applies to unstrained material, makes use of the property of transitivity in band alignments, and the observed experimental correlation between barrier heights and band gap discontinuities, to consolidate a wide range of data. The figure should be very useful in the design of novel heterostructure electronic and optical devices.

The behavior of band discontinuities in semiconductors has been a subject of extensive experimental and theoretical research. Experimentally, reliable measurements exist for a number of lattice-matched III–V heterostructures; most notable of these are the $Ga_{1-x}Al_xAs/GaAs$ system and the $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$, $Ga_{0.51}In_{0.49}P/GaAs$, $InP/Ga_{0.47}In_{0.53}As$, and GaSb/InAs interfaces which have been employed in semiconductor device structures. Some of these measurements are included in Refs. 1, 2, and 3 which summarize data on both lattice-matched and mismatched conditions. This information is very useful in designing devices for specific characteristics. As an example, positions of subband energy levels in quantum-well laser diodes and resonant tunneling structures are strongly related to the discontinuities and directly affect the operating characteristics of these devices. Unfortunately, new device designs often require this information for alloy combinations for which no experimental data is available. Consequently, device designers are forced to perform several trial-and-error experiments. The objective of this paper is to provide this information in an approximate form, by consolidating a wide range of data into a single figure. This empirical figure is a consolidation of data based primarily on two principles: the properties of transitivity and commutativity, which are supported by experimental evidence to date, and the strong correlation observed between the *p*-type semiconductor barrier height, the transition impurity levels, and the valence band discontinuity.

The property of transitivity for band offsets means that the sum of the band offset from material *A* to material *B* plus the band offset from material *B* to material *C* is equal to the band offset from material *A* to material *C*. The commutative property means that the band offset between two materials is independent of the order in which they are grown. References 2 and 3 contain excellent summaries of the experimental tests of these properties, from which it appears that they are generally valid, at least to within about 100 meV. For a given lattice constant, these two properties taken together allow one to determine, in principle, the relative band-edge positions of all III–V alloy semiconductors that have that lattice constant. Only the absolute position of the energy scale is arbitrary. This idea can also be extended to include nonlattice matched semiconductors,[3] but we have chosen not to do so here in order to reduce the number of degrees of freedom and because of the difficulty of taking into account strain-related effects. One other property of heterojunctions that has been assumed is lattice orientation independence. If the offsets are not independent of lattice direction, then separate figures would need to be drawn for each orientation of interest.

Existing experimental measurements of band-edge discontinuities fall naturally into four lattice-constant groups. The materials are nearly lattice matched within each group, and the relative alignments can be determined. Table I contains a summary of these alignments. These values were chosen by careful consideration of available experimental data with additional emphasis on its agreement with accumulated information on experimental abrupt heterostructure devices, and by requiring consistency ($\Delta E_g = \Delta E_c + \Delta E_v$, and transitivity) within each group. The $Ga_{1-x}Al_xAs/GaAs$ system follows within 10 meV the estimate of Wang and Stern[4] across the range of AlAs mole fraction. The discontinuity for $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$ is based on the measurements of People *et al.*[5] $InP/Ga_{0.47}In_{0.53}As$ is based on the measurements of Hasse, Pan, and Stillman[6] and $Ga_{0.51}In_{0.49}P/GaAs$ follows the limit of the range proposed by Rao *et al.*[7] Some of the rest of the estimates are derived by requiring consistency; the values chosen are within the range of the estimates in the literature. In particular, the values for $Al_{0.52}In_{0.48}As/InP$ and AlSb/InAs were chosen primarily on the basis of transitivity.

The zero point for energy at each lattice constant has been chosen based on Schottky barrier-height data at that lattice constant. Since the valence-band barrier heights have been shown to be well correlated with the valence-band discontinuities, this is expected to enable Fig. 1 to be predictive for band alignments that have not been measured. This strong correlation between valence-band discontinuity and *p*-type metal–semiconductor barrier heights and transition impurity levels has been conjectured to be the result of the continuity of the "bulk neutrality level." Briefly, Tersoff's argument[8] is as follows. In metal–metal junctions, the Fermi level serves as a neutrality level since there is unimpeded motion of free carriers, and thermal equilibrium leads to an interface dipole that is equal to the difference in work functions. In the case of one-dimen-

 0003-6951/92/050630-03$03.00

TABLE I. Discontinuity references ($T = 300$ K).

Lattice constant of group (Å)	Material system	ΔE_g (eV)	ΔE_c (eV)	ΔE_v (eV)
5.44	GaP/Si	1.148	0.798	0.35
5.66	GaAs/Ge	0.758	0.268	0.49
	AlAs/Ge	1.48	0.55	0.93
	$Ga_{0.7}Al_{0.3}As/GaAs$	0.395	0.263	0.132
	AlAs/GaAs	0.73	0.29	0.44
	$Ga_{0.51}In_{0.49}P/GaAs$	0.463	0.223	0.24
5.87	$Al_{0.48}In_{0.52}As/InP$	0.106	0.30	−0.194
	$InP/Ga_{0.47}In_{0.53}As$	0.600	0.20	0.40
	$Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$	0.706	0.50	0.206
6.10	AlSb/GaSb	0.887	0.487	0.40
	GaSb/InAs	0.370	0.88	−0.51
	AlSb/InAs	1.257	1.367	−0.11

TABLE II. Band gap and lattice data ($T = 300$ K).

