# Effects of alloy disorder on Schottky-barrier heights

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The effects of alloy disorder on the Schottky barriers at semiconductor-alloy—metal interfaces are investigated within the defect model of Schottky-barrier formation. The deep levels and the associated wave functions for surface antisite defects, which are believed to be responsible for the barriers considered here, were previously calculated for various III-V semiconductor alloys using the theory of deep levels and treating the alloy host in the virtual-crystal approximation. In the present paper, perturbation theory is used to treat the effect of the random local environment of each defect on these deep levels. For the cation and anion antisite defects at the (110) surfaces of six different III-V semiconductor alloys, the inhomogeneous broadening of the associated deep levels is found to range from nearly 0 to about 0.3 eV, depending on the alloy composition and the material considered. The corresponding effect on the Schottky-barrier heights which result from Fermi-level pinning by these deep levels should be a slight bowing with composition. Typically, this bowing effect is estimated to be of the order of 0.1 eV at intermediate alloy compositions.

## I. INTRODUCTION

Understanding the formation of Schottky barriers at semiconductor-metal interfaces is a problem of considerable technological, as well as fundamental, importance. It is now believed that Schottky barriers are usually due to Bardeen Fermi-level pinning[1] by extrinsic surface states associated with defects.[2-6] The phenomenological defect model for Fermi-level pinning and Schottky barrier formation, developed by Spicer and coworkers,[2] has been given a microscopic foundation by Allen, Sankey, and Dow.[7] In particular, it has been shown that the observed Schottky barriers at III-V semiconductor-alloy—metal interfaces are remarkably well described by a model which attributes the barriers to the dangling-bond deep-level states associated with antisite defects at the alloy surface.[7] In this paper, we (1) develop a simple perturbation-theory approach to the calculation of the effects of alloy disorder on these deep-level states, (2) obtain quantitative estimates for the magnitude of these effects at the surfaces of six semiconductor alloys, and (3) show that the inclusion of these effects does not substantially alter the picture of Schottky-barrier formation and Fermi-level pinning due to surface antisite defects in the materials for which experimental data is currently available. However, we find that in some cases the effects of alloy disorder on Schottky-barrier heights may be large enough to be observable. We predict, for example, relatively large alloy-disorder effects in $GaAs_{1-x}Sb_x$.

In the calculations of Allen *et al.*,[7] the alloy host was treated in the virtual-crystal approximation (VCA), and the antisite defect was assumed to be the composition-weighted average defect. In this approximation, effects of alloy disorder on the deep levels associated with Fermi-level pinning and Schottky-barrier formation are completely neglected. It is the purpose of the present paper to remedy this situation by extending the VCA theory[7] to include these effects, and to obtain estimates of their magnitude for a number of III-V semiconductor alloys.

The motivation for the present work is twofold. First, the alloy disorder in the neighborhood of bulk defects in semiconductor alloys has been shown, both experimentally and theoretically, to be important for understanding the associated deep electronic energy levels in these materials. For example, in recent years, several workers have observed and studied the effects of such disorder on optical absorption and luminescence from excitons bound to impurities in the III-V alloys, and have found that such spectra are inhomogeneously broadened ("alloy broadened") by the disorder.[8-10] In addition, Ford and Myles[11-13] have recently developed a quantitative theory to treat the effects of alloy disorder on deep levels in bulk semiconductor alloys. Calculations made by these workers of the inhomogeneous alloy broadening of deep energy levels due to substitutional impurities in bulk $Al_{1-x}Ga_xAs$ (Ref. 11) and $Hg_{1-x}Cd_xTe$ (Ref. 12) indicate that this effect can be of the order of 0.1 eV or greater for some alloy compositions in some materials. Second, the remarkable agreement between the predictions of Ref. 7 and the experimental data for a number of III-V semiconductor alloys provides one of the most convincing arguments for the defect model of barrier formation. Yet, because this theory does not include the effects of alloy disorder, a potentially important ingredient is missing.

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This is true from both the quantitative and the philosophical viewpoints. Quantitatively, if the alloy broadening of the surface defect states were found to be more important than the comparable effect in the bulk, this could substantially alter the previous results,[7] and thus have an impact on the interpretation of the defect model for Schottky-barrier formation. Philosophically, a theory which makes predictions of chemical trends with alloy composition needs to include the effects of alloy disorder in order to be complete. The simple theory derived below gives a means of estimating the importance of these effects within the framework of the model which produced the earlier predictions.

The deep levels[7] and the associated wave functions[14,15] for the surface antisite defects have previously been calculated using the theory of deep levels and treating the alloy host in the VCA. In our approach, perturbation theory is used to treat the effects of the random local environment of the defect on these deep levels. The effects of this environment on all four deep levels associated with each defect are estimated.

