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Vacancies near semiconductor surfaces

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We present a calculation of the bound-state energy levels of ideal vacancies near and on a semiconductor surface. We consider the (110) surface of GaAs and also a model for more ionic semiconductors with the zinc blende crystal structure. We find that the vacancy energy levels are not greatly perturbed (by less than 0.1 eV) as the vacancy is moved toward the surface until the vacancy reaches the second layer of atoms from the surface. At this point the highest occupied level in the neutral anion vacancy moves to lower energy, and the highest-energy state occupied in the neutral cation vacancy moves to higher energy. As more ionic materials are considered, we find that the anion vacancy levels move toward and eventually into the conduction band, while the cation vacancy levels move toward and eventually into the valence band. These results suggest that the recently proposed defect model for Schottky-barrier formation is capable of accounting for experimentally observed trends in Schottky-barrier behavior.

I. INTRODUCTION

Because of their importance in the fabrication of semiconductor devices, there has been a great deal of interest in Schottky barriers formed at metal-semiconductor contacts. Experimentally, the Schottky-barrier height on covalent semiconductors has been found to depend on the semiconductor but to be rather insensitive to the metal forming the contact. On ionic semiconductors, however, the Schottky-barrier height was found to be sensitive to the metal forming the contact.[1-4] The transition between covalent and ionic behavior occurs rather suddenly, at a fixed value of the electronegativity difference between the cation and anion forming the semiconductor. The transition between covalent and ionic behavior has also been correlated with the heat of formation of the semiconductor.[5-7] Recently, Schottky-barrier formation has been studied at submonolayer coverages. The Schottky barrier was found to be formed at a small fraction of a monolayer in III-V semiconductors.[7-9]

A new model for Schottky-barrier formation has been proposed.[7-9] In this model, defects in the semiconductor are created when the semiconductor-metal contact is formed. These defects induce localized electronic levels in the band gap of the semiconductor which pin the Fermi level at the energy of the defect level. Such a model would account for the insensitivity of the Schottky-barrier height on the metal overlayer in covalent semiconductors since the pinning position would be determined by the defect energy level in the semiconductor. It would also account for the barrier's being formed at a fraction of a monolayer coverage. The precise nature of the defects responsible for Fermi-level pinning was not proposed. However, it was shown that atoms from the semiconductor can diffuse through a rather thick layer of gold on the semiconductor surface. In GaSb, the Sb atoms were found to diffuse preferentially through the gold; in InP, the P diffusion was somewhat preferred; and in GaAs, Ga, and As diffusion appeared to be about equal.[7-8] These observations suggest considering vacancies and vacancy complexes (especially anion vacancies).

In this paper we present a calculation of the bound-state energy levels of ideal vacancies near or on a semiconductor surface. We consider the (110) surface of GaAs and also a model for more ionic semiconductors with the zinc blende crystal structure. The calculations were performed using the tight-binding approximation.

For bulk GaAs we find that the As vacancy introduces a partially filled level about 0.4 eV below the conduction-band minimum and the Ga vacancy introduces a partially filled level about 0.5 eV above the valence-band maximum. The energy of these states is found not to change significantly until the vacancy is put at the second atomic layer from the surface. At this point the highest filled level in the neutral As vacancy moves to lower energy, and the highest filled level in the neutral Ga vacancy moves to higher energy. As the ionicity of of the semiconductor is increased, the anion vacancy levels are found to move to higher energy and eventually into the conduction band, whereas, the cation vacancy levels move to lower energy and eventually into the valence band. These results suggest that vacancy-related defects can pin the Fermi level in the gap of a covalent semiconductor, whereas the analogous defect would not pin the Fermi level in the gap of an ionic semiconductor. This suggests that the defect model can account for the covalent-ionic transition in Schottky-

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barrier formation.

The paper is organized in the following way: In Sec. II we describe the method by which the calculations were done, in Sec. III we present the results, and in Sec. IV we present our conclusions.

II. METHOD OF CALCULATION

We consider ideal vacancies near the (110) surface of GaAs. The calculations were performed in the tight-binding approximation using one S and three P functions on each atom. The tight-binding parameters of Ref. 10 were used.[11] The vacancies were described using the Green's function approach introduced by Koster and Slater.[12-14] The vacancy potential is described in the manner used in Ref. 15. We have performed calculations of vacancy energy levels for vacancies near the surface and in the bulk. The bulk calculations differ from those of Ref. 15 only because different tight-binding parameters are used.