Material	Lattice constant (Å)	$E_g(\Gamma)$ (eV)	$E_g(L)$ (eV)	$E_g(X)$ (eV)	ϕ_{bv} (eV)
AlP	5.463 5	3.6	3.5[a]	2.45	1.27[a]
AlAs	5.660 5	3.00	2.36	2.15	1.002
AlSb	6.135 8	2.3	2.21	1.612	0.47
GaP	5.451 0	2.78	2.6	2.272	0.797
GaAs	5.653 25	1.424	1.708	1.900	0.562
GaSb	6.096 02	0.725	0.810	1.032	0.07
InP	5.868 9	1.350	1.95	2.15	0.857
InAs	6.058 3	0.355	1.43[a]	2.0[a]	0.58
InSb	6.479 43	0.170	1.0[a]	1.7	0.04
Si	5.431 1	4.1	2.0	1.124	0.447
Ge	5.657 9	0.805	0.666	0.89	0.072

[a]Indicates theoretical estimate.

sional small band gap model semiconductors,[9,10] this occurs with the neutrality level at the center of the band gap; the center of the band gap delineates states that are conduction-like and valence-like, and hence, leads to a neutral line-up. The tight-binding theory suggests the sp^3 hybrid energy as this neutrality level since it correlates with the electronegativity and is continuous across the interface if the electronegativity difference is equal to the interface dipole. This energy also correlates with dangling bond energies at a semiconductor interface and with the energies of transition impurities. It should be noted that there are other models[11] that also predict this correlation between barrier heights and valence-band discontinuities. Regardless of the theoretical underpinning, we expect that the correlation between pinned barrier heights, transition impurity energies, and discontinuities measured in the heterostructure systems will persist, and that it therefore provides a reasonable basis upon which to develop a general and predictive set of values for device design.

Figure 1 is the culmination of the above principles. It summarizes the behavior of the unstrained band-edge discontinuities as a function of the lattice constant, and simultaneously provides an estimate of the Schottky barrier heights. The figure also includes unstrained $Ge_{1-x}Si_x$ alloys, a material system in which there is considerable current interest. The band alignment of any two lattice-matched alloys can be obtained by observing the relative

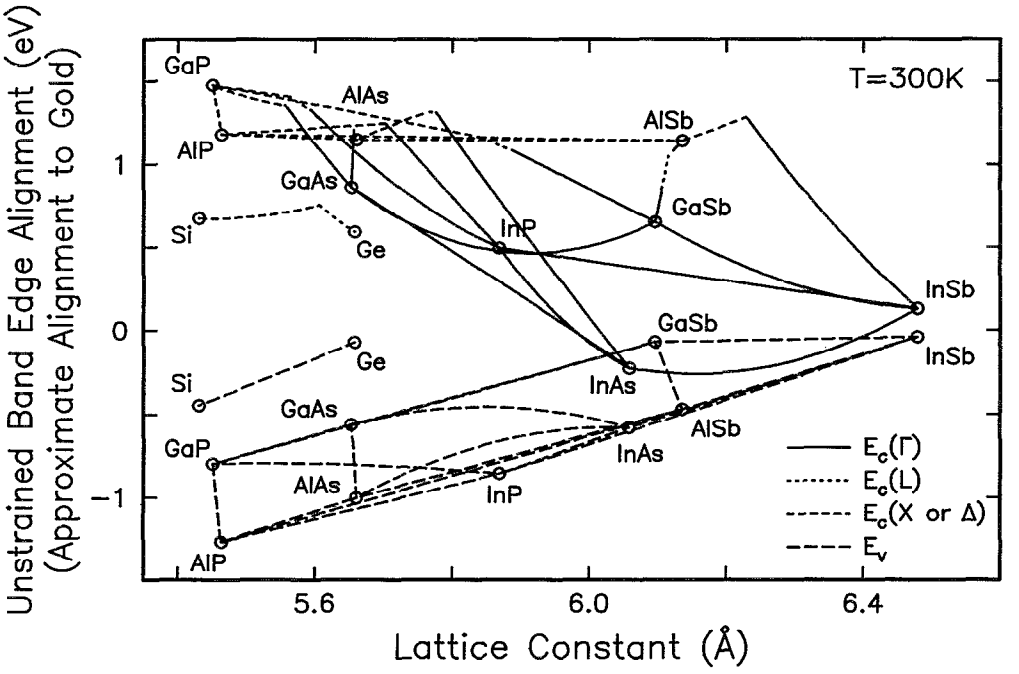

FIG. 1. The conduction band edge and valence band edge energies plotted as a function of the lattice constant of semiconductors. The circles indicate the band edges of the binary semiconductors and the lines show the band edges of the ternary alloys. The two endpoints of each ternary line are the binary constituents of that ternary. Discontinuities between two lattice matched or nearly matched semiconductor alloys may be found from the difference in energy between their band-edge energies. The zero energy point represents the approximate gold Schottky barrier position in the band gap of any given alloy.

