Transition-Metal Impurities in Semiconductors—Their Connection with Band Lineups and Schottky Barriers

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The dependence of cation-substitutional transition-metal impurity levels upon the host semiconductor is calculated self-consistently in a defect-molecule approach. Heterojunction band lineups and Schottky-barrier heights can be calculated within the same tight-binding model. In all three systems, the characteristic behavior is determined by an approximate local charge-neutrality condition imposed by electrostatic self-consistency ("pinning"), with a dangling-bond level playing the role of the "neutrality level." In this way we explain the observed correlation between transition-metal impurity levels, heterojunction band lineups, and Schottky barriers.

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Transition-metal (TM) impurities in semiconductors have been the focus of intense interest in recent years, because of their interesting physical properties and their importance in semiconductor devices. Particular attention has focused on the trends in TM impurity energy levels as the metal atom is varied, and these trends are now rather well understood.[1-3]

However, more recently, a somewhat different question has assumed pressing importance. Zunger and coworkers,[3,4] Langer and Heinrich,[5] and Tersoff[6] have noted that the trends in impurity levels for a given TM atom, as the host semiconductor is varied, can shed light on apparently unrelated interface properties. In particular, it was found that TM levels in compound semiconductors could serve as reference levels, with which heterojunction band lineups and even Schottky-barrier heights could be predicted with some accuracy.[3-6]

Here we present the first unified physical explanation for the connection between TM levels and both band lineups and Schottky barriers. We calculate the host dependence of cation-substitutional TM impurity levels within a self-consistent tight-binding model. Because of bond polarization, the charge in the *d* shell depends on the position in energy of the TM level relative to the host bands (and, in particular, relative to the ideal vacancy level). Electrostatic self-consistency requires approximate charge neutrality within the TM *d* shell, so the impurity level is forced to assume that unique energy which yields neutrality within the *d* shell.

This electrostatic "pinning" mechanism is almost precisely analogous to that by which the charge-transfer dipole at a semiconductor interface determines the band lineup[7-9] or Schottky barrier.[10,11] Moreover, the neutrality level for the TM impurity is shown to be nearly identical to that of the interface. Such an explanation is in direct contrast to previous suggestions, which neglected the effects emphasized here, and concluded that the impurity level measured some "internal vacuum level" of the semiconductor.[4]

Our main interest is in developing simple ideas and explicit relationships between different measurable quantities. We therefore use the powerful but transparent "defect-molecule" approach, following closely the work of Picoli, Chomette, and Lannoo[1] (PCL). In fact, we are able to treat the heterojunction problem and the defect problem within essentially the same model. In this way, we can draw a very direct connection between the two.

We begin with a cation vacancy, which will be occupied by the TM atom. There are four inward-pointing dangling bonds on the four anions surrounding the vacancy, which give rise to four levels. Ignoring for now the coupling between dangling bond and host, the defect problem reduces to a much simpler problem, involving only the TM atom and the four dangling bonds, which form the defect "molecule." Later the coupling to the host is included by a renormalization of the dangling-bond properties. Also, we begin with a spin-restricted Hartree-Fock analysis, following PCL.

The four sp^3 hybrids form two representations under the tetrahedral point group, of A_1 and T_2 symmetry. The TM *s* level has A_1 symmetry, while the five *d* levels split into T_2 and E representations. Since the crucial physics here involves the *d* levels, as seen below, we can neglect the two states of A_1 symmetry, which have no contribution from the TM *d* levels. While the position of the E level is of interest, it is obtained trivially from the self-consistent potential, since there is no host level for it to couple to. (In the real crystal, there are, of course, host states of E symmetry, but they lie at rather high energies, and so couple very weakly to the TM level.)

We therefore need only consider the 2×2 Hamiltonian describing the states of T_2 symmetry,

$$\begin{bmatrix} E_d & V \\ V & E_h \end{bmatrix}, \tag{1}$$

where E_d is the energy of the d level $|d\rangle$, E_h is the energy of the anion sp^3 hybrid level $|h\rangle$ (the dangling bond), and V is the coupling between these. The resulting two T_2 eigenstates are

$$|t^*\rangle = \beta|d\rangle - \alpha|h\rangle, \quad |t\rangle = \alpha|d\rangle + \beta|h\rangle. \tag{2}$$