The remainder of this paper is organized as follows. In Sec. II the basic model we employ for these calculations is briefly reviewed and the theoretical approach is outlined. In Sec. III we present the results of our calculations for the alloy broadening of the deep levels associated with both the cation and the anion antisite defects at the (110) surfaces of six III-V semiconductor alloys. We then discuss these results and their implication for the Allen *et al.*[7] model of Fermi-level pinning, within the Spicer defect model[2] of Schottky-barrier heights at semiconductor-alloy—metal interfaces. Finally, in Sec. IV we give a brief summary.

## II. THEORY

### A. Deep-level calculations

The starting point for our theory is the results of previous calculations[7] of deep levels and their associated wave functions[14,15] for both types of antisite defects at the (110) surfaces of ternary III-V semiconductor alloys, $A_xB_{1-x}C$. In these calculations, both the defect and the host were treated in the VCA, which replaces them by their composition-weighted averages. For example, the cation-on-anion-site defect in $Al_{1-x}Ga_xAs$ was treated as an average cation (with weights $1-x$ and $x$ for Al and Ga, respectively) sitting on an As site in a material whose Hamiltonian matrix elements are averages of those for the two binary semiconductors (with weights $1-x$ for AlAs and $x$ for GaAs). The deep levels and the resulting Schottky-barrier heights have been previously published[7] for the alloys $Al_{1-x}Ga_xAs$, $GaAs_{1-x}P_x$, $Ga_{1-x}In_xP$, $InP_{1-x}As_x$, and $In_{1-x}Ga_xAs$. The electronic wave functions associated with these deep levels in GaAs have been calculated by S.-Y. Ren,[15] and will be published elsewhere.

For completeness, we briefly summarize here the method used in Ref. 7. The surface Green's-function matrix, $G(E)=(E-H)^{-1}$, including the effects of the (110) surface relaxation,[16] was first calculated in the Vogl *et al.*[17] $sp^3s^*$ semiempirical nearest-neighbor tight-binding basis using a method developed earlier.[18] Here $E$ is an energy and $H$ is the Hamiltonian describing the surface. The deep levels $E$ due to each defect were then determined from the eigenvalue equation

$$\det[1-G(E)U]=0 . \tag{1}$$

In Eq. (1), $U$ is a defect potential matrix, localized at the impurity site, which is constructed according to the prescription given by the Hjalmarson *et al.*[19] deep-level theory. (In this prescription, lattice distortion around the impurity is neglected so that $U$ is a diagonal matrix in a local representation and the three $p$ diagonal elements are equal to one another. The $s^*$ diagonal element is taken to vanish, and each $p$ diagonal element is taken to be one half the $s$ diagonal element.) Finally, the deep-level wave functions associated with the defects were calculated by S.-Y. Ren[15] using an extension of his method for bulk defect wave functions.[14]

The alloy composition dependence of the Schottky-barrier height (the conduction-band edge minus the lowest empty defect level for $n$-type material, and the highest occupied defect level minus the valence-band edge for $p$-type material) which results from these calculations is shown (straight thick lines) in Fig. 1 for the alloys $Al_{1-x}Ga_xAs$, $GaAs_{1-x}P_x$, $Ga_{1-x}In_xP$, $InP_{1-x}As_x$, $In_{1-x}Ga_xAs$, and $GaAs_{1-x}Sb_x$. Superimposed on these curves are the experimental data (solid circles connected by a dashed line) for the barrier heights, taken from the work cited in Ref. 7. As has been previously discussed,[7] the theory reproduces the chemical trends in the data remarkably well for both $n$-type and $p$-type materials and for a variety of metals at the interface. The quantitative agreement between theory and experiment is fortuitous, since the theory contains uncertainties of several tenths of an eV. The thin

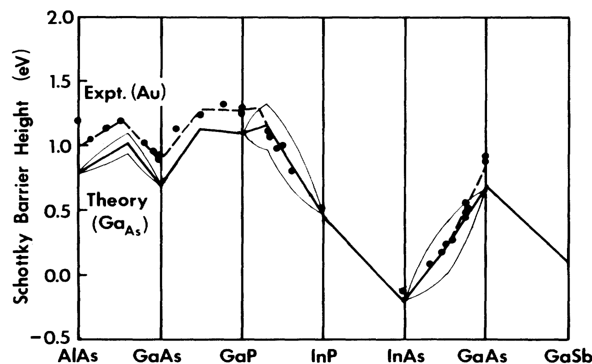


FIG. 1. Alloy broadening of state + 1 at the anion site. The experimental data for Schottky-barrier heights of Au contacts to the various alloys $Al_{1-x}Ga_xAs$, $GaAs_{1-x}P_x$, etc., indicated by points and fitted with the dashed line, are from the papers cited in Ref. 7. The thick solid lines represent the theoretical calculations for the dangling-bond acceptor level associated with a cation atom on the anion site—e.g., Ga on the As site—as calculated in the virtual-crystal approximation (Ref. 7). The thin solid lines represent the root-mean-square alloy broadening of this defect level as calculated here.

curved lines shown in the figure are the results of the calculation described below and are discussed in detail in Sec. III.

