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Intrinsic limits on electron mobility in dilute nitride semiconductors

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A fundamental connection is established between the composition-dependence of the conduction band edge energy and the n-type carrier scattering cross section in the ultradilute limit for semiconductor alloys, imposing general limits on the carrier mobility in such alloys. From the measured nitrogen composition dependence of the bandgap in $GaAs_{1-x}N_x$, the carrier scattering cross section of substitutional nitrogen defects in GaAs is estimated to be 0.3 nm^2. Within an independent scattering approximation, the carrier mobility is then estimated to be $\sim$1000 $cm^2/V\,s$ for a nitrogen atomic concentration of 1%, comparable to the highest measured mobility in high-quality GaInNAs samples at these N concentrations, but substantially higher than that found in many samples. This gives an intrinsic upper bound on the carrier mobility in these materials. [DOI: 10.1063/1.1622444]

There is considerable interest in dilute nitride alloys, both because of their fundamental physical properties and potential device applications. When a small fraction of As atoms in Ga(In)As are replaced by N, the energy gap decreases rapidly; for example, by about 150 meV when 1% of N is added to GaAs.[1] This opens the possibility of 1.3 and 1.5 μm telecommunication lasers based on GaAs,[2] and also of extending the wavelength range of GaAs-based solar cells further into the infrared.[3] There has been substantial progress in understanding many of the properties of dilute nitrides and related alloys. Much of this understanding is based on the band anticrossing model developed by Shan *et al.*,[4] who used hydrostatic pressure techniques to show that the reduction in energy gap can be described by an interaction between the conduction band edge (CBE) and a higher lying set of localized nitrogen resonant states. This, and alternative, models have provided significant insight into these materials,[5–7] but there has been little progress in developing models to describe their transport and mobility properties. Even for idealized random alloy crystals, these properties are difficult to analyze precisely because N introduces such a strong perturbation to the band structure of Ga(In)As. This must lead to strong alloy scattering. There is a well-established model,[8] based on the Born approximation, to describe the relatively weak alloy scattering that occurs in conventional semiconductor alloys. We confirm here that this model is entirely insufficient for extreme alloys such as GaNAs, showing that it underestimates the alloy scattering cross section by over two orders of magnitude. We conclude that the strong scattering due to N atoms substantially limits the electron mobility in dilute nitride alloys, consistent with the maximum mobility observed experimentally of order 1000 $cm^2/V\,s$.[9]

We begin by calculating the scattering cross section for an isolated N impurity in GaAs using S-matrix theory (distorted Born wave approach). This has previously been applied to describe resonant scattering due to conventional impurities in GaAs.[10,11] We derive here a simple general expression for scattering in the ultradilute regime. We show that the scattering rate in this limit is proportional to $|dE_c/dx|^2$, the square of the variation of the CBE energy E_c with alloy composition x. While this result is only strictly valid at very low concentrations, at which each N atom scatters independently, it allows us to extrapolate towards higher N concentrations. We estimate a scattering cross section of order 0.3 nm^2 for an isolated N atom, equivalent to a classical hard sphere scatterer of radius 0.3 nm, and two orders of magnitude larger than the scattering cross section in a conventional alloy.

We use the S-matrix formalism[12] to calculate the elastic scattering cross section. The scattering rate between two ideal crystal states, ϕ_k and $\phi_{k'}$, of equal energy in the ideal crystal, is proportional to the S-matrix element squared, $|S(k,k')|^2=|\langle\psi_k|\Delta V|\phi_{k'}\rangle|^2$, where ΔV is the perturbing impurity potential and ψ_k is the exact eigenstate in the presence of the impurity, with $\psi_k(\mathbf{r})\sim\phi_k(\mathbf{r})$ at points $\mathbf{r}$ very far from the impurity. For low-energy electron scattering, both k and k' are approximately zero. For a sufficiently localized perturbation ΔV (i.e., where the range of the perturbation is less than $2\pi/|k-k'|$), $S(k,k')$ is then independent of k and k' and may be replaced by $S(0,0)$. The total scattering cross section σ for an isolated impurity is then given by

$$\sigma=4\pi\left(\frac{m^*}{2\pi\hbar^2}\right)^2|\langle\psi_0|\Delta V|\phi_0\rangle|^2\Omega^2, \tag{1}$$

where m^* is the electron effective mass at the CBE and Ω is the volume of the region in which the wave functions are normalized. The state ϕ_0 is the Γ-point CB Bloch wave function (in the absence of the N atom) and ψ_0 is the exact CBE state in the presence of the N atom.

We note that the Born approximation is equivalent to setting $\psi_0=\phi_0$ in the required matrix elements. It is often

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used in the discussion of impurity scattering,[8] but is entirely inadequate in the calculation of resonant scattering.[10,11] We will show below for the case of N defect scattering in GaAs, that the Born approximation underestimates the scattering cross section by two orders of magnitude, and that a full calculation of the state ψ_0 is essential.