We describe the semiconductor surface using a finite slab of atoms. The surface geometry is taken to be that suggested by the energy-minimization calculations in Ref. 16; this structure is consistent with quantum chemistry calculations[17] and with low-energy electron diffraction (LEED) results.[18] The tight-binding parameters at the surface are linear combinations of the bulk parameters, analogous to the transformation of components of a rotated vector modulated by a d^{-2} scaling relation.[19] The scaling had little effect on the results because nearest-neighbor bond lengths are constant to within 3%. The results of our calculation for the finite slab are similar to the results of previous calculations.[19,20] Prior to relaxation, occupied As-derived and empty Ga-derived surface states occur in the band gap. The surface relaxation pushes the Ga-derived states into the conduction band and the As-derived states into the valence band.

In the Koster-Slater approach, defect energy levels are determined from the Green's function for the unperturbed case.[11-15] This Green's function can be written as

$$G_{\alpha\alpha'}(E)=P\int\frac{A_{\alpha\alpha'}(S)dS}{E-S}-i\pi A_{\alpha\alpha'}(E), \tag{1a}$$

where

$$A_{\alpha\alpha'}(E)=\sum_{nk}\langle\alpha|nk\rangle\langle nk|\alpha'\rangle\delta(E-E_n(k)). \tag{1b}$$

Here $|nk\rangle$ are unperturbed eigenstates with energies $E_n(\vec{k})$; $\vec{k}$ labels wave vectors (two-dimensional for the surface case); n labels bands; and $|\alpha\rangle$ is an atomic function. The energy of a bound defect state can be determined by solving[12-15]

$$\det|1-G(E)V|=0, \tag{2}$$

where V is the defect potential. In our case, the vacancy potential is defined by raising to infinity on-site energies of the atom to be removed. This prescription is mathematically equivalent to setting all the interaction matrix elements with the removed atom equal to zero.[15] For this model, the condition for a bound state becomes

$$\det|g(E)|=0, \tag{3}$$

where $g(E)$ (a 4×4 matrix in our case) is the block of $G(E)$ confined to the vacancy site in the tight-binding representation.

To perform the calculations, we first construct the spectral functions $A_{\alpha\alpha'}(E)$. The integral over the wave vector was replaced with a Simpson's rule sum; 49 points in the irreducible part of the Brillouin zone were used in the surface calculation; 70 points in the irreducible part of the Brillouin zone were used in the bulk calculations. The δ function in Eq. (1b) was replaced by a band-pass function with a width of 0.1 eV. The remaining part of the Green's function was computed from the principal-part integral in Eq. (1a). The surface calculations were performed using a slab of nine atomic layers. Numerical results for vacancy bound states converged to within 0.1 eV.

The matrix $g(E)$ in Eq. (3) contains information not only on the energy of a bound state but also on its symmetry. For ideal bulk vacancies, $g(E)$ is diagonal in the S-P atomic basis. However, in the surface case it is not diagonal in this basis. It is useful to diagonalize g; then the determinant consists of a product of four functions, and we look for zeros in each of the four. For bulk vacancies, symmetry requires that three of these four functions are identical, giving rise to triplet (t_2 symmetry) and singlet (a_1 symmetry) levels. Near the surface, the bulk symmetry is broken and the a_1 and t_2 states mix to form nondegenerate levels which we label as $\alpha^{(+)}$, $\tau_D^{(+)}$, $\tau_B^{(+)}$, and $\tau_T^{(-)}$. The sign indicates the parity of the level under the mirror symmetry of the (110) surface. Loosely speaking, the a_1 bulk level goes into the level labeled $\alpha^{(+)}$, and the degenerate t_2 levels split and form the τ levels as the vacancy is moved near the surface.