### B. Alloy disorder effects

#### 1. Energy shifts of deep levels via perturbation theory

In this section we outline a perturbation-theory approach to the calculation of the energy shifts, with respect to their values obtained using the VCA for the alloy host, of the deep levels associated with the surface antisite defects. For a given configuration of alloy atoms surrounding the defect, a particular shift is obtained for each deep level. When all such configurations are included, an inhomogeneously broadened deep-level spectrum is obtained. Possible configurations in the bulk alloy are illustrated schematically in Fig. 2.

In the following discussion, we explicitly consider the case of a ternary alloy $A_xB_{1-x}C$ with cation disorder. The resulting formalism is obviously applicable to an alloy with anion disorder when one interchanges cation and anion labels. In the absence of antisite defects or impurities, atoms $A$ and $B$ are regarded as randomly occupying the cation sites ($c$ sites), with the anion sites ($a$ sites) always occupied by atom $C$. In this paper, we consider only antisite defects, although a similar formalism can be applied to other substitutional defects. We thus calculate below the alloy-disorder effects on the deep levels for a cation ($A$ or $B$ atom) occupying an $a$ site.

In our approximate treatment, we will consider only the alloy-disorder effects on the above-discussed deep levels which are associated with the defect site and with its nearest-neighbor sites. (Calculations in the bulk[11-13] indicate that second- and higher-neighbor effects are small.)

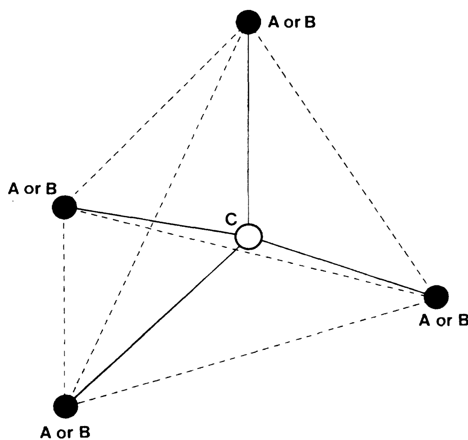


FIG. 2. Configurations in the alloy $A_xB_{1-x}C$. In the bulk atom $C$ is surrounded by four neighbors, all in equivalent tetrahedral sites, each of which may be either an $A$ or $B$ atom. At the (110) surface (e.g., when the atom furthest right in the figure is missing), $C$ has one dangling bond, is bonded to two surface atoms at equivalent sites (denoted as 1 and 2 in the text), and is bonded to one subsurface atom at a site (denoted as 3 in the text) which is inequivalent to sites 1 and 2.

At the (110) surface of a III-V semiconductor, an atom has one dangling bond and three nearest neighbors, two of which are in the surface plane with it and one of which is in the first subsurface plane. This can be seen in Fig. 2 if the surface is imagined to coincide with the plane which passes through the $C$ atom, the uppermost $A$ ($B$) atom, and the lowermost $A$ ($B$) atom, so that the $A$ ($B$) atom at the right of the figure is missing. (See also Fig. 1 of Ref. 15.) We thus focus our attention on a four atom cluster of alloy constituents at the (110) surface of the semiconductor alloy under consideration. Before an antisite defect has formed, such a cluster consists, in the present case where we are considering cation-disordered alloys, of an anion and three nearest-neighbor cations. The anion (atom $C$ in Fig. 2) and two of the cations [the upper and lower $A$ ($B$) atom in Fig. 2] are in the plane of the surface, while the third cation [the $A$ ($B$) atom at the left in Fig. 2] occupies a site which is one atomic layer below the surface. The two surface cations thus occupy geometrically equivalent $c$ sites, while the subsurface cation occupies a $c$ site which is inequivalent to the other two. A particular $c$ site can be randomly occupied by an $A$ or a $B$ atom, with probabilities $x$ and $1-x$, respectively, in analogy to Fig. 2. In the derivation which follows, the two equivalent surface-layer $c$ sites and the inequivalent subsurface-layer $c$ site are numbered with site indices 1, 2, and 3, respectively.