Here t^* is the state at higher energy, and the respective energies are

$$\epsilon = \bar{\epsilon} \pm \Delta, \tag{3}$$

where $\bar{\epsilon} = (E_d + E_h)/2$, $\Delta = (\delta^2 + V^2)^{1/2}$, and $\delta = (E_d - E_h)/2$, and

$$\alpha^2 = \tfrac{1}{2}(1 - \delta/\Delta), \quad \beta^2 = \tfrac{1}{2}(1 + \delta/\Delta). \tag{4}$$

Within the restricted Hartree-Fock picture, the only remaining issue is electrostatic self-consistency. For the present analysis it suffices to follow PCL and consider only on-site Hubbard-type terms. Specifically, we write

$$E_d = E_d^0 + U_d(n_d - n_d^0), \quad E_h = E_h^0 + U_h(n_h - n_h^0), \tag{5}$$

where E_d^0 and E_h^0 are the diagonal matrix elements for the TM d and host sp^3 hybrid levels, in the absence of any charge transfer; U_d and U_h are the corresponding on-site Coulomb integrals; and n_d^0 and n_h^0 are the numbers of electrons in the respective levels (excluding the A_1 contribution) in the absence of any charge transfer. Solving for the occupancies of the orbitals, one finds

$$n_d = n_B\alpha^2 + n_A\beta^2 + n_E, \quad n_h = n_B\beta^2 + n_A\alpha^2, \tag{6}$$

where n_B, n_A, and n_E designate occupancies of the bonding and antibonding T_2 levels and of the E level, respectively. For the cases of interest, the first will be filled, so that its occupancy is equal to its degeneracy, $n_B = 6$.

Solving (4)-(6) with $n_B = 6$ yields the self-consistent shift of the TM potential relative to the host,

$$\begin{aligned} \delta - \delta_0 &= U_d(n_d - n_d^0) - U_h(n_h - n_h^0) \\ &= U_d \tfrac{1}{2}[\tfrac{1}{2}(n_A + 6) + \tfrac{1}{2}(n_A - 6)\delta/\Delta + n_E - n_d^0] + U_h \tfrac{1}{2}[\tfrac{1}{2}(n_A + 6) - \tfrac{1}{2}(n_A - 6)\delta/\Delta - n_h^0]. \end{aligned} \tag{7}$$

Configuration effects and spin polarization act primarily to lift degeneracies, without changing the self-consistent charge transfer.[1] Thus, while such effects are crucial for the description of differences between different TM impurities in a given host,[1-3] the same effects are virtually irrelevant when we discuss the *differences* between respective levels of a given TM atom in different hosts. We therefore omit them here.

Now let us restrict consideration to a single class of semiconductors, e.g., only III-V's or only II-VI's. Then n_h^0 and U_h will be essentially identical for all semiconductors in that class, and may be taken as constants. Moreover, V depends primarily upon the bond length,[12] and so may be taken as approximately constant if we consider only semiconductors with similar lattice constants. Also, the splitting between A_1 and T_2 states (which we have neglected in identifying E_h with the T_2 state) is nearly constant within the class, so that the effect of splitting on E_h levels is negligible except for an irrelevant additive constant.

As we change semiconductors, then, we are basically only changing E_h. However, the self-consistent response of the system to this change is as important as the change itself. For example, if we raise E_h, this polarizes the bonds via (4), resulting in a charge transfer (6) into the d shell. The resulting Coulomb repulsion (5) causes the d-shell energy E_d to rise along with E_h.

Now the crucial point is that if $U_d \to \infty$, then (7) simplifies to

$$\tfrac{1}{2}(n_A + 6) + \tfrac{1}{2}(n_A - 6)\delta/\Delta + n_E - n_d^0 \to 0. \tag{8}$$

This is just the condition of charge neutrality within the d shell, $n_d \to n_d^0$, which completely determines δ. Thus δ is independent of δ_0, and hence of E_h^0. In this limit, then, δ is approximately the same for all III-V or all II-VI semiconductors.

The use of realistic parameter values[1] merely confirms the validity of the $U_d \to \infty$ limit for description of the actual systems of interest. Note that U_d is the *unscreened* Coulomb integral, of order 10 eV, and not the screened interaction which determines the small differences among charge states.[1] The dominance of the U_d term also justifies the neglect of the much smaller interatomic Coulomb terms, and of the A_1 symmetry states. On the other hand, U_h is very small (roughly[1] 0.2 eV), because of the delocalized nature of the dangling-bond level, which is described below.

