AIP | Applied Physics Letters

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Citation: Applied Physics Letters **45**, 671 (1984); doi: 10.1063/1.95351
View online: http://dx.doi.org/10.1063/1.95351
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/45/6?ver=pdfcov
Published by the AIP Publishing

A universal trend in the binding energies of deep impurities in semiconductors

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(Received 7 June 1984; accepted for publication 28 June 1984)

Whereas the conventional practice of referring binding energies of deep donors and acceptors to the band edges of the host semiconductor does not produce transparent chemical trends when the same impurity is compared in different crystals, referring them to the vacuum level through the use of the photothreshold reveals a remarkable material invariance of the levels in III-V and II-VI semiconductors. It is shown that this is a consequence of the *antibonding* nature of the deep gap level with respect to the impurity atom-host orbital combinations.

Whereas, since the early days of atomic and molecular physics, electronic energy levels have been naturally referred to the vacuum state (vacuum referred binding energies, or VRBE), in impurity physics, it has long become customary to refer acceptor or donor levels to either the valence (v) or the conduction (c) host band edges (hereafter denoted as host referred binding energies, or HRBE). This latter choice has been motivated not only by the paradigms of effective mass theory (which associated the generic evolution of shallow levels from these band edge states), but also by the obvious relation of electron/hole emission and capture processes to such band edges. The organization of a large body of observed electric levels with reference to E_v or E_c (see for example, recent compilations in Refs. 1–3) had unravelled many well-known chemical trends in the binding energies of *shallow* impurities (central cell effects). At the same time, this traditional choice of HRBE has revealed obscure trends in the material dependence of the HRBE for *deep* impurities,[1–3] which have since been accepted as part of the complex reality of the physics of deep centers. We show here that the VRBE is a more natural reference system and that it organizes many of the puzzling material-dependent trends in terms of the different positions of the *host states* relative to vacuum (photothreshold).

Recently, first-principles self-consistent electronic structure calculations have become possible[4] for series (e.g., V through Cu) of deep transition atom centers in semiconductors such as Si [5] and GaP.[6] Among others, they have shown that the impurity levels are not[7] "pinned" to the host vacancy level (as previously suggested[8]), nor are the host band edges the physically relevant states that determine generically the *position* of such levels. Instead, it was found that many of the results of the detailed calculations could be qualitatively understood in terms of a model of three "effective levels." This can be used here to illustrate that the physical invariant is the VRBE and not the HRBE. For impurity levels of a given symmetry Γ (say, t_2) associated with a certain site S in the host crystal (say, cation substitutional), these zero-order states are the $3d\Gamma$ orbitals of the effective impurity (I) ion[5] with energy ϵ_I, and the host (H) states ϵ_H^v and ϵ_H^c showing up as the largest peaks in the S-centered, Γ-projected local density of states in the valence (v) and conduction (c) bands, respectively. When ϵ_I is not too close to ϵ_H^c, a two-level model (ϵ_I and ϵ_H^v) suffices.[5] Having the same symmetries (Γ around S), they will interact (Fig. 1) through the coupling element $V = \langle I|\Delta V|H\rangle$. This will result in an impurity-like bonding state in the valence band (t_2^{CFR} of Refs. 5 and 6), and in an antibonding gap level (the t_2^{DBH} dangling bond hybrid of Ref. 5) at the energy $E_{\text{imp}} = \bar{\epsilon} + [\Delta^2 + V^2]^{1/2}$. Here $\bar{\epsilon} = (\epsilon_I + \epsilon_H^v)/2$ and $\Delta = (\epsilon_I - \epsilon_H^v)/2$ are the zero-order centroid and level separation, respectively. The energy E_{VBM} of the valence-band maximum (VBM) is at a fixed distance from ϵ_H^v. All energies are referred to the vacuum. The antibonding character of the gap level implies that its energy E_{imp} is decided by two opposing and partially cancelling effects. This is illustrated in Fig. 1. If ϵ_H^v is well above ϵ_I [host anion with shallow p orbital, such as in ZnTe, Fig. 1(a)] then $\bar{\epsilon}$ is shallow, but Δ is large, leading to a weak level repulsion $R = [\Delta^2 + V^2]^{1/2}$. If, on the other hand, ϵ_H^v is closer to ϵ_I [host anion with deeper p orbitals, such as ZnS, Fig. 1(b)], then $\bar{\epsilon}$ is deeper, but Δ is smaller, increasing thereby the level repulsion R. Hence, the positions of E_{imp} relative to vacuum in cases (a) and (b) (VRBE, depicted as shaded areas in Fig. 1) are expected to be considerably closer to one another than the HRBE's (cross-hatched area in Fig. 1). The cancellation is particularly effective when ϵ_I of the *effective* impurity ion (where all s electrons occupy the d shell[5]) is above ϵ_H^v. *No cancellation is expected to occur if the gap level is not antibonding.* Such is the case in hydrogenic impurities that merely split an *already existing* host state into the gap. Hence, their energy will follow the HRBE. Note that since the coupling V and the Coulomb repulsion energies U vary considerably in going from one class of crystals to the other[3] (e.g., the more ionic II-VI relative to the III-V), this invariance may be restricted to one class of materials at a time.