The unitary transformation which diagonalizes $g(E)$ is significant in determining the wave function for a bound state. The amplitude for the atomic function labeled by ν (both atom and type of function) included in the bound state is given by

$$C_\nu=G'_{\nu j}(E_j)\left(\sum_\lambda|G'_{\lambda j}(E_j)|^2\right)^{-1/2}, \tag{4a}$$

where C_ν is the amplitude (ν cannot refer to the removed atom), and

$$\underline{G}'(E)=\underline{U}(E)\underline{G}(E)\underline{U}^{-1}(E), \tag{4b}$$

where

$$\underline{U}(E)=\begin{pmatrix}\underline{u}(E) & 0\\ 0 & 1\end{pmatrix}. \tag{4c}$$

Here $u(E)$ is the 4×4 unitary matrix which diagonalizes $g(E)$ (for E in the band gap). In Eq. (4c), the 4×4 block in the upper-left corner refers to the four atomic functions on the removed atom. In Eq. (4a), j labels the transformed set of atomic functions for which $G'_{jj}(E_j)$ vanishes and E_j is the corresponding bound-state energy. With this notation, the condition for a bound state in the energy gap [Eq. (3)] can be written as

$$\sum_{lk}\left(\int_{\text{VB}}\frac{u_{jl}(E_j)a_{lk}(S)u_{kj}^{-1}(E_j)dS}{E_j-S}+\int_{\text{CB}}\frac{u_{jl}(E_j)a_{lk}(S)u_{kj}^{-1}(E_j)dS}{E_j-S}\right)=0, \tag{5}$$

where $a_{lk}(S)$ is the 4×4 block of $A_{\alpha\alpha'}(S)$ for which α and α' refer to atomic functions on the removed atom and VB (CB) indicates the energy integral is to go over the valence (conduction) band.

Finally, we wish to investigate the behavior of the vacancy levels in semiconductors of increasing ionicity in order to compare the behavior expected in the defect model of Schottky-barrier formation with experimental trends. To do this we use the ionicity parameter χ defined in Ref. 21, that is, χ is defined as the difference in the anion P and cation S on-site parameters in the tight-binding Hamiltonian. For our GaAs parameters, $\chi=-3.6$ eV. To generate the model Hamiltonian for other ionicities, we change the cation on-site levels, keeping both atomic S-P spacings constant. All other parameters are held fixed. We use the same surface relaxation as for GaAs. The calculations of Ref. 22 suggest that the relaxation of the (110) surface of various III-V and II-VI semiconductors are qualitatively similar. The parameter χ represents a single quantity which can be varied to investigate systematic trends and to compare with observed behavior. The advantage of having a single parameter representing ionicity seemed to us to outweight the advantage for a more accurate treatment of specific materials in this calculation.

III. RESULTS

The results of our calculation for the bound-state energies of ideal vacancies near the GaAs (110) surface are shown in Fig. 1. A Ga vacancy on the fifth layer from the surface induces an essentially triply degenerate bound state 0.4 eV above the valence-band maximum. There is also a well defined singlet resonance 0.4 eV below the valence band edge. An As vacancy on the fifth layer induces an essentially triply degenerate bound state 1.1 eV above the valence band edge and a singlet level at the valence band edge. The energy positions of the bound vacancy levels on the fifth layer of the slab are essentially the same (to better than 0.1 eV) as those for the bulk. The bulk vacancy levels we find are similar to those found by Jaros and Brand using a pseudopotential calculation.[23] The biggest discrepancy is in the As t_2 level. Jaros and Brand found this level somewhat above the conduction band edge; in our calculation it is about 0.4 eV below the conduction band edge.

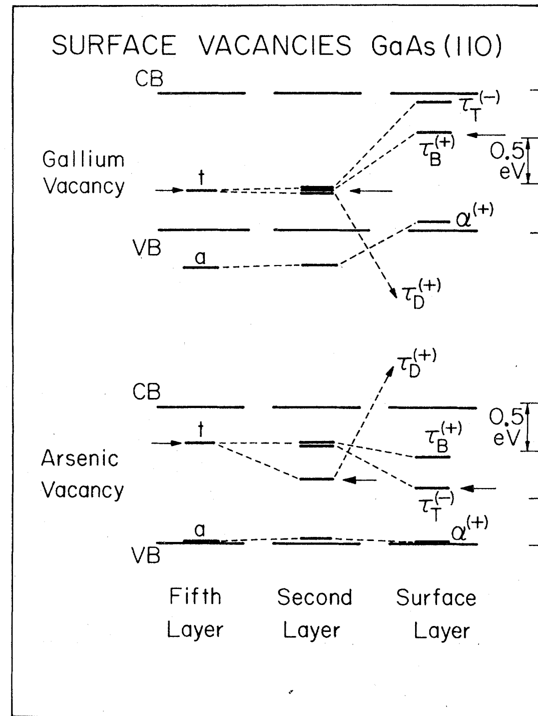

FIG. 1. Energy positions, relative to the band edges, of ideal vacancies near the (110) surface of GaAs. The bound-state energy positions for the vacancies are essentially the same as that of the bulk until the vacancy reaches the second atomic layer from the surface. The arrow indicates the highest energy state occupied in the neutral vacancy.