Thus, if we measure the impurity level for a given charge state of a given TM impurity in different III-V semiconductors, this will actually provide a measure (up to an additive constant) of the host dangling-bond energy E_h. (Since U_d is large and U_h is small,[1] we can ignore the difference between E_h and E_h^0, or at least the variation of this difference among semiconductors.) While the spin-restricted Hartree-Fock approach is inadequate to determine the absolute position of an impurity level, the *differences* between semiconductors should be described well.

It is worthwhile to compare this picture with previous models. Hjalmarson *et al.*[13] proposed that levels of *sp*-bonded substitutional impurities tend towards the vacancy level. While this seems superficially similar to the conclusion here, the two models are in fact antithetical. Hjalmarson *et al.* completely neglected charge transfer, which plays the dominant role here because of the very large U_d; and, in fact, they did not propose that their approach was applicable to TM impurity levels.

On the other hand, it is observed[4,14] in several cases that, as the host is varied, a given TM level tends to maintain a relatively constant energy with respect to the vacuum level (as measured for the cleaved surface). Several authors have suggested[4,14] that this may be a general rule for TM impurity levels. In particular, Caldas, Fazzio, and Zunger[4] have presented qualitative theoretical arguments for such a rule. However, those arguments neglect self-consistency with respect to charge transfer, which we have argued is crucial here. Within the present theory, the vacuum level plays a somewhat accidental role, because the TM levels follow E_h, and E_h falls at a somewhat constant energy with respect to the vacuum level for semiconductors of similar lattice constant, for reasons discussed elsewhere.[9]

In fact, as Freeouf and Woodall[15] have stressed, similar behavior is observed in the case of Schottky barriers, where the Fermi-level position at the interface falls at a roughly constant energy, relative to the vacuum, for a variety of semiconductors. One can no more conclude that the impurity level is fixed by the vacuum level than that the Schottky-barrier height is.

The only remaining problem here is to relate E_h to the properties of the host, in particular to those properties which determine the interface band lineup or barrier height. Within the approximations made so far, E_h is just the anion sp^3 hybrid energy, which we denote ϵ_h^a. However, this hybrid is coupled to the host, with the coupling depending upon the difference between anion s and p term values.[12] That difference is large, giving a substantial coupling, so the correct value of E_h turns out to be more characteristic of the semiconductor bulk than that of the isolated anion hybrid.

We have calculated the dangling-bond energy, including the coupling to the host, within a standard tight-bonding model,[12] by increasing the size of the "molecule" to include all sixteen anion orbitals of the four atoms surrounding the impurity, and the twelve cation sp^3 hybrids which interact directly with these. The resulting renormalized dangling-bond energies E_h are plotted for several semiconductors in Fig. 1, and compared with ϵ_h^a and ϵ_h^c. In general, E_h is seen to be very nearly midway between the two atomic hybrid levels. The reason is that the dangling-bond state is actually rather delocalized, and so has considerable cation character. Thus

$$E_h \simeq \bar{\epsilon}_h, \tag{9}$$

where $\bar{\epsilon}_h \equiv (\epsilon_h^a + \epsilon_h^c)/2$. The relationship (9) is not exact, but is obeyed here rather accurately in Fig. 1. The largest deviations occur for phosphides, but even these are well within the expected accuracy, given the approximations inherent in tight binding and the modest size of the host volume included in the calculation.

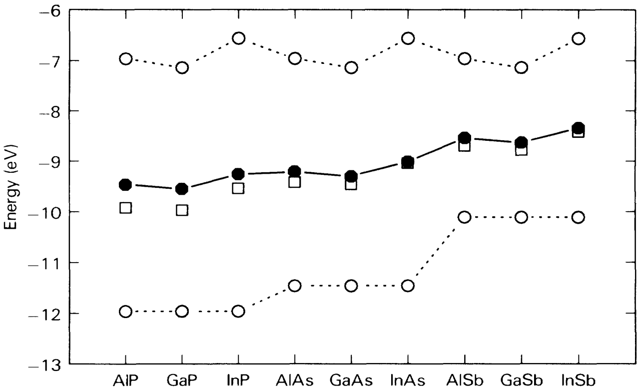

FIG. 1. The semiconductor host properties for compounds indicated at the bottom, relative to the nominal vacuum level. The squares are renormalized cation-vacancy dangling-bond levels E_h. The upper open circles are cation hybrid levels ϵ_h^c, and the lower open circles are anion hybrid levels ϵ_h^a. The filled octagons are average hybrid energy $\bar{\epsilon}_h = (\epsilon_h^a + \epsilon_h^c)/2$. The circles are connected for ease of viewing.