To be explicit, let us consider the case of the antisite cation ($A$ or $B$ atom) defect occupying the central $a$ site of the cluster. Alloy disorder effects will give rise to energy shifts in the resulting deep levels associated with this defect. In our approximation, these energy shifts can be divided into two categories: (1) shifts due to effects on the defect site (on-site effects), and (2) shifts due to effects on the nearest-neighbor sites (off-site effects). We assume that both types of disorder-induced energy shifts are small enough that first-order perturbation theory provides an adequate description for calculating them. In order to include the on-site effects, the average antisite cation $[xA+(1-x)B]$ used in the VCA calculations[7] is replaced by each of the actual cations $A$ and $B$, and the energy shift of the associated deep level with respect to the VCA level is calculated in first-order perturbation theory. The energy shifts due to off-site effects originate because a defect can be surrounded by one of numerous possible local environments of alloy constituents. Each distinct local environment will give rise to a different defect-associated energy level, resulting in a spectrum of deep levels. This is interpreted as an inhomogeneous broadening of the deep level associated with that defect. In the formalism given below, we approximate this effect by calculating the energy shift of a particular level which is produced by each possible nearest-neighbor environment which can surround the defect. For the four-atom cluster discussed above with the $a$ site occupied by either an $A$ or a $B$ atom antisite defect, there are six distinct configurations. These, along with their probabilities of occurrence (assuming a completely random alloy) are listed in Table I; the numbers in parentheses indicate the site indices defined above, with $c$ site 3 not equivalent to $c$ sites 1 and 2 because of the lack of symmetry at the surface.

TABLE I. The six possible configurations of a $C$ atom surrounded by a disordered nearest-neighbor shell of $A$ or $B$ atoms, and their probabilities of occurrence, at the (110) surface of the alloy $A_xB_{1-x}C$. Here "1" and "2" are equivalent surface neighboring sites, and "3" is an inequivalent subsurface neighboring site, as is discussed in the text.

| Configuration number | Configuration | Probability of occurrence |
|---|---|---|
| 1 | $A(1),A(2),A(3)$ | $x^3$ |
| 2 | $B(1),A(2),A(3)$ | $2x^2(1-x)$ |
| 3 | $A(1),A(2),B(3)$ | $x^2(1-x)$ |
| 4 | $B(1),B(2),A(3)$ | $x(1-x)^2$ |
| 5 | $A(1),B(2),B(3)$ | $2x(1-x)^2$ |
| 6 | $B(1),B(2),B(3)$ | $(1-x)^3$ |

For a particular antisite defect and for a particular nearest-neighbor cluster configuration, the first-order perturbation theory results for the combined energy shift due to both on-site and off-site effects can be written as

$$\Delta E = \langle \Psi | V | \Psi \rangle , \tag{2}$$

where $|\Psi\rangle$ is the wave function associated with the particular deep level being considered and $V$ is a potential representing the change in the local environment of the defect, surrounded by that particular cluster configuration, with respect to its local environment in the VCA medium. In our approach, we adopt the framework of Hjalmarson *et al.*[19] and construct this potential using the atomic energies of the alloy constituents. We thus write

$$V = \sum_i |i,a\rangle \Delta\epsilon_i \langle i,a| + \sum_{i,n} |i,c(n)\rangle \Delta\epsilon_{i,n} \langle i,c(n)| . \tag{3}$$

Here $a$ refers to the $a$ site of the cluster, $c(n)$ refers to $c$ site $n$ of the cluster ($n=1,2,3$), $i$ is an orbital index ($s,p_x,p_y,p_z$), and $|i,a\rangle$ and $|i,c(n)\rangle$ are atomiclike orbitals centered at the appropriate sites. In Eq. (3), we have defined the symbols

$$\Delta\epsilon_i = \beta_i(\epsilon_i^c - \bar{\epsilon}_i^c) , \tag{4a}$$

and

$$\Delta\epsilon_{i,n} = \beta_i(\epsilon_{i,n}^c - \bar{\epsilon}_i^c) , \tag{4b}$$

where $\epsilon_i^c$ is the $i$th orbital atomic energy of the cation antisite defect on the $a$ site of the cluster, $\epsilon_{i,n}^c$ is the $i$th orbital atomic energy for the cation which occupies $c$ site $n$ for this configuration, $\bar{\epsilon}_i^c$ $[=x\epsilon_A+(1-x)\epsilon_B]$ is the $i$th orbital cation atomic energy in the VCA, and $\beta_i$ is a semiempirical proportionality constant. Following Hjalmarson *et al.*[19] we take $\beta_s=0.8$ and $\beta_p=0.6$. The atomic energies used in the numerical calculations discussed in the next section were taken from Table 3 of Ref. 17.

