Electronic properties of the quaternary semiconductor alloy $GaSb_{1-x-y}As_xP_y$: Coherent-potential approximation

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A coherent-potential-approximation (CPA) calculation, based upon a generalization of the Chen-Sher formalism to the quaternary alloy case, is presented for the electronic properties of the quaternary semiconductor alloy $GaSb_{1-x-y}As_xP_y$. The results obtained indicate that alloy disorder effects, as measured by the CPA self-energy, are large for this alloy.

The technological importance of quaternary semiconductor alloys has stimulated considerable interest in the basic physics of these materials, and many experimental studies of their properties have been carried out.[1] However, there have been only a few systematic, theoretical treatments of these properties.[2,3] Obtaining an understanding of the electronic properties of these alloys is clearly of importance for understanding electronic transport phenomena in these systems, and could thus indirectly contribute to the improvement of devices manufactured from these materials. There have been, to our knowledge, no published treatments of the electronic properties of the quaternary semiconductor alloys which have both utilized realistic band structures for the alloy constituents and attempted to realistically account for the effects of alloy disorder on these properties. Other than coherent-potential-approximation (CPA) formalisms developed for treating simple one-dimensional models of these alloys,[4] the usual approximation in theoretical analyses[2,3] is to make the virtual-crystal approximation (VCA),[5] which neglects all alloy disorder.

The purpose of the present paper is to improve upon this situation by presenting the results of a calculation of the electronic properties of the quaternary semiconductor alloy $GaSb_{1-x-y}As_xP_y$ which realistically accounts for the effects of alloy disorder by utilization of the CPA[5] and which also uses realistic band structures for the alloy constituents. The calculation is based upon a generalization of the Chen-Sher[6] CPA formalism, originally developed to treat the electronic properties of ternary semiconductor alloys, and it utilizes the semiempirical, sp^3s^* nearest-neighbor tight-binding band structures of Vogl, Hjalmarson, and Dow[7] as input. In the present paper, this generalized formalism is only briefly discussed, with the details left for a later paper.[8]

We have chosen to present the results for $GaSb_{1-x-y}As_xP_y$ as a first illustration of our method because an analysis of the relative scattering strengths of the alloy constituents indicates that it should be in the strong-scattering limit. Thus, alloy disorder effects, as measured by the CPA self-energy, are expected to be large for this system, and the deviations in the state density and other properties from their values obtained using the VCA are expected to be significant.

Our formalism[8] shares the advantage with the original formalism of Chen and Sher[6] in that it is capable of yielding detailed predictions of a wide range of properties, yet it is simple enough to be practical to implement on a repeated basis for a large number of alloys. The primary disadvantage of our approach, also shared with the Chen-Sher[6] formalism, is that it reduces the CPA calculation to one with diagonal disorder only. In particular, off-diagonal disorder due to structural differences in the alloy constituents is neglected in the present theory. However, for alloys where such differences are small compared to the diagonal randomness, our formalism[8] should provide an adequate means of estimating the effects of disorder on the electronic properties. We note that Hass, Lempert, and Ehrenreich[9] have developed a molecular coherent-potential approximation (MCPA) for the III-V ternary alloys, wherein off-diagonal disorder effects are included by applying the CPA to a unit cell of alloy constituents. In principle, this formalism could be generalized to treat quaternary alloys of the type considered here. However, this would be accomplished at the expense of computational labor, as the formalism of Hass *et al.*[9] requires the self-consistent determination of an 8×8 energy-dependent complex self-energy. By contrast, our formalism[8] only requires the calculation of two scalar self-energies. Furthermore, the present theory should provide an adequate first step in the study of the effects of alloy disorder on the electronic properties of the quaternary semiconductor alloys.