We can now make a direct connection between the TM impurity levels and heterojunction band lineups. Specifically, Harrison and Tersoff[9] showed that, within the same tight-binding theory used here, the correct self-consistent prescription to obtain the band lineup in a heterojunction is to align the average hybrid energy, $\bar{\epsilon}_h$, in the two semiconductors. According to (9), this is approximately the same as the alignment of E_h in the two semiconductors, which in turn corresponds to the alignment of the respective TM impurity levels in the two semiconductors, as discussed above. But this is precisely the rule arrived at empirically for the prediction of band lineups from TM impurity levels.[3,5]

We have therefore succeeded in explaining how the observed correlation is a direct consequence of the theory of impurity levels and band lineups. It should be stressed, however, that according to this theory, the alignment of TM levels is by no means an exact prescription for obtaining the band lineup, since E_h and $\bar{\epsilon}_h$ are not in general identical. It is seen in Fig. 1 that the rule should be particularly accurate for band lineups of "common anion" heterojunctions. Thus the success of the correlation for the AlAs-GaAs interface, which has been stressed by several authors,[3,5] is not a stringent test of the rule in general.

Harrison and Tersoff also pointed out that $\bar{\epsilon}_h$ provided a good measure of the energy at which the Fermi level is "pinned" to form the Schottky barrier.[9] Thus the difference of TM levels or of $\bar{\epsilon}_h$'s provides a good predictor of the difference in Schottky-barrier heights, as ob-

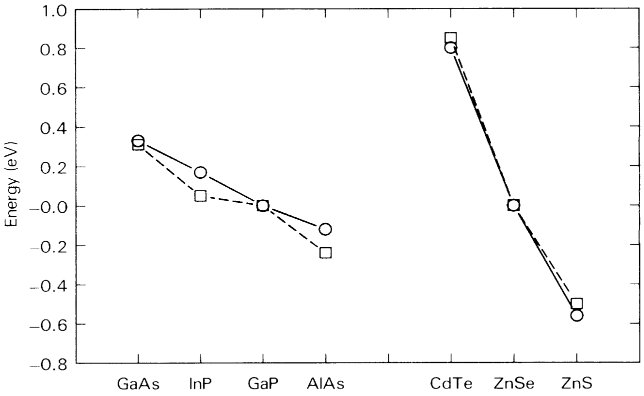

FIG. 2. Comparison of the calculated (Refs. 8 and 11) charge-neutrality level E_B (squares) with the measured (Ref. 5) TM impurity levels (circles). The data are connected for ease of viewing. Following Ref. 5, TM levels are taken relative to the valence maximum, normalized by the subtraction of their value from that in GaP (for III-V's) or ZnSe (for II-VI's), and averaged over different impurities.

served empirically.[6] In fact, $\bar{\epsilon}_h$ is, in essence, the center of the dielectric gap,[9,12] and is closely analogous to the midgap energy or neutrality level E_b which arises in the context of semiconductor heterojunctions[7,8] and Schottky barriers.[10,11] We therefore *speculate* that TM levels could be calculated by replacing E_h with the neutrality level E_B, and proceeding as in Ref. 1. If correct, this would permit greater accuracy than is possible with tight binding alone, while avoiding the difficulties of an *ab initio* impurity calculation.

One would like to compare theory and experiment directly. While the present tight-binding scheme is ideal for general analyses, it does not describe individual semiconductors with high numerical accuracy. We therefore make use of the above speculation, and conclude that a given TM level should fall roughly at E_B, up to a single additive constant for all III-V or all II-VI semiconductors. In Fig. 2, we compare calculated values[8,11] of E_B with the measured TM impurity levels.[5] For the data available, the trends are described very well. These results certainly tend to support the present picture.

In conclusion, a very simple model suffices to show that the host dependence of a TM impurity level is determined by the same basic mechanism as the band lineup at a semiconductor heterojunction. In both cases, there is a charge transfer which depends on the relative energies of the states of the two systems. Any charge transfer results in a large energy shift, so that the relative energies of the levels are almost entirely fixed by the requirement of approximate local charge neutrality within the TM d shell.

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