According to Eqs. (2)–(4), the alloy disorder-induced energy shift in the deep level under consideration, for a particular antisite defect and cluster configuration, can be written as

$$\Delta E = \Delta E_1 + \Delta E_2 , \tag{5a}$$

where we have defined

$$\Delta E_1 = \sum_i \Delta\epsilon_i \, |\langle i,a | \Psi\rangle|^2 , \tag{5b}$$

and

$$\Delta E_2 = \sum_{i,n} \Delta\epsilon_{i,n} \, |\langle i,c(n) | \Psi\rangle|^2 . \tag{5c}$$

The quantities $\Delta E_1$ and $\Delta E_2$ are, respectively, the shifts produced by on-site and off-site disorder.

For an antisite anion (C atom) defect occupying a $c$ site, there is no alloy broadening in the present model for the case of cation disorder, because our cluster consists of an anion surrounded by neighboring anions, i.e., there is only one configuration.

*2. Calculations of alloy broadening of deep levels: Width of the spectrum*

Given the wave functions $\langle i,a|\Psi\rangle$ and $\langle i,c(n)|\Psi\rangle$,[14,15] and the appropriate atomic energies from Table 3 of Ref. 17, the energy shifts $\Delta E_1$ and $\Delta E_2$ are easily calculated via Eqs. (5a)—(5c) for a particular antisite defect on the $a$ site of the cluster, and for a particular configuration of cations on the $c$ sites. These energy shifts are first calculated for both possibilities of the antisite defect and for each cluster configuration. Then average moments of the resulting spectrum are calculated by weighting each of these shifts by the probability of occurrence of the configuration which produced it. These moments will give an estimate of the size of the inhomogeneous broadening for a given composition.

When this procedure is followed, it is not difficult to show that the average energy shifts due to the two contributions to the broadening separately vanish. Thus, on the average, the center of the alloy-broadened deep-level spectrum is at the energy for the deep level predicted using the VCA description for the alloy host. This is a consequence of our use of perturbation theory to calculate the broadening. A more complete, nonperturbative calculation, such as that done by Ford and Myles[11–13] for the alloy broadening of deep levels in the bulk, would probably produce a small but nonzero average shift.

A good measure of the magnitude of the alloy disorder effects on the alloy broadened spectrum is the root-means-square (rms) width. Like the energy shifts, this has an on-site and an off-site contribution, and each of these can be calculated from the appropriate mean-square energy shift. For on-site disorder effects, the mean-square energy shift has the form

$$\langle (\Delta E_1)^2 \rangle = x(\Delta E_1^A)^2 + (1-x)(\Delta E_1^B)^2 , \tag{6}$$

where the angular brackets indicate a configuration average, and $\Delta E_1^A$ and $\Delta E_1^B$ are the on-site energy shifts of Eq. (5b) calculated with cation $A$ and cation $B$, respectively, replacing the anion on the $a$ site. In Eq. (6) we have assumed that, in the alloy $A_xB_{1-x}C$, the probability that the antisite defect is an $A$ atom is $x$, and that it is a $B$ atom is $1-x$. Similarly, for off-site disorder effects, the mean-square energy shift has the form

$$\langle(\Delta E_2)^2\rangle=\sum_\alpha P_\alpha(\Delta E_2^\alpha)^2\;, \tag{7}$$

where $P_\alpha$ is the probability of occurrence, listed in Table I, of the $\alpha$th configuration of cations in the four-atom cluster, $\Delta E_2^\alpha$ is the off-site energy shift of Eq. (5c), calculated for the $\alpha$th configuration, and the sum on $\alpha$ runs over all six configurations shown in Table I. The total rms width of the alloy-broadened deep-level spectrum thus has the form

$$\Delta=\Delta_1+\Delta_2\;, \tag{8a}$$

where

$$\Delta_j=\langle(\Delta E_j)^2\rangle^{1/2}\quad(j=1,2)\;. \tag{8b}$$

It should be noted that the probabilities $P_\alpha$, listed in Table I, assume a completely random alloy. Obviously, if the alloy were nonrandom, Eqs. (6)—(8) would still apply with different $P_\alpha$ and the numerical results presented in the next section would be changed.

### 3. *Effect on Schottky-barrier heights*

As is mentioned above, the Schottky-barrier height is approximately equal to the conduction-band edge at the surface minus the lowest-lying empty defect level for an $n$-type semiconductor, and the highest occupied defect level minus the valence-band edge for a $p$-type material.