The neutral Ga vacancy has five electrons, and the neutral As vacancy has three electrons in the eight (including spin) bound or resonant states associated with the vacancy. The highest-energy occupied state in the neutral vacancy is indicated by an arrow in Fig. 1. In all cases this level (twofold degenerate because of spin) is partially occupied in the neutral vacancy.

As a vacancy is moved near the surface, the

bound-state energy levels are not much changed (by less than 0.1 eV), until the vacancy is put on the second layer from the surface. For an atom on the third atomic layer from the (110) surface, the closest atom absent because of the surface is a fifth-nearest neighbor (and only 1 of 12 fifth-nearest neighbors is absent). For an atom on the second atomic plane, a second-nearest neighbor is removed because of the surface and the degenerate triplet levels split by an appreciable amount. The highest occupied level of the Ga vacancy moves to higher energy as the vacancy is moved toward the surface, while the highest occupied level of the As vacancy moves to lower energy.

The labeling of the states in Fig. 1 is made on the basis of the character of the wave functions of the states. We examined the unitary transformation $u(E)$ which diagonalizes the Green's function $g(E)$ and determines the orbital decomposition of the atomic functions on the vacancy site which generates the bound state [in the sense of Eq. (4)]. In the bulk, this decomposition consists of the S state and the three P states which generate the a_1 and t_2 levels, respectively. Near the surface the decomposition is mixed and depends both on the position and type of vacancy. However, the states labeled $\alpha^{(+)}$ are generated largely by the S level. The states labeled $\tau_T^{(-)}$ are generated by the P orbital which lies in the plane of the surface and changes sign under the mirror symmetry of the (110) surface. The states labeled $\tau_B^{(+)}$ are generated largely by the P orbital which lies in the plane of the surface and is even under the mirror symmetry. The states labeled $\tau_D^{(+)}$ are generated largely by the P orbital which is orthogonal to the surface (i.e., the surface dangling-bond state). In Fig. (2) we show the partial density of states for the orbitals that generate the $\tau_D^{(+)}$ and $\tau_T^{(-)}$ states of the vacancy on the surface [i.e., $u(E_j)a(E)u^{-1}(E_j)$, which appears in Eq. (5)]. We compare the surface functions with the corresponding bulk functions (pure P orbitals in the bulk). The large contribution from surface resonance states is evident in the decomposition for the $\tau_D^{(+)}$ states. These strong peaks [see Eq. (5)] push the $\tau_D^{(+)}$ states well out of the gap. By comparing the surface and bulk decompositions for the $\tau_T^{(-)}$ states in Fig. 2, we see why the anion $\tau_T^{(-)}$ state is pushed to lower energy at the surface and the cation $\tau_T^{(-)}$ state is pushed to higher energy at the surface.

In Fig. (3) we show the energy levels of ideal bulk vacancies as the ionicity parameter χ is varied. The anion vacancy levels move to higher energy and the cation vacancy levels move to lower energy as χ is increased.[24] When χ becomes slightly positive the levels move outside of the band gap. The bulk band structure remains qualitatively similar as χ is changed, although the size of the band gap increases with increasing χ. The character of the valence- and conduction-band states is rather sensitive to the value of χ. For $\chi < 0$, the valence-band states are somewhat more anionic and the conduction-band states somewhat more cationic,