To check the idea of material invariance of the VRBE's, we have used our calculated levels of GaP:Fe and InP:Fe,

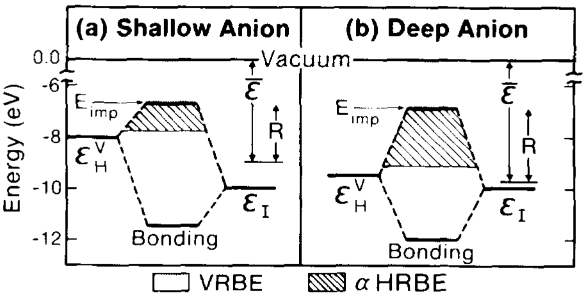

FIG. 1. Schematic two-level model for a deep impurity in a semiconductor with (a) shallow anion (e.g., ZnTe) and (b) deep anion (e.g., ZnS).

TABLE I. Observed[13] photothreshold values Φ, band gaps E_g, and single acceptor (A), single donor (D), and double acceptor (AA) energies (in eV, relative to the valence-band maxima) of deep transition atom impurities.[1-3,15]

Host	E_g (eV)	Φ (eV)	Impurity V	Cr	Mn	Fe	Co	Ni	Type
ZnS	3.85	7.5	2.11	1.0	– 0.6[a]	1.75	⋯	0.75[b]	*D*
			⋯	2.78[c]	⋯	⋯	⋯	2.48	*A*
ZnSe	2.80	6.82	1.6[a]	0.44	– 0.86[a]	1.25	0.3	0.16	*D*
			⋯	2.24[c]	⋯	⋯	⋯	1.85	*A*
CdSe	1.98	6.62[d]	1.4	0.64	⋯	0.64	0.15	0.3	*D*
			⋯	⋯	⋯	⋯	⋯	1.81	*A*
CdTe	1.48	5.78	0.74	⋯	⋯	⋯	⋯	⋯	*D*
			⋯	1.3	⋯	⋯	⋯	⋯	*A*
InP	1.41	5.69	⋯	0.94	0.2	0.7	0.24	⋯	*A*
GaP	2.35	5.9[e]	⋯	1.12	0.4	0.85	0.41	0.5	*A*
			⋯	1.85		2.25		1.55	*AA*
GaAs	1.50	5.49	1.29	0.81	0.1	0.46	0.16	0.22	*A*

[a] Predicted in Ref. 3.
[b] Tentative, see Ref. 3.
[c] Optical value.
[d] Wurtzite structure, Ref. 15.
[e] Extrapolated from Fig. 10–13 in Ref. 14.

referring all one-electron energy levels to the *electrostatic potential of each host crystal at its interstitial site.* The potential at the empty interstitial site has been shown[9] to be a reasonable approximation to an internal (surface independent) vacuum level, and had produced reasonable predictions for band alignments at interfaces.[9] We found that whereas their HRBE differ substantially ($E_c - 1.22$ and $E_c - 0.28$ eV, for GaP:Fe and InP:Fe, respectively), their VRBE are much closer (-2.98 and -2.86 eV, respectively). A similar insight has been derived by Jaffe and Zunger[10] by analyzing the band-gap anomaly in ternary chalcopyrites.