We use Eq. (1) to derive a general relation between the electron scattering cross section and the initial CBE shift due to alloying. Consider a perfect crystal for which the electron Hamiltonian is H_0 and the CBE state has wave function ϕ_0 and energy E_{c0}. When we introduce a single alloy or impurity atom into a large volume Ω of the otherwise perfect lattice, the new Hamiltonian $H_1 = H_0 + \Delta V$, leads to a modified CBE state ψ_0 with energy E_{c1}. We can therefore rewrite the scattering matrix element as

$$\langle \psi_0 | \Delta V | \phi_0 \rangle = \langle \psi_0 | H_1 - H_0 | \phi_0 \rangle = (E_{c1} - E_{c0}) \langle \psi_0 | \phi_0 \rangle. \tag{2}$$

Because $\langle \psi_0 | \phi_0 \rangle \rightarrow 1$ for sufficiently large Ω, we derive that at low impurity concentrations

$$\Omega \langle \psi_0 | \Delta V | \phi_0 \rangle = \frac{dE_c}{dn}, \tag{3}$$

where E_c is the CBE energy and n is the number of impurities per unit volume. Substituting Eq. (3) in Eq. (1), and noting that n is related to the concentration x by $n = 4x/a_0^3$, where a_0 is the GaAs unit cell dimension, the scattering cross section for an isolated impurity is then given by

$$\sigma = \frac{\pi}{4} \left(\frac{m^*}{2\pi\hbar^2} \right)^2 \left[\frac{dE_c}{dx} \right]^2 a_0^6. \tag{4}$$

We emphasize that this result is completely general for any localized perturbation, whether it be a substitutional impurity or any other kind of defect, and is independent of any details of how the defect is formed. We note a few caveats regarding Eq. (4). Firstly, it assumes that ΔV is localized compared to the typical distances between impurities. Thus, long-range strain fields, which are included in the band-energy shift, may not contribute to the scattering at moderate impurity densities. Secondly, we need to know dE_c/dx and not just the bandgap variation dE_g/dx, in order to apply Eq. (4). We shall see later that neither of these issues is critical when considering scattering in ultradilute nitride alloys.

The two-level, band-anticrossing model describes well the composition dependence of the bandgap in GaN_xAs_{1-x}, with the measured composition dependence of the energy gap given for small x by the lower eigenvalue E_- of the equation

$$\det \begin{pmatrix} E_N - E & \beta x^{1/2} \\ \beta x^{1/2} & E_c - \alpha x - E \end{pmatrix} = 0, \tag{5}$$

where E_c is the bandgap in pure GaAs (=1.42 eV at RT), and $E_N = 1.65$ eV is the energy of an isolated nitrogen resonant defect level.[13] The off-diagonal matrix element $\beta x^{1/2}$ represents the interaction of the CBE with the N resonant defect level, varying as $x^{1/2}$ because the interaction is between localized and extended levels. The experimental variation of energy gap with composition is well fitted by setting $\alpha = -1.45$ eV and $\beta = 2.45$ eV, in good agreement with the magnitude predicted by tight-binding calculations.[7] The derivative of the bandgap with respect to N composition is then given as $x \rightarrow 0$ by

$$\frac{dE_-}{dx} = -\alpha + \frac{\beta^2}{E_c - E_N}. \tag{6}$$

We note that in the Born approximation, $dE_-/dx = -\alpha$, where this term includes the valence band edge contribution to the change in energy gap, as well as the effects of the long-range strain field. For an isolated N defect, the additional, CB-related term $\beta^2/(E_c - E_N)$ is an order of magnitude larger, increasing the scattering cross section by two orders of magnitude. With the parameters given above for Eq. (5), the derivative of the CBE with respect to atomic composition is $dE_-/dx = -24.6$ eV as $x \rightarrow 0$. When substituted into Eq. (4) this gives an electron scattering cross section $\sigma = 0.3$ nm^2 for the isolated N defect in GaAs.

The estimate here was derived explicitly using the two-level model. However, we emphasize that our main conclusion is largely independent of the two-level model. The scattering cross section depends only on dE_-/dx, which has a similar value whether we use the experimentally observed variation or the calculated variation of the CBE energy from empirical pseudopotential[5] or tight-binding calculations.[7]

We now wish to extend the isolated N result of Eq. (4) to the case of a dilute nitride alloy, GaN_xAs_{1-x}. The mean free path l of carriers depends in an independent scattering model on the scattering cross section σ for a single defect and the number of defects n per unit volume as $l^{-1} = n\sigma$. Assuming such a classical model and the values of m^* and dE_c/dx at $x = 0$, we estimate for a N content of 1% a mean free path of only 15 nm. This is still more than an order of magnitude larger than the average N separation, suggesting that an independent scattering model should remain appropriate in the dilute random alloy. The mobility μ is related to the mean free path l as $\mu = e\tau/m^*$, with the scattering time $\tau = l/\overline{u}$, where $\overline{u}$ is the mean electron velocity. Setting $\overline{u}^2 = 3kT/m^*$, we then estimate that the mobility μ is given by

$$\mu^{-1} = \frac{\sqrt{3m^*kT}}{e} \pi \left(\frac{m^*}{2\pi\hbar^2} \right)^2 \left[\frac{dE_c}{dx} \right]^2 a_0^3 x. \tag{7}$$