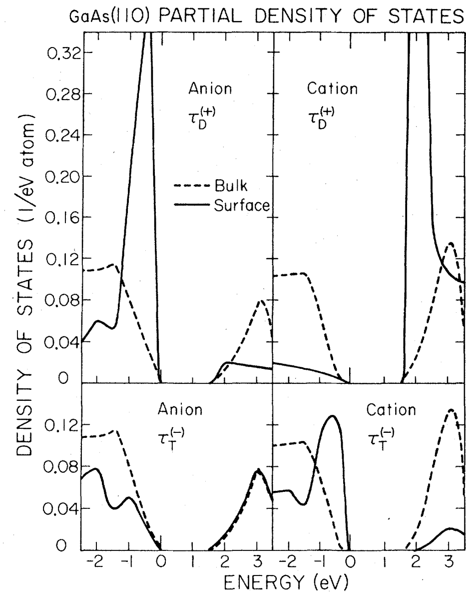

FIG. 2. Partial density of states for the orbital combination which generates [in the sense of Eq. (4)] the surface vacancy states $\tau_D^{(+)}$ and $\tau_T^{(-)}$ at the GaAs (110) surface. The corresponding bulk (P orbital in both cases) partial density of states is also shown.

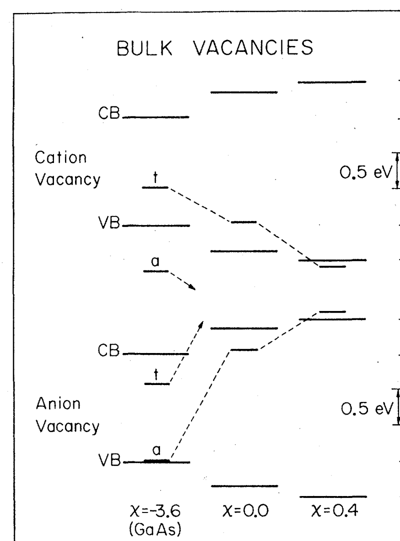

FIG. 3. Ideal bulk vacancy energy levels, relative to the band edges, as the ionicity parameter χ is changed. The absolute position of the band edges is arbitrary.

but the mix is fairly equal. The splitting between valence- and conduction-band states is primarily due to hybridization (i.e., bonding and antibonding states).[21] In the ionic case $\chi > 0$, the conduction-band states are very heavily cationic, and the valence-band states are very heavily anionic. In this case the splitting of valence- and conduction-band states is due primarily to the difference in the anion and cation on-site energy levels.[21] If one views the vacancy levels as formed from dangling bonds in the defect molecule picture,[25] the behavior indicated in Fig. 3 is to be expected. For the covalent case, the dangling-bond states occur between the bonding (valence-band) and antibonding (conduction-band) states, that is, in the band gap. In the more ionic case ($\chi > 0$), the anion vacancy states (formed primarily from cation dangling bonds) occur in the band of cationic states, that is, the conduction band. Likewise, the cation vacancy states (formed primarily from anion dangling bonds) occur in the band of anionic states, that is, the valence band. We expect that this general trend will hold for other defect states formed from dangling-bond orbitals.

In Fig. 4, we show the energies of the ideal vacancies near the (110) surface in the $\chi = 0$ case. As for the GaAs case, there is little change in the energy levels until the vacancy is on the second layer from the surface. The overall behavior is similar to that for GaAs. The strongest change with the ionicity parameter is the general motion of the anion vacancy levels toward the conduction band and of the cation vacancy levels toward the valence band with increasing χ.

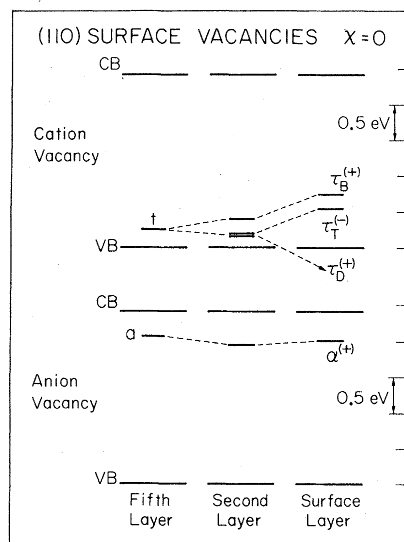

FIG. 4. Energy positions, relative to the band edges, of the ideal vacancies near the (110) surface for the $\chi = 0$ case. The bound-state energy positions are essentially the same as that of the bulk until the vacancy reaches the second atomic layer from the surface.