Motivated by the above considerations, we follow recent suggestions[11,12] and refer the experimentally determined HRBE of transition atom acceptors [first (o/ –) and second (– / =)] and donors [(o/ +)] levels in III-V and II-VI semiconductors to an approximate vacuum level, taken as the experimentally determined[13] photothreshold Φ for the (110) surface (Table I). We neglect material variations in surface corrections because (i) the experimental precision for surface corrections is poorer[13] than for Φ, (ii) Φ has proven to correlate well[14] with E_{VBM} for a given sequence of common-cation compounds, (iii) only relative *shifts* in the vacuum level from one material to the other are needed here. The reliability of this approximation has already been verified in the study of vacancies in III-V materials[15] where empirical band structures of III-V materials were fit to Φ. We show in Fig. 2 the results for eight semiconductors for which reliable data exist,[1-3,16] indicating the oxidation states that exist at each region of the gap. Note that the 1 +, 2 +, and 3 + oxidation states shown in Fig. 2 correspond to the $A^{=}$, A^{-}, and A^{0} charge states in III-V semiconductors, and to A^{-}, A^{0}, and A^{+} charge states in II-VI's. The remarkable result is that *within a class of compounds, the VRBE of each impurity are nearly constant, despite significant variations in HRBE.*

Few chemical trends become apparent. (i) Shallow acceptors in CdTe and ZnTe (e.g., Cu, with[1,2] $E_A = E_v + 0.15$ eV) become deep acceptors in ZnS and ZnSe (around[17] $E_v + 1.3$ and $E_v + 0.7$ eV, respectively for Cu in ZnS and ZnSe) merely because the VBM in the latter systems recedes, decreases Δ, and repells $E_{\rm imp}$ upwards, deep inside the gap. This is why CdTe can be made low resistivity *p* type by cation substitution, whereas sulphides cannot.[10] On the other hand, isovalent substitutional elements lacking a deep ϵ_l (e.g., Li, Na) can form shallow acceptors in II-VI's, having hence similar HRBE and different VRBE. The same is true for Mn acceptors in III-V's: they are deep in GaP but shallow in GaAs because $\Phi_{\rm GaP} > \Phi_{\rm GaAs}$. (ii) Cr, Co, and Ni impurities that exist as deep donors in ZnS, ZnSe, and CdSe, but were not observed in CdTe, are indeed predicted here to be inside the CdTe valence band. (iii) Iron impurity forms a midgap (semi-insulating) level in InP, but Cr is needed to form a midgap level in GaAs (despite the similarities in band gaps), since the VBM of InP is lower than that of GaAs. (iv) Impurities in CdTe and ZnTe have similar HRBE (hence only one is

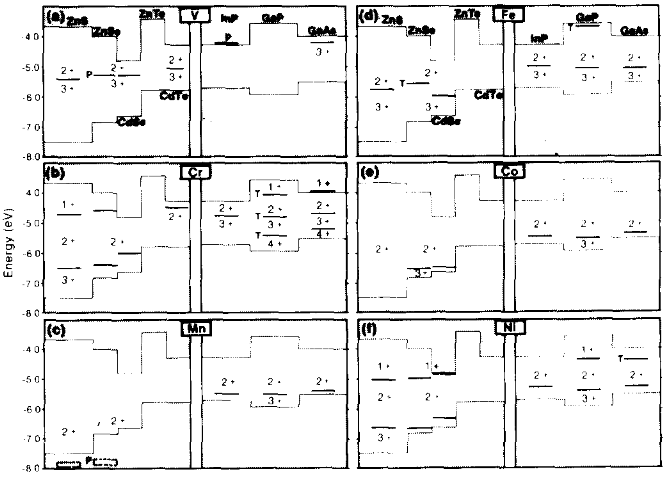

FIG. 2. Vacuum related binding energies of six 3*d* impurities in eight host semiconductors (cf. Table I), showing that the regions of stability of the 1 +, 2 +, and 3 + oxidation states are very similar in materials of the same class. (T) tentative experimental value; (P) predicted.