If there is a very high concentration of defects at the surface, alloy broadening will lead to a downward bowing as a function of alloy composition of the lowest unfilled (acceptor) levels and to an upward bowing of the highest filled (donor) levels. Thus, in this case, there should be an *upward* bowing of the Schottky barrier for both $n$-type and $p$-type semiconductor alloys as $x$ varies from either 0 or 1 towards the center of the alloy diagram. If the defect concentration were extremely large, we would expect this bowing to be comparable to the maximum rms alloy broadening of the deep level responsible for the barrier height. However, this is essentially an upper limit, and for a more reasonable concentration of defects one expects the alloy broadening of the deep levels to have more modest effects on the Schottky-barrier height. Also, if the number of defects changes with the sample, alloy broadening can lead to a scatter among the barrier heights measured in different samples, rather than a bowing. Finally, if the number of defects were relatively small, but the Schottky barrier was still mainly due to defects, alloy broadening of the deep levels should produce a *downward* bowing of the barrier height as a function of alloy composition $x$. (However, the present model requires a reasonably large number of defects.[7]) As will be seen below, our results indicate that, for the semiconductor alloys that have been studied experimentally, all of these effects of the alloy broadening of deep levels on the barrier heights are expected to be small ($\sim$0.1 eV or less). For $GaAs_{1-x}Sb_x$, however, we predict that these effects are larger—perhaps large enough to be observable.

In interpreting the results presented below in terms of bowing of the Schottky-barrier heights, one should bear in mind that it is well known that there is a downward bowing of the conduction band and an upward bowing of the valence band as a function of composition in semiconductor alloys.[20] As is discussed above, the band edges with respect to which we compute our barrier heights are those computed in the VCA, which *does* account for *some* of this band bowing.[20] However, in order to obtain an accurate prediction of the bowing of the band edges in these materials, it is necessary to perform coherent potential approximation[20] (CPA) calculations of the electronic structure of the alloy host. Such calculations show that the CPA corrections to the band bowing over those predicted by the VCA can in some cases be of a similar size ($\sim$0.1 eV) as the rms alloy-broadened widths which we predict below, but for most compositions in most materials they are smaller. The effect of these band bowings on the deep-level—induced Schottky-barrier heights could thus, *in some cases,* be comparable to the bowing induced by the disorder effects considered here. If this were the case, the extra downward bowing of the conduction band and the extra upward bowing of the valence band would, for $n$-type and $p$-type materials, respectively, tend to *partially cancel* the upward bowing of the Schottky-barrier heights predicted here for large concentrations of defects.

At one end of the alloy diagram ($x\rightarrow0$ or $x\rightarrow1$), the disorder-shifted deep level which lies at one edge or the other of the alloy-broadened deep-level spectrum will deviate significantly from the VCA deep level, but the probability of occurrence of the cluster which produced it will be zero. At the other end of the alloy diagram ($x\rightarrow1$ or $x\rightarrow0$), this level will merge with the VCA level and the probability of occurrence of the cluster which produced it will be unity. Thus, the greatest correction to the Schottky-barrier heights calculated in the VCA will occur near $x=0.5$.

## III. RESULTS AND DISCUSSION

We have applied the formalism just described to obtain estimates of the alloy broadening for the four deep levels associated with each of the antisite defects at the (110) surfaces of the semiconductor alloys $Ga_xAl_{1-x}As$, $GaAs_{1-x}P_x$, $Ga_{1-x}In_xP$, $InP_{1-x}As_x$, $In_{1-x}Ga_xAs$, and $GaAs_{1-x}Sb_x$. Our results for the alloy broadened rms widths are summarized in Tables II and III for $x=0.5$, the composition at which alloy-disorder effects are the largest.

Table II is for a cation-on-anion-site defect, and Table III is for an anion-on-cation-site. In both tables we separately show the on-site contribution $\Delta_1$, the off-site contribution $\Delta_2$, and the total alloy-broadened rms width $\Delta$. The notation of these tables follows that of Ref. 15: The state denoted as $+1$ is the mainly $p$-like defect state associated with the defect dangling bond, the states denoted as $+2$ and $+3$ are two other defect states having positive parity with respect to the $[1\bar{1}0]$ reflection plane perpendicular to the (110) surface, and the state denoted as $-1$ is the remaining purely $p$-like defect state, having negative parity. The $p$-like dangling-bond state $(+1)$ is the one which is interpreted as pinning the Fermi level and producing the observed Schottky barriers for Au contacts to $n$-type semiconductor alloys.[7]