IV. SUMMARY AND CONCLUSIONS

Our main results are in the form of trends which should be independent of the calculational details. We find that vacancy energy levels are not greatly perturbed (by less than 0.1 eV) as the vacancy is moved from the bulk to the surface until the vacancy reaches the second layer of atoms from the surface. At this point, the highest energy state occupied in the neutral anion vacancy moves to lower energy and the highest energy state occupied in the neutral cation vacancy moves to higher energy. As more ionic materials are considered, we find that the anion vacancy levels move toward and eventually into the conduction band while cation vacancy levels move toward and eventually into the valence band. Characterizing the material by the ionicity parameter χ, we find that the vacancy levels leave the band-gap region for χ slightly positive. These general trends should also occur for other defect states which are made up from dangling bonds. The common III-V semiconductors have negative values for χ and the common II-VI semiconductors have positive values of χ. These results suggest that vacancies should form deep levels in the III-V semiconductors. In the II-VI semiconductors, cation vacancies should form shallow acceptors and anion vacancies should form shallow donors. (We have not included the Coulomb interaction responsible for forming shallow impurity bound states. Thus, we interpret an occupied level moving into the conduction band or an empty level moving into the valence band as leading to the formation of shallow donors and acceptors, respectively.)

In the defect model of Schottky-barrier formation, it is proposed that defects, created in the semiconductor when the semiconductor-metal contact is formed, pin the Fermi level at the energy position of the defect bound electronic state.[7-9] Our results indicate that this model is capable of accounting for the covalent-ionic transition observed in Schottky-barrier formation. For covalent materials, with $\chi < 0$, the vacancies form deep trap levels in the semiconductor band gap which can pin the Fermi level in the gap. For ionic materials, with $\chi \gtrsim 0$, the vacancy levels should be near the band edges and the Fermi level is not determined by the semiconductor alone. The transition between covalent and ionic Schottky-barrier behavior does indeed occur at $\chi \approx 0$.[21]

Furthermore, if one associates the defects responsible for Fermi-level pinning in the III-V semiconductors with an anion vacancy[26] (or more

generally, a defect state involving dangling cation bonds), a second experimentally observed trend can be explained. In the series GaSb, GaAs, and InP (listed in order of increasing χ) the pinned Fermi level (insensitive to the metal forming the contact) has been observed to proceed from near the valence-band maximum to near midgap to near the conduction-band minimum.[7-9] A similar increase in the Fermi-level pinning position is seen in the other common III-V semiconductors (see Table I). Since the anion vacancy level moves to higher energy with increasing χ (see Fig. 3), this behavior is expected if the Fermi level is pinned by a state derived from an anion vacancy. It seems reasonable that anion vacancies should occur near the surface of the common III-V semiconductors since the vapor pressure of the anion materials is much higher than that of the cation materials in these semiconductors. Also preferential diffusion of the anion through an Au film has been observed in Schottky barriers made of Au on GaSb and InP.[7,8]

Of course, associating Fermi-level pinning with a simple anion vacancy is probably oversimplified. However, the general trends of bound-state energies with semiconductor ionicities should occur for other defect states involving dangling-bond orbitals. We conclude that the defect model is capable of accounting for the experimental trends observed in Schottky-barrier formation. This does not, of course, prove the validity of the defect model. But it does suggest that it is a promising model worthy of further investigation.

TABLE I. Comparison of the surface Fermi level relative to valence-band maximum (E_F) with the scaled electronegativity parameter χ for the common III-V semiconductors. The value for E_f from Ref. 9 is for oxidized surfaces; the numbers in parentheses (without parentheses) are for n-type (p-type) material. All numbers are in units of eV.

	χ[a]	E_f Ref. 3	E_f Ref. 9	E_g
GaSb	−5.0	0	0.1(0.1)	0.67
InSb	−4.0	0		0.16
AlSb	−3.5	0.55		1.63
GaAs	−3.5	0.5	0.5(0.7)	1.43
GaP	−2.7	0.7		2.24
InAs	−2.6	0.5		0.33
AlAs	−2.2	1.1[b]		2.16
InP	−2.0	0.8	1.1(1.2)	1.34

[a] Reference 21.
[b] From the n barrier, assuming n and p barriers add to the band gap.

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materials. They suggest that at least two defect levels must be considered to interpret this result. It is certainly possible that more than one defect is responsible for the Fermi-level pinning. However, the result can also be accounted for by a single defect with three charge states (say neutral, plus, and minus one electron charge), since more energy would be required to remove an electron from the neutral center than would be gained in binding an electron to the neutral center.