We utilize the sp^3s^* band structures[7] as input into our CPA calculations because this band-structure model has previously been used successfully to predict a large number of bulk, surface, and defect properties of numerous semiconductor materials.[3,7,10] In particular, the chemical trends in the electronic properties of such materials are known to be well described by this model. Thus, CPA calculations for quaternary alloys based on these band structures form the basis for a natural extension of previous studies of these materials, which utilized the VCA.[3]

Our formalism[8] considers substitutionally disordered quaternary semiconductor alloys of the form A_xB_y-$C_{1-x-y}D$ and assumes implicitly that the underlying crystal lattice is zinc blende. Thus, for this type of alloy, one of the two sublattices is substitutionally disordered and randomly occupied by atoms of the types A, B, and C with probabilities x, y, and $1-x-y$, respectively, while the second sublattice is always occupied by atoms of the type D.

Briefly stated, the calculational procedure is first to

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form the VCA Hamiltonian using the Vogl et al.[7] parameters as input, and then to calculate the fluctuations about the VCA using our generalized[8] formalism. We thus begin with an alloy Hamiltonian which is the sum of the VCA Hamiltonian, and a potential V which represents the alloy fluctuations about the VCA. Following Ref. 6, we assume that the potential V contains diagonal disorder only, so that it can be written as a sum of single-site terms. Furthermore, we assume that it can be written in a bonding-antibonding basis so that each single-site term can be decomposed into bonding and antibonding parts which can be treated independently.

As in all CPA theories,[5] the next step in implementing the generalized formalism is to replace the alloy Hamiltonian by an effective, energy-dependent Hamiltonian given by

$$H_{\text{eff}}(E) = H_V + \Sigma(E) , \qquad (1)$$

where H_V is the sp^3s^* Hamiltonian of Vogl et al.[7] for the

alloy $A_x B_y C_{1-x-y} D$, calculated in the VCA, and $\Sigma(E)$ is the complex, energy-dependent CPA self-energy which is to be determined. Again, following Ref. 6, we make the single-site approximation so that $\Sigma(E)$ can be written as the sum of single-site self-energies. Furthermore, we assume that the effective medium defined by Eq. (1) is periodic so that these quantities are independent of lattice site and that, like V, each single-site self-energy can be decomposed into bonding and antibonding parts. We denote the bonding and antibonding parts of the single-site self-energy as $\sigma_b(E)$ and $\sigma_a(E)$, respectively.

As is usual in CPA theories,[5] the self-energies $\sigma_b(E)$ and $\sigma_a(E)$ are determined self-consistently in our formalism[8] by requiring that the average atomic scattering matrix vanish. By considering each bond as an independent scattering center, it can be shown after considerable manipulation that this results in scalar self-consistency equations for the bonding (valence band) and antibonding (conduction band) CPA self-energies which have the form[8]

$$\sigma_j(E) = [(x-1)\delta_j^A + y\delta_j^B - \sigma_j(E)]G_j(E)[x\delta_j^A + (y-1)\delta_j^B - \sigma_j(E)]G_j(E)[x\delta_j^A + y\delta_j^B - \sigma_j(E)]$$
$$+ [(3x-1)\delta_j^A + (3y-1)\delta_j^B - 2\sigma_j(E)]G_j(E)\sigma_j(E) + [x(1-x)(\delta_j^A)^2 + y(1-y)(\delta_j^B)^2 - 2xy\delta_j^A\delta_j^B]G_j(E) , \qquad (2)$$

where $j = b$ or $j = a$, and we have introduced the Green's function

$$G_j(E) = \frac{1}{4} \int \frac{D_j(E')dE}{E - E' - \sigma j(E)} . \qquad (3)$$

Here, $D_j(E)$ is the VCA state density for the valence-band $(j = b)$ or the conduction-band $(j = a)$ states. In Eq. (2), we have introduced the disorder parameters for the bonding or antibonding states as (where CD is the reference crystal)

$$\delta_j^A = \varepsilon_j(CD) - \varepsilon_j(AD) , \qquad (4a)$$

and

$$\delta_j^B = \varepsilon_j(CD) - \varepsilon_j(BD) , \qquad (4b)$$

where $\varepsilon_j(CD)$, $\varepsilon_j(AD)$, and $\varepsilon_j(BD)$ are, respectively, the average bonding or antibonding energies of the semiconductors CD, AD, and BD. For substance CD, this is defined as

$$\varepsilon_j(CD) = \frac{1}{4} \int E D_j^{CD}(E)dE , \qquad (5)$$

where $D_j^{CD}(E)$ is the state density for substance CD for states of type j. The quantities $\varepsilon_j(AD)$ and $\varepsilon_j(BD)$, are similarly defined.