In Figs. 1, 3, and 4 we reproduce the VCA results of Ref. 7 for the three principal antisite-defect-produced

deep levels that are thought to be associated with Fermi-level pinning and Schottky-barrier formation for III-V semiconductors. The first two of these are associated with antisite dangling bonds, and the third is an $s$-like bulk-derived level.[7] We recall that the Schottky-barrier height $\phi_B$ is given by

$$\phi_B^n = E_c^s - E_F^s \tag{9a}$$

for an $n$-type semiconductor and

$$\phi_B^p = E_F^s - E_v^s , \tag{9b}$$

for a $p$-type material, where $E_c^s$, $E_v^s$, and $E_F^s$ are, respectively, the conduction-band minimum, valence-band maximum, and Fermi energy at the surface. The theoretical barrier heights of Figs. 1, 3, and 4 are obtained in the limit of an infinite concentration of defects—i.e., in the approximation $E_F^s = E_a$ ($n$-type) or $E_F^s = E_d$ ($p$-type), where $E_a$ is the lowest unfilled acceptor level and $E_d$ the highest filled donor level. Our estimates of the alloy broadening are indicated by the thin curved lines of Figs. 1, 3, and 4, obtained by using Eqs. (9a) and (9b) together with the rms broadening of the defect levels $E_a$ and $E_d$ exhibited for $x=0.5$ in Tables II and III. As is discussed above, we expect the broadening shown in Figs. 1, 3, and 4 for the *defect levels* to be larger than the resulting bowing or scatter in the experimentally measured *barrier heights*, with the predicted disorder effects on the defect levels serving as an upper limit on the expected effects on the barrier heights.

In making these predictions, we have used the wave functions for the antisite defects calculated by Ren.[15] The results of these surface defect-state wave function calculations (as well as those of previous bulk defect-state wave functions[14]) indicate that for a given (cation or anion) antisite defect, the wave function of a given character depends most strongly on the defect site, and only weakly on the semiconductor host and the energy. In our calculations we have therefore neglected the dependence of the wave functions on the alloy composition, the material which contains the defect, and the energy, and have used the wave functions calculated for the surface antisite defects at midgap in GaAs.[15] While not rigorously correct, this approximation should give us a good *estimate* of the alloy-broadened rms widths of the deep levels.

The magnitudes of the results for the alloy broadening listed in Tables II and III and shown in Figs. 1, 3, and 4, can be qualitatively understood on a case-by-case basis in terms of the $s$ and $p$ orbital atomic energy differences between the appropriate atoms in the alloys listed,[17] together with the magnitudes of the various orbital contributions

TABLE II. Alloy broadening in three semiconductor alloys for deep levels associated with the cation-on-anion-site antisite defect at the (110) surface. The rms alloy-broadened width, in eV, is evaluated at $x=0.5$ for the four deep-level states of the ternary semiconductor alloys listed. The on-site contribution is denoted as $\Delta_1$, the off-site contribution as $\Delta_2$, and the total width as $\Delta$. The labeling of the states is explained in the text. The surface dangling-bond state is denoted as $+1$.

| Contribution | Width (eV) State $+1$ | $+2$ | $+3$ | $-1$ |
|---|---|---|---|---|
| | | $Ga_xAl_{1-x}As$ | | |
| $\Delta_1$ | 0.073 | 0.000 | 0.000 | 0.000 |
| $\Delta_2$ | 0.008 | 0.063 | 0.058 | 0.067 |
| $\Delta$ | 0.081 | 0.064 | 0.059 | 0.067 |
| | | $Ga_xIn_{1-x}P$ | | |
| $\Delta_1$ | 0.171 | 0.000 | 0.005 | 0.000 |
| $\Delta_2$ | 0.028 | 0.131 | 0.131 | 0.132 |
| $\Delta$ | 0.199 | 0.131 | 0.136 | 0.133 |
| | | $In_{1-x}Ga_xAs$ | | |
| $\Delta_1$ | 0.171 | 0.000 | 0.005 | 0.000 |
| $\Delta_2$ | 0.028 | 0.131 | 0.131 | 0.133 |
| $\Delta$ | 0.199 | 0.131 | 0.136 | 0.133 |

TABLE III. Alloy broadening in three semiconductor alloys for deep levels associated with the anion-on-cation-site antisite defect at the (110) surface. The notation is explained in the caption for Table II.

| Contribution | Width (eV) State $+1$ | $+2$ | $+3$ | $-1$ |
|---|---|---|---|---|
| | | $GaAs_{1-x}P_x$ | | |
| $\Delta_1$ | 0.106 | 0.024 | 0.004 | 0.000 |
| $\Delta_2$ | 0.013 | 0.047 | 0.067 | 0.117 |
| $\Delta$ | 0.120 | 0.071 | 0.071 | 0.118 |
| | | $InP_xAs_{1-x}$ | | |
| $\Delta_1$ | 0.106 | 0.024 | 0.004 | 0.000 |
| $\Delta_2$ | 0.013 | 0.047 | 0.067 | 0.117 |
| $\Delta$ | 0.120 | 0.071 | 0.071 | 0.118 |
| | | $GaAs_{1-x}Sb_x$ | | |
| $\Delta_1$ | 0.188 | 0.175 | 0.006 | 0.000 |
| $\Delta_2$ | 0.034 | 0.103 | 0.128 | 0.184 |
| $\Delta$ | 0.222 | 0.278 | 0.134 | 0.184 |