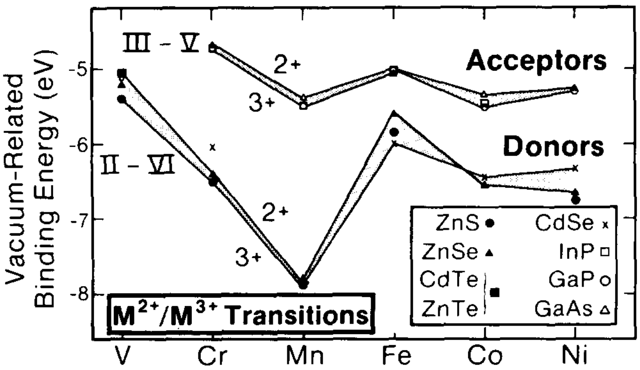

FIG. 3. Universal binding energy curve for deep acceptors in III-VI's and deep donors in II-VI's.

shown in Fig. 2), since their Φ's are nearly identical. Other common-anion semiconductors (e.g., InP and GaP) show variations in HRBE of deep level, since their Φ's are different. (v) The failure to detect a V acceptor in InP (despite its existence in GaAs) is consistent with the prediction that it lies just above the CBM; however, an experimental search for the V acceptor level in GaP would be important to shed light on its position GaAs. (vi) Cr in GaP can appear in the 1 + oxidation state, whereas it does not exist in GaAs and InP (but could be forced into the gap by applying pressure) since the conduction-band minima of the latter materials are lower than in GaP. (vii) we predict that the VRBE of transition atom impurities in mixed alloys (e.g., ZnS_xSe_{1-x} or $GaAs_xP_{1-x}$) will follow the variations with x in Φ and not the HRBE (e.g., the CBM or any CB in particular).

Figure 3 shows the universal trends in the VRBE of donors (M^{2+}/M^{3+}) in II-VI's, and of acceptors (M^{3+}/M^{2+}) in III-V's. (Similar trends are obtained for acceptors in II-VI's except that the jump is between Cr and Mn.) The overall trend, including the local minima in Mn parallels that in free-ion ionization energies[18]; the jump is larger in the more ionic II-VI systems since the impurity Mott–Hubbard Coulomb repulsion energies U are larger ($U \sim 10$–20 eV in free ions, 2–3 eV in II-VI's, and 1–2 eV in III-V's[3]). The overall width of the distribution of VRBE is dictated by the host covalency. One hopes that the universality of VRBE could be used to predict the approximate location of unknown deep centers in crystals and alloys from the knowledge of Φ and the level position in related semiconductors.

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Titanium disilicide formation by sputtering of titanium on heated silicon substrate

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(Received 19 April 1984; accepted for publication 9 July 1984)

We have sputter deposited titanium on bare silicon substrates at elevated temperatures. We find that at a substrate temperature of about 515 °C titanium silicide is formed due to the reaction of the titanium with the Si. The resistivity of the silicide is about $15\,\mu\Omega$ cm and it is not etchable in a selective titanium etch. This process can have applications in low-temperature, metal-oxide-semiconductor self-aligned silicide formation for very large scale integrated

The deposition and processing of the refractory metal silicides have become the topic of many recent investigations due to their vital role in the future of very large scale integration (VLSI) technology.[1] The initial use of the silicide films was intended for the gate metallization in metal-oxide-semiconductor (MOS) devices. The next generation of silicide films will be used to shunt the gate of the MOS devices as well as the source and drain thus reducing their resistance,