In order to evaluate the Brillouin-zone sums which are necessary to compute the state densities which enter Eqs. (3) and (5), we have used a technique developed originally by Lehmann and Taut[11] and later modified by Hjalmarson.[12] Once these are obtained, the self-energies $\sigma_b(E)$ and $\sigma_a(E)$ can be easily calculated by iterating Eq. (2) to self-consistency, utilizing standard techniques. Once the self-energies are obtained, essentially any properties of the alloy under consideration, such as state densities and band structures, can be obtained by using standard techniques.[5]

Two final points on the implementation of the above formalism should be made. First, it should be pointed out that before one solves Eqs. (2)–(5), it is necessary to shift all energies, which for compound semiconductors are usually referred to a zero at the valence-band maximum, to the vacuum scale.[6,13] Following Chen and Sher,[6,13] we define this scale using experimental photothresholds.[14] Second, we note that although the calculations presented below utilized the Vogl et al.[7] band structures, the formalism discussed above is independent of any particular choice of band-structure model and can be used with any reasonable choice for the electronic structure of the alloy constituents. However, if one were to use another band-structure model as input into our formalism, quantitative differences in the numerical results would be expected in comparison with those obtained here, reflecting quantitative differences in the band structures.

Here, we present results for the CPA self-energies and state density for GaSb$_{1-x-y}$As$_x$P$_y$ for $x = y = 0.33$ only. Results for this alloy for other compositions, results for other properties, and similar results for other quaternary alloys will be discussed elsewhere.[8] The values of the disorder parameters defined by Eqs. (4) and (5) for the valence and conduction bands are, respectively (letting the reference material CD be GaSb, with $C = $ Sb and $D = $ Ga), $|\delta_b^{As}| = 1.07$ eV, $|\delta_b^P| = 1.21$ eV, $|\delta_a^{As}| = 0.42$ eV, and $|\delta_a^P| = 0.69$ eV. The sizes of these parameters in comparison with those of the corresponding bonding and antibonding disorder parameters for the ternary alloy GaAs$_{1-x}$P$_x$ (Ref. 15) ($|\delta_b| = 0.14$ eV and $|\delta_a| = 0.28$ eV) indicate that the presence of the semiconductor GaSb in the quaternary alloy GaSb$_{1-x-y}$As$_x$P$_y$ produces large alloy disorder effects in comparison with those present in the GaAs$_{1-x}$P$_x$ alloy. This type of effect on alloying GaP and GaSb has been noted elsewhere.[15]
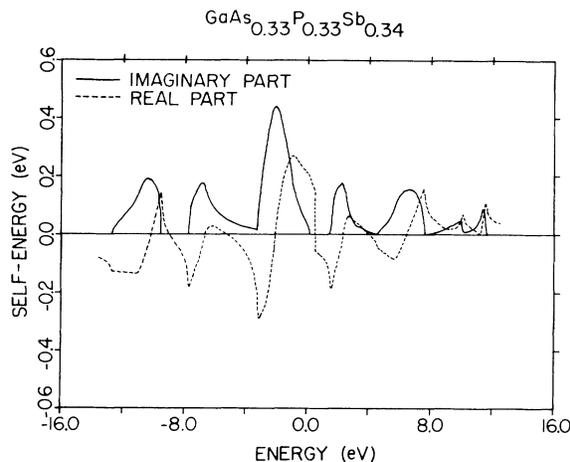
GaAs$_{0.33}$P$_{0.33}$Sb$_{0.34}$

FIG. 1. The real (dashed curve) and negative of the imaginary (solid curve) parts of the CPA self-energy as a function of energy relative to the top of the VCA valence band for GaSb$_{0.34}$As$_{0.33}$P$_{0.33}$.

