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Band structure of highly mismatched semiconductor alloys: Coherent potential approximation

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The many-impurity Anderson model is applied to compound semiconductor alloys in which metallic anion atoms are partially substituted by highly electronegative atoms at low concentrations. The interaction between the localized states derived from the electronegative atoms and the Bloch states of the semiconductor matrix is treated in a single-site coherent-potential approximation. The solution for the Green's function provides dispersion relations and broadenings for the conduction-band states. The calculations validate the dispersion relations previously obtained from the two-level band anticrossing model. The restructured dispersion relations and optical absorption coefficient are calculated and compared with experimental results of $GaAs_{1-x}N_x$ alloys.

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Over the past several decades, the physics of randomly disordered crystals has been studied extensively. An especially intense effort has been directed towards the understanding of the electronic structure of random semiconductor alloys. One of the simplest treatments of such alloys is based on the virtual crystal approximation (VCA), which is applicable to perfectly random alloys.[1,2] In this approximation, the electronic properties of the alloys are given by the linear interpolation between the properties of the end-point materials. Most of the experimental studies of semiconductor alloy systems have been restricted to the cases where there are only small differences between properties of the end-point semiconductor materials. Such well-matched alloys can be easily synthesized and their properties are close to the VCA predictions. Recent progress in the epitaxial growth techniques has led to successful synthesis of semiconductor alloys composed of materials with distinctly different properties. The properties of these highly mismatched alloys (HMA's) drastically deviate from the linear predictions of the VCA. The most prominent class of HMA's comprises the III-V_{1-x}-N_x alloys, in which electronegative nitrogen substitutes group V anions in standard group III-V compounds. One of the striking effects of nitrogen incorporation into III-V semiconductors is a dramatic reduction in the fundamental band gap. A band-gap reduction of more than 180 meV has been observed in $GaAs_{1-x}N_x$ alloys with only 1% N.[3] Similar effects were observed in $GaP_{1-x}N_x$,[4] $InP_{1-x}N_x$,[5] $GaSb_yAs_{1-x-y}N_x$,[6] and $InSb_{1-x}N_x$ (Ref. 7) alloys.

The energy-band structure of HMA's has been explained in terms of the band anticrossing (BAC) model.[8,9] The model accurately describes the composition and pressure dependencies of the fundamental band gaps of HMA's. Furthermore, it predicted several effects such as a N-induced enhancement of the electron effective mass[10] and an improvement in the donor activation efficiency[11] in $In_yGa_{1-y}As_{1-x}N_x$ alloys, and the change in the nature of the fundamental band gap from indirect to direct in $GaP_{1-x}N_x$.[12] All these predictions have now been confirmed experimentally.

In the BAC model, the restructuring of the conduction band is a result of an anticrossing interaction between highly localized A_1 states of the substitutional N atoms and the extended states of the host semiconductor matrix. The interaction between these two types of states has been treated in the simplest possible manner that does not account for the expected severe level broadening effects. These effects profoundly affect the line shape of the observed optical transitions and they entirely dictate energy dissipative processes such as free-carrier transport.

To address these issues and to put the BAC model on a firmer theoretical base, we have studied the HMA's based on the many-impurity Anderson model that has been widely used to treat the interaction between impurity states and band states. The original Anderson model has been proposed to describe a single impurity atom of a transition metal or a rare-earth element in a nonmagnetic metal.[13] The electron system is separated into a delocalized part of the matrix metal, which is described in terms of the band theory, and a localized level of the *d* shell electrons of the transition-metal impurity atom. A dynamical mixing term is introduced into the Hamiltonian of the system to describe the hybridization between the band states and the localized impurity states. A many-impurity Anderson model has also been developed to describe the electronic properties of semiconductor crystals with low concentrations of deep-level transition-metal impurities.[14,15] In this paper, we use the many-impurity Anderson model to evaluate the interaction between the randomly distributed localized states and the extended states in HMA's. We solve this problem within the single-site coherent-potential approximation (CPA). The calculations reproduce the BAC model results for the restructuring of the conduction band. The imaginary part of the Green's function also yields information on the electronic level broadening that is used to determine the broadening of the optical transitions and to calculate the free-electron mobility.