This is the main result of the present letter and is an estimate of the alloy-scattering-limited mobility in dilute nitride alloys. It includes, via the S-matrix formalism, the strong perturbative effect that each N atom has on the band structure, while assuming that all N atoms scatter independently of each other. Equation (7) predicts that the scattering rate $1/\tau$ at low N composition x, is proportional to $m^{*3/2}$, $(dE_c/dx)^2$, and x. The solid line in Fig. 1 shows the estimated variation of the RT electron mobility with x in GaN_xAs_{1-x}, using the $x = 0$ values of m^* and dE_c/dx. However, both m^* and dE_c/dx vary strongly with N composition, with m^* increasing and dE_c/dx decreasing. The dashed line in Fig. 1 shows the estimated variation of μ when we allow m^* and dE_c/dx to vary with x based on the two-level model of Eq. (5). [The effective mass is calculated by allowing the CBE matrix element in Eq. (5) to vary with k as $E_c - \alpha x + \hbar^2 k^2/2m_c^*$, with m_c^* set equal to the bulk GaAs value. For example, at $x = 0.01$, $m^* = 1.425 m_c^*$ and $dE_c/dx = -10.2$ eV, giving a value for the mobility from Eq. (7) that is 2.4 times larger

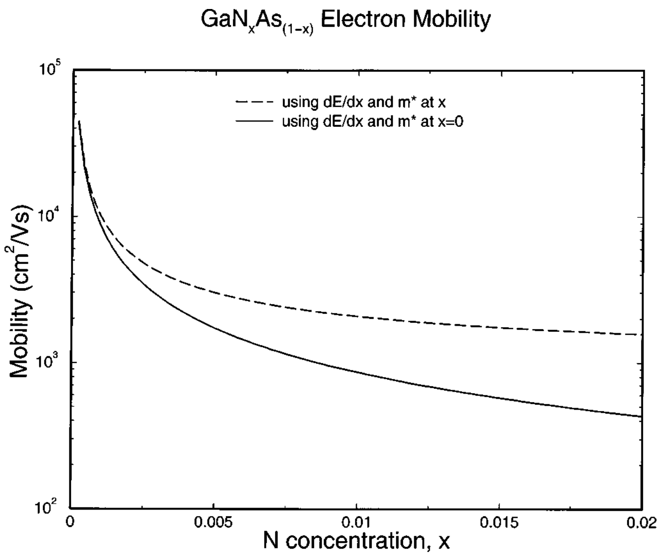

FIG. 1. Variation of alloy-scattering-limited electron mobility in GaN_xAs_{1-x}, calculated assuming GaAs (solid line) and composition-dependent (dashed line) values of m^* and dE_c/dx.

than if we use the $x=0$ values for m^* and dE_c/dx.] Using either approach, the electron mobility is estimated to be of order 1000 $cm^2/V\,s$ when $x=0.01$, of similar magnitude to the highest values observed to date in dilute nitride alloys,[9] but substantially higher than that found in many samples.[3,14–18] We therefore conclude that, in the highest quality samples, random alloy scattering, rather than film quality or other factors, dominates the carrier mobility and is an intrinsic limiting factor in these materials.

The intrinsically low electron mobilities in dilute nitride alloys have significant consequences for potential device applications. The low electron mobility, combined with the short nonradiative lifetimes observed to date, limit the electron diffusion lengths and efficiency achievable in GaInNAs-based solar cells. Further efforts may lead to increased nonradiative lifetimes, but are unlikely to see significant further improvements in the alloy-scattering-limited mobility.[9] The low electron mobility may, however, lead to reduced surface recombination in mesa structures containing GaInNAs quantum wells, of benefit for ultracompact photonic device applications.

Finally, we suggest that significant further insight can be obtained by systematically investigating the transport properties of GaAs:N samples, both in the impurity limit, with nitrogen compositions $\lesssim 10^{19}$ cm^{-3}, and also with increasing x. The separation $E_N - E_c$ between the nitrogen resonant state and the CBE can for instance be modified through the application of hydrostatic pressure. The two-level model, in which the scattering radius is dominated by the term $\beta^2/(E_c - E_N)$, thus predicts a virtual quenching of the mobility in GaAs:N as the N level passes through the CBE. The influence of N–N pairs and other clusters,[5] which may substantially increase resonant carrier scattering at higher N concentrations, can also be explored via pressure measurements, both in the impurity limit and also in dilute nitride alloys. (In the analysis presented here, we have assumed that all nitrogen present in the sample is incorporated in single, unpassivated, substitutional defects.)

In summary, we have used the S-matrix formalism to derive an exact relation between the scattering cross section for low-energy electrons and the derivative of the alloy bandgap in a general system. Applying the method to dilute nitride alloys, we derive a scattering cross section of order 0.3 nm^2 for an isolated substitutional N defect in GaAs. We conclude that the strong bandgap bowing that makes GaInNAs attractive for semiconductor laser and solar cell applications must also intrinsically limit the electron mobility in such systems, and that this limit is close to being achieved experimentally in the best quality GaInNAs samples.

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