TABLE III. Bowing parameters for band edges ($T = 300$ K). Unfilled Table positions indicate an absence of experimental values; zeros were assumed for purposes of generating Fig. 1.

Material system	c_{Γ_v} (eV)	$c_{\Gamma_c-\Gamma_v}$ (eV)	$c_{L-\Gamma_v}$ (eV)	$c_{X-\Gamma_v}$ (eV)
$Ga_{1-x}Al_xP$	...	...	...	...
$In_{1-x}Al_xP$	...	...	...	...
$In_{1-x}Ga_xP$	0.098	0.77	1.15	0.207
$Ga_{1-x}Al_xAs$	0	0.37	0.055	0.245
$In_{1-x}Al_xAs$	0.479	0.675	...	...
$In_{1-x}Ga_xAs$	0.460	0.431	0.5	0.08
$Ga_{1-x}Al_xSb$	...	0.47	0.7	
$In_{1-x}Al_xSb$	...	0.43	...	...
$In_{1-x}Ga_xSb$	...	0.413	0.33	0.13
$AlAs_{1-x}P_x$	...	...	...	...
$AlSb_{1-x}As_x$	...	...	...	...
$AlSb_{1-x}P_x$	...	...	...	...
$GaAs_{1-x}P_x$	...	0.19	0.16	0.21
$GaSb_{1-x}As_x$	...	1.15	...	...
$GaSb_{1-x}P_x$	...	...	...	...
$InAs_{1-x}P_x$	...	0.32	...	...
$InSb_{1-x}As_x$	...	0.65	...	...
$InSb_{1-x}P_x$	...	...	...	...
$Ge_{1-x}Si_x$	...	...	0.33	0.17

position of their band edges on this figure. The zero energy level indicates the approximate position at which a gold Schottky barrier would align to the band gap of each semiconductor. Using this information, one can carry out first pass designs for novel devices in which the heterojunction offsets are designed to meet very specific goals, as, for example, was done in Ref. 12 using an early version of this figure.

This figure is based on the band-edge discontinuities given in Table I, the band gap data of Table II, and the band gap bowing parameters listed in Table III. The band gap and bowing parameters are selected from the data in Landolt-Börnstein.[13,14] Except for three cases in which barrier-height data or offset data dictated otherwise, we placed all of the bowing into the conduction bands. This is in accord with the observation in the $Ga_{1-x}Al_xAs/GaAs$ system that both the valence-band barrier height and the valence-band discontinuity[15] with GaAs follow the composition linearly. The zero position for each binary semiconductor is indicated in the last column of Table II. This was determined by averaging all of the Schottky barrier height[16] estimates of the zero position that were available in each lattice constant group.

This figure consolidates data involving discontinuities, barrier heights, and band gap under unstrained conditions. It is consistent with the criteria mentioned previously and the data in the tables. However, we emphasize that it is an empirical fit and should be treated as such. The available data at $Ga_{1-x}Al_xAs/GaAs$, $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$, $Ga_{0.51}In_{0.49}P/GaAs$, $InP/Ga_{0.47}In_{0.53}As$, and GaSb/InAs interfaces is fairly complete and reliable, while data on GaP, AlP, and the antimonides is prone to more uncertainty because of fewer reports, and incomplete and inconsistent data. The worst case is AlP, which has two significantly different reported lattice constants, and no reported barrier heights or offsets (forcing us to use a theoretical estimate[8]). We have made a judicious selection, but there are certain to be changes as future experimental results are reported. We estimate the band alignment accuracy of Fig. 1, for unstrained heterostructures, to be ≈ 100 meV. Near the well-measured regimes, the accuracy should be substantially better. The barrier height estimates are expected to be slightly less accurate. For strained conditions, however, the changes in the behavior of valence and conduction bands become important. These changes should result in modification of the discontinuities. Polar interfaces, such as at a GaAs/Ge junction, may also alter the discontinuities. Transitivity, used as a basis for these figures, may be broken by such strain or polarization effects. Thus, these figures should necessarily be used with caution. They are a good guideline for the unstrained condition, but may be relatively inaccurate when the underlying assumptions are violated.

In summary, we have described a useful figure that allows us to predict the conduction and valence-band discontinuities at unstrained heterostructure interfaces, and to estimate the Schottky barrier heights of III–V alloys in the absence of barrier lowering effects. The results presented should be helpful in heterostructure device design. Tables of the parameters necessary to create the figure have been included; this should simplify the task of updating the figure as new data become available.

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