It has been predicted by Hjalmarson *et al.* that incorporation of isoelectronic impurities into semiconductors gives rise to highly localized levels.[16] The energy of these levels depends on the electronegativity of the substitutional impurity. In the case of highly electronegative impurities substituting metallic anions in compound semiconductors, the energy levels are located close to the conduction-band edge.[16]

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For example, substitutional nitrogen as an isoelectronic impurity in GaAs generates an A_1-symmetry localized level resonant with the conduction band of GaAs at ~0.23 eV above the conduction-band edge. This resonant level has been observed in optical experiments when the level is moved into the GaAs band gap by applying hydrostatic pressure[17] or alloying with GaP.[18]

We describe the electronic structure of HMA's (e.g., $GaAs_{1-x}N_x$) by considering an interaction between the localized and extended states within the many-impurity Anderson model. The total Hamiltonian of the system is the sum of three terms,[14,15]

$$H=\sum_{\mathbf{k}} E^c_{\mathbf{k}} c^+_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{j}} E^d_{\mathbf{j}} d^+_{\mathbf{j}} d_{\mathbf{j}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{j},\mathbf{k}} (e^{i\mathbf{k}\cdot\mathbf{j}} V_{\mathbf{k}j} c^+_{\mathbf{k}} d_{\mathbf{j}} + \text{H.c.}), \tag{1}$$

where the first term is the Hamiltonian of the electrons in the band states with energy dispersion $E^c_{\mathbf{k}}$, and the second term corresponds to the energy of the electron localized on the jth impurity site with energy E^d_j. The third term describes the change in the single-electron energy due to the dynamical mixing between the band states and the localized states. Following Anderson's scheme, the hybridization strength is characterized by the parameter $V_{\mathbf{kj}}$ defined by the following equation,[13]

$$V_{\mathbf{kj}} = \sum_l e^{i\mathbf{k}(\mathbf{l}-\mathbf{j})} \int a^*(\mathbf{r}-\mathbf{l}) H_{\text{HF}}(\mathbf{r}) \varphi_d(\mathbf{r}-\mathbf{j}) d\mathbf{r}, \tag{2}$$

where $a(\mathbf{r}-\mathbf{j})$ and $\varphi_d(\mathbf{r}-\mathbf{j})$ are the Wannier functions belonging to the band and the localized wave function of the impurity on the jth site, respectively. $H_{\text{HF}}(\mathbf{r})$ is the single-electron energy described in the Hartree-Fock approximation.[13]

For the single-impurity case, the Hamiltonian described in Eq. (1) can be solved analytically and the exact solution has been obtained by various methods.[13] The dynamical term presents a profound effect on the electronic structure of the system.[13] In general, we shall consider finite but dilute concentrations of impurities, $0<x\ll 1$. The impurities are assumed to be distributed randomly in space, so that we can carry out a configurational averaging, neglecting correlations between positions of the impurities. In this case, the single-site CPA is adequate for the many-impurity system.[19,20] The CPA treatment leads to the result that,[14,19,20] after the configurational averaging, the average Green's function partially restores the space translational invariance, and **k** resumes its well-defined properties as a good quantum number. In momentum space, the diagonal Green's function in CPA can be written as[14,19,20]

$$G_{\mathbf{kk}}(E) = \left[E - E^c_{\mathbf{k}} - \frac{V^2 x}{E - E^d - i\pi\beta V^2 \rho_0(E^d)} \right]^{-1}. \tag{3}$$

The dispersion relations are determined by the poles of $G_{\mathbf{kk}}(E)$, and the solutions are given by an equivalent two-state-like eigenvalue problem,

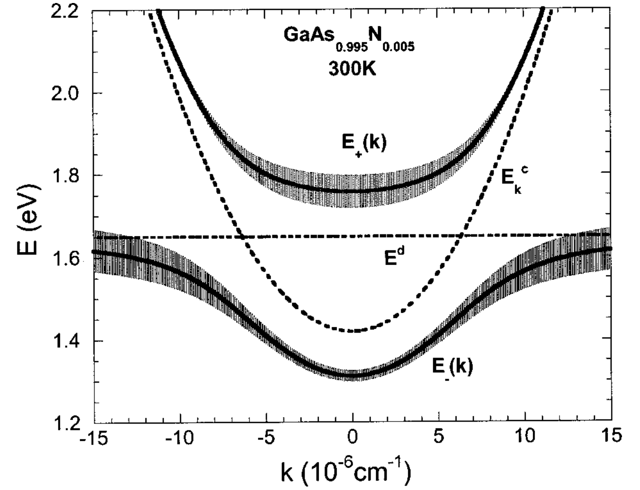

FIG. 1. Conduction-band restructuring according to Eq. (6) for $GaAs_{0.995}N_{0.005}$. The broadening of the dispersion curves of the newly formed subbands illustrates the energy uncertainties defined in Eq. (7). All the energies are referenced to the top of the valence band of GaAs.