GaAs$_{0.33}$P$_{0.33}$Sb$_{0.34}$

FIG. 2. The CPA (dashed curve) and VCA (solid curve) density of states as a function of energy relative to the top of the VCA valence band for the alloy GaSb$_{0.34}$As$_{0.33}$P$_{0.33}$.

The origin of large disorder effects for alloys containing GaSb is traceable to the large differences in the s- and the p-orbital atomic energies of P and Sb and of As and Sb which were used by Vogl et al.[7] to partially determine the tight-binding parameters for GaP, GaAs, and GaSb. We note that such effects should not be unique to CPA calculations which utilize the Vogl et al.[7] band structures, but should also occur if other semiempirical schemes which are partially based on atomic energies are used. For example, Harrison's universal model[16] would also be expected to predict large alloy disorder effects for semiconductor alloys containing GaSb.

In Fig. 1, we plot on the same graph the real part (dashed curve) and the negative of the imaginary part (solid curve) of the CPA self-energy for the alloy GaSb$_{0.34}$As$_{0.33}$P$_{0.33}$ as a function of energy. In that figure, the results are displayed after shifting all energies back to a scale where the top of the VCA valence band is taken as the zero of energy. An examination of Fig. 1 shows clearly that alloy disorder has a significant effect on the electronic properties of GaSb$_{1-x-y}$As$_x$P$_y$. In particular, the magnitude of the maximum values of the CPA self-energies $\sigma_b(E)$ and $\sigma_a(E)$ are of the order of 0.4 and 0.2 eV, respectively. These values are, respectively, approximately 80 and 20 times the corresponding values found by Shen and Myles[15] in CPA calculations using the same band structures for the ternary alloy GaAs$_{0.5}$P$_{0.5}$. The fact that the alloy disorder effects for GaSb$_{0.34}$As$_{0.33}$P$_{0.33}$, as measured by the self-energy, are greatest for the valence band, and are smaller (but still very large) for the conduction band, is consistent with the above analysis of the disorder parameters for this alloy.
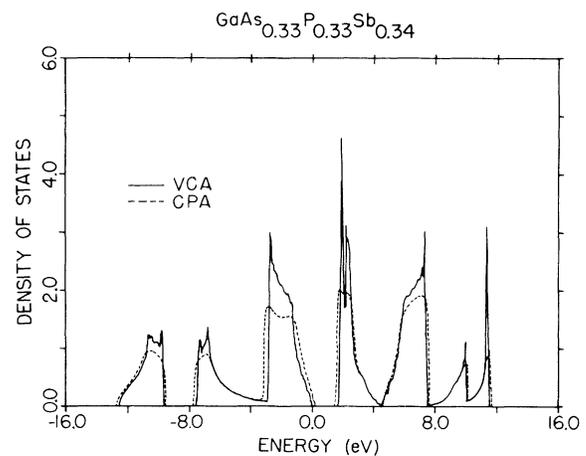
In Fig. 2 we display our results for the CPA state density for GaSb$_{0.34}$As$_{0.33}$P$_{0.33}$ (dashed curve) as a function of energy. In that figure, the results have again been shifted back to an energy scale referenced to the top of the VCA valence band. Also plotted in Fig. 2 for comparison is the state density for the same alloy obtained in the VCA (solid curve). The results just discussed for the self-energies are reconfirmed in Fig. 2 for the density of states. In particular, it can be clearly seen from that figure that the alloy disorder effects accounted for by the CPA have a significant effect on the electronic state density. It is especially noticeable that essentially all of the peaks due to Van Hove singularities, which occur in the VCA state density, are smoothed out in the CPA state density, as is typical of the effects of strong alloy disorder on such peaks.[5]

It is clear from the results presented in Figs. 1 and 2 that alloy disorder effects are extremely important for understanding the electronic properties of GaSb$_{1-x-y}$As$_x$P$_x$. In particular, any analysis of this alloy utilizing the VCA would clearly be inadequate. Unfortunately, to our knowledge, there is no detailed experimental data available for this alloy with which to confirm the predictions we make here. It would be interesting to see the results of experiments on this material which are designed to confirm these predictions. Further details of our generalized CPA formalism and its application to other quaternary semiconductor alloys will be discussed elsewhere.[8]

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