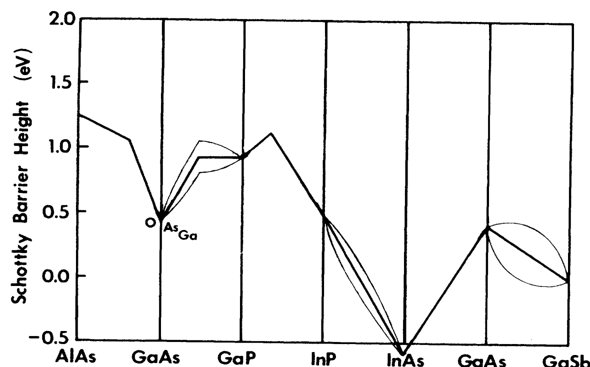


FIG. 3. Alloy broadening of state $+1$ at the cation site. The open circle indicates that this is the acceptor level associated with the anion dangling-bond state. Otherwise, the interpretation is as in Fig. 1.

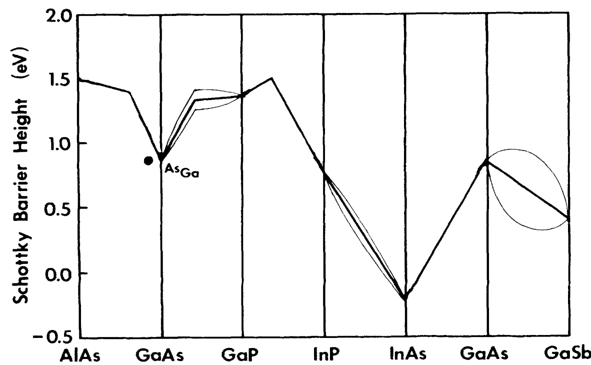


FIG. 4. Alloy broadening of state +2 at the cation site. The solid circle indicates that this is the donor level associated with the anion $s$-like state. Otherwise, the interpretation is as in Fig. 3.

to the wave functions[15] entering Eqs. (5b) and (5c).

It should be noted that the results shown in Tables II and III and in Figs. 1, 3, and 4 indicates that the alloy broadening of deep levels at semiconductor-alloy surfaces is a small effect in most cases, but that for some states associated with some defects in some materials, it can be as large as about 0.3 eV. Clearly the magnitude of these alloy-disorder effects depends on the following factors: (1) the alloy composition $x$, (2) the constituents of the alloy, and (3) the symmetry of the state. These predictions indicate that, for the alloys considered, these effects should be largest in $GaAs_{1-x}Sb_x$ and smallest in $Ga_xAl_{1-x}As$. Furthermore, it is clear from our calculations that the detailed microscopic physics of the material under consideration must be considered n order to predict the size of these effects. Finally, it should again be noted that the results predicted here for the bowing of the Schottky-barrier heights resulting from the alloy broadening of the defect-induced deep levels could be altered if CPA corrections to the VCA band bowing with alloy composition were taken into account.[20] As is discussed in the preceding section, in all cases we expect this extra band bowing to *reduce* the expected bowing of the Schottky-barrier height.

## IV. SUMMARY AND CONCLUSIONS

We have used a simple perturbation-theory approach to calculate the effects of alloy disorder ("alloy broadening") on deep electronic energy levels due to defects at semiconductor-alloy surfaces. As an application of our approach, we have estimated the rms widths of the levels produced by antisite defects at the (110) surfaces of six ternary III-V semiconductor alloys.

Our results show that, in principle, the alloy broadening of the defect levels can produce a bowing of the Schottky-barrier height $\phi_B$ as a function of the alloy composition $x$ (or a scatter in the measured heights if the concentration of defects varies from sample to sample). In particular, for a very large concentration of defects, one expects an upward bowing of $\phi_B$ as a function of $x$ for both $n$-type and $p$-type semiconductor alloys. However, CPA corrections to band bowing, not included in the present theory, are expected to reduce the bowing of $\phi_B$ that we predict here. For those alloys for which experimental data is currently available, our calculations indicate that alloy disorder should have only a small effect on the barrier heights, in agreement with the nearly linear dependence of $\phi_B$ on $x$ that is observed. There are exceptions, however. For example, we predict a relatively large effect for $GaAs_{1-x}Sb_x$ in Figs. 3 and 4 that may be observable.

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