$$\begin{vmatrix} E^c_{\mathbf{k}} - E(\mathbf{k}) & V\sqrt{x} \\ V\sqrt{x} & E^d + i\Gamma_d - E(\mathbf{k}) \end{vmatrix} = 0, \tag{4}$$

where $\Gamma_d = \pi\beta V^2 \rho_0(E^d)$ is the broadening of E^d in the single-impurity Anderson model, V is the value of $V_{\mathbf{kj}}$ averaged over **k** and **j**, and ρ_0 is the unperturbed density of states (DOS) of $E^c_{\mathbf{k}}$. In this approximation, the effective contribution of the DOS is represented by the value evaluated at E^d and multiplied by a prefactor β. If $\Gamma_d = 0$, Eq. (4) is reduced to the BAC model[9] with two restructured dispersions for the upper and lower conduction subbands,

$$E_\pm(\mathbf{k}) = \frac{1}{2}\{(E^c_{\mathbf{k}} + E^d) \pm \sqrt{(E^c_{\mathbf{k}} - E^d)^2 + 4V^2 x}\}. \tag{5}$$

If the broadening Γ_d is nonzero but small, so that $2V\sqrt{x} \gg \pi\beta V^2 \rho_0(E^d)$ and $|E^c_{\mathbf{k}} - E^d| \gg \pi\beta V^2 \rho_0(E^d)$, we obtain an approximate analytical solution for Eq. (4),

$$\tilde{E}_\pm(\mathbf{k}) \approx E_\pm(\mathbf{k}) + i\Gamma_d \frac{[E_\pm(\mathbf{k}) - E^c_{\mathbf{k}}]}{[E_\pm(\mathbf{k}) - E^c_{\mathbf{k}}] + [E_\pm(\mathbf{k}) - E^d]} \equiv E_\pm(\mathbf{k}) + i\Gamma_\pm(\mathbf{k}), \tag{6}$$

where the real part $E_\pm(\mathbf{k})$ is defined in Eq. (5). The imaginary part of the dispersion relations defines the hybridization-induced uncertainty of the energy. We note that the imaginary part in Eq. (6) is proportional to the admixture of the localized states to the restructured wave functions in the two-state-like-perturbation picture described by Eq. (4),

$$\Gamma_\pm(k) = |\langle \varphi_d | E_\pm(\mathbf{k}) \rangle|^2 \Gamma_d. \tag{7}$$

As an example, Fig. 1 shows the dispersion relations given by Eq. (5) for $GaAs_{0.995}N_{0.005}$ near the Brillouin-zone center. The broadening of the dispersion relations is given by the

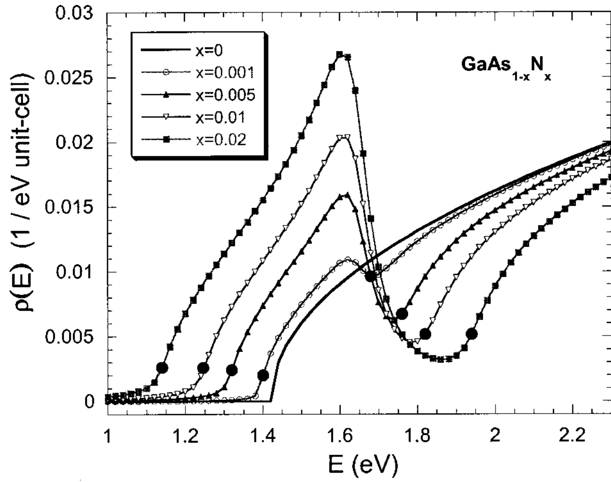

FIG. 2. Density of states of $GaAs_{1-x}N_x$ alloys for a range of values of x as compared with the unperturbed DOS. The two black dots on each curve indicate the energy positions of the E_- and E_+ subband edges.

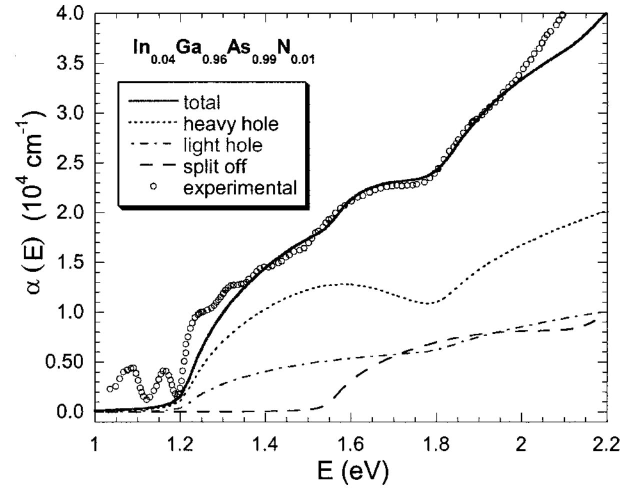

FIG. 3. Calculated optical absorption coefficient in comparison with room-temperature experimental data for freestanding $In_{0.04}Ga_{0.96}As_{0.99}N_{0.01}$. The oscillations below the absorption edge are due to Fabry-Perot interference.

imaginary part of Eq. (6). In the calculation, the hybridization parameter $V=2.7$ eV is taken to be an experimentally determined constant.[9]

The restructured density of states can be calculated from the imaginary part of the Green's function and is given by the expression

$$\rho(E)=\frac{1}{\pi}\mathrm{Im}\sum_{\mathbf{k}} G_{\mathbf{kk}}(E)=\frac{1}{\pi}\int \rho_0(E_{\mathbf{k}}^c)\mathrm{Im}[G_{\mathbf{kk}}(E)]dE_{\mathbf{k}}^c. \tag{8}$$

The integration converges rapidly with $E_{\mathbf{k}}^c$ in a small range that is in proportion to x. The calculated perturbed DOS for $GaAs_{1-x}N_x$ with several small values of x is shown in Fig. 2. Note that the anticrossing interaction leads to a dramatic redistribution of the electronic states in the conduction band. The most striking feature of the DOS curves is the clearly seen gap between E_+ and E_-, which evolves with increasing N content.

In order to illustrate the effect of the state broadening on the optical properties, we consider the spectral dependence of the interband absorption in $In_yGa_{1-y}As_{1-x}N_x$ alloys. The optical absorption coefficient due to the transitions from the valence bands to the restructured conduction bands can be written in the form of the joint DOS summed over the contributions from the heavy-hole, the light-hole, and the spin-orbital split-off valence bands. Assuming parabolic forms for the dispersions of the valence bands near the Brillouin-zone center, we have calculated the optical absorption for $In_{0.04}Ga_{0.96}As_{0.99}N_{0.01}$ for which experimental results are available.[21] The comparison between the calculation and the experimental data is shown in Fig. 3. In the calculation, the only parameter that has been adjusted is the prefactor β used to scale the energy broadening. The best fitting with the experimental data is obtained with $\beta=0.22$. The calculation clearly reproduces the two bumps on the absorption curve, i.e., the one starting at ~1.8 eV due to the onset of the transitions from the heavy-hole and light-hole valence bands to E_+, and the one starting at ~1.5 eV due to the onset of the transition from the split-off valence band to E_-. The more rapid rise of the experimental data at the absorption edge near 1.2 eV is most likely due to the continuum exciton absorption effect, which is not considered in the calculation.

In the Green's-function calculation, the **k** dependence of $V_{\mathbf{kj}}$ is assumed to be weak on the momentum scale we are interested in. In Eq. (2), the parameter $V_{\mathbf{kj}}$ is averaged over the impurity sites and in **k** space. It can be assumed that the Hartree-Fock energy varies slowly in space and can be replaced by a constant. Due to the localized character of both $a(\mathbf{r})$ and $\varphi_d(\mathbf{r})$, the overlap integral in Eq. (2) is essentially zero when $a(\mathbf{r})$ and $\varphi_d(\mathbf{r})$ are located on two sites far apart from each other. In an attempt to model the **k** dependence of $V_{\mathbf{k}}$, we replace the integral in Eq. (2) by an exponentially decaying function, $\sim\exp(-l/l_d)$, and obtain $V_{\mathbf{k}}=V_0/(1+l_d^2k^2)^2$. There is experimental evidence indicating that the values of $V_{\mathbf{k}}$ at the L point in $GaAs_{1-x}N_x$ (Ref. 22) and the X point in $GaP_{1-x}N_x$ (Ref. 23) are about 3–4 times smaller than the $V_{\mathbf{k}}$ at the Γ point. This ratio corresponds to a wave-function decay length of the order of the lattice constant. This result indicates that the off-zone-center conduction-band minima are affected by the anticrossing interaction only when their energies are close to the localized level. This is consistent with recent measurements of the optical properties of $In_yGa_{1-y}As_{1-x}N_x$ alloys, which have shown that alloying with N has only very small effects on the high-energy transitions at large **k** vectors.[24]

In summary, we have applied the many-impurity Anderson model to the electronic structure of highly mismatched semiconductor alloys. The band restructuring and energy broadening effects are investigated within the coherent-potential approximation. The dispersion relations calculated using the coherent-potential approximation reproduce the results of the two-level band anticrossing model.[9] The band restructuring leads to a strongly perturbed DOS for the conduction band. We show that the conduction band restructuring and the energy broadening have to be included to explain the spectral dependence of the absorption coefficient of

$In_yGa_{1-y}As_{1-x}N_x$ alloys. The energy broadening function can also be used to calculate the effects of the hybridization on the transport properties of these highly mismatched alloys.

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