Full-band-structure calculation of Shockley–Read–Hall recombination rates in InAs

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We report a calculational procedure to obtain the rate of electron–hole recombination, mediated by the Shockley–Read–Hall (SRH) mechanism. Our method uses a combination of first-principles calculations and accurate empirical band structures. First, we use *ab initio* calculations to identify the point defects, their densities and energy levels in the gap. Then we parametrize the tight-binding interaction between defect and the host atoms in a Green's function approach to obtain the defect levels as identified by the first-principles calculations. Finally, the resulting tight-binding Hamiltonian is used to obtain the dipole matrix element between the conduction and valence band states, mediated through the defect levels in the gap, in second-order perturbation theory. The states are integrated over the entire Brillioun zone, subject to energy and momentum conservation, to obtain the limiting lifetimes of the carriers. This method is applied to study the minority carrier lifetimes in *n*-doped InAs. The calculated effective lifetimes that include Auger and SRH recombinations as functions of temperature agree reasonably well with experiment. Our calculation of lifetimes in 3.5×10^{16} and $2.0\times10^{16}\,\mathrm{cm}^{-3}$ *n*-doped InAs indicate that SRH is dominant at low temperatures and that the lifetimes vary between 10^{-8} and 10^{-7} s. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1381051]

I. INTRODUCTION

Minority carrier lifetimes in semiconductors play a vital role in controlling the efficiency of various classes of devices. Most common recombinations are mediated by the radiative process, the Auger process, and the Shockley–Read–Hall (SRH) mechanism. The radiative process, in which an electron and a hole recombine to release energy equal to (or greater than) the band gap E_g, dominates in large gap materials as the rate varies as E_g^4, whereas the rate of recombination by the other two processes decreases exponentially with the band gap. In small band gap material such as InAs and HgCdTe, recombination by Auger and SRH processes are considered important. The Auger process involves two majority carriers and a minority carrier and becomes dominant at high temperature and in heavily doped material. The SRH mechanism, in which electron–hole recombination is mediated by defect levels in the gap, is believed to be important at low temperature.

Since the pioneering work of Hall[1] and Shockley and Read,[2] the effect of the SRH mechanism on the electron lifetimes has been studied intensely both theoretically[3–5] and experimentally in InAs,[6–11] HgCdTe,[12–15] and other semiconductors.[16–20] There are still some unresolved issues. The SRH rate depends crucially on the defect density, the defect energy levels in the gap, and the electron and hole scattering cross sections. So far, these parameters have been adjusted, in combination with Auger and radiative lifetimes, to explain observed lifetimes. While this approach can sometimes be useful in studying trends,[12–15] the parametrization can lead to contradicting conclusions on the relative importance of various recombination mechanisms.[7–9]

This article describes a method for calculating the parameters needed to evaluate SRH lifetimes. We use a combination of first-principles calculations to evaluate defect densities and their energy level and an accurate empirical band structure to calculate the defects-mediated radiative recombination scattering rates. The calculated minority carrier lifetimes, limited by both Auger and SRH mechanisms, in *n*-doped InAs are compared with experiment.

II. THE METHOD

A. SRH lifetime

When the excess carrier density is small, SRH recombination lifetime has been shown[1,2] to be

$$\tau_p=\frac{\tau_{p0}(n_0+n_1+n_tf_1)+\tau_{n0}(p_0+p_1)}{n_0+p_0+n_tf_1f_2},$$
$$\tau_n=\frac{\tau_{p0}(n_0+n_1)+\tau_{n0}(p_0+p_1+n_tg_1)}{n_0+p_0+n_tg_1g_2}, \tag{1}$$

where τ_{p0} and τ_{n0} are the limiting hole and electron lifetimes, respectively, in highly *n*-doped and *p*-doped samples. These fundamental lifetimes depend on the defect density, n_t, in the sample. n_0 and p_0 are the equilibrium electron and hole densities, given by

$$n_0=\int f(E)\rho_c(E)dE,$$
$$p_0=\int [1-f(E)]\rho_v(E)dE,$$
$$f(E)=[1+e^{\beta(E-E_f)}]^{-1}, \tag{2}$$

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$$\beta = \frac{1}{k_B T},$$

where E_f is the equilibrium Fermi level and $\rho_{c(v)}$ is the density of conduction (valance) band states. The parameters n_1, p_1, f_1, f_2, g_1, and g_2 in Eq. (1) are given by

$$n_1 = n_0 e^{\beta(E_t - E_f)}, \quad p_1 = p_0 e^{-\beta(E_t - E_f)},$$
$$f_1 = (1 + n_0/n_1)^{-1}, \quad f_2 = (1 + n_1/n_0)^{-1}, \tag{3}$$
$$g_1 = (1 + p_0/p_1)^{-1}, \quad g_2 = (1 + p_1/p_0)^{-1}.$$

We see that from Eqs. (1)–(3) the SRH lifetimes can be calculated in terms of four parameters, τ_{p0}, τ_{n0}, n_t, and E_t. In the literature, all efforts to estimate SRH lifetimes involve adjusting these four parameters to yield a good fit to the experiment. The following sections describe a method for calculating the parameters n_t and E_t from first-principles and from the known processing conditions and the parameters τ_{p0} and τ_{n0} from defect state assisted recombination rates.

B. Calculation of n_t and E_t

We recently[21] applied *ab initio* methods to calculate the equilibrium native point-defect densities in InAs as functions of constituent partial pressure and temperature. The neutral and excited state energies for native point defects in InAs were calculated by using the full-potential linearized muffin-tin orbital method within the local density approximation (LDA). The calculations include gradient corrections to the LDA so that the vapor pressure of the arsenic monomer could be used to compare the results with experiment. The calculation of n_t proceeds in two steps. First, we calculate the formation energies (also known as enthalpies) of various point defects: In and As vacancy, In and As antisite, and In and As interstitials. Then, we calculate the temperature-dependent vibrational free energies using a valence force-field model. The entropy of formation of these defects calculated in the presence of vapor at a pressure, P, and temperature, T, is then combined with enthalpies to get free energy. The values of n_t are obtained by minimizing the free energy for the known P-T diagram.

The defect levels in the gap are also obtained from first-principles calculations. All excited state energies are partitioned into ground state (or neutral) contribution and a sum of one-electron excitations. E_t is obtained from the difference in energies corresponding to charged and neutral states. In this one-electron picture, the donor and acceptor levels are assumed to track the conduction and valance bands, respectively, for all temperatures.

C. Calculation of τ_{n0} and τ_{p0}

The fundamental lifetime of a single electron (hole) in highly p-type (n-type) material depends on n_t and E_t. We calculate these lifetimes from the scattering rate for electron–hole recombination mediated by defect states. The rate calculated in a second-order perturbation theory requires knowledge of the wave functions in the conduction band (CB), valance band (VB), and at the defects. While the wave functions in the bands are easily obtained from tight-binding (TB) band structures, the wave function at the defect states needs to be evaluated in detail. In our model, we assume that, in the presence of point defects, the site energy (also called term values) and the first neighbor interactions are affected. Then the perturbing potential in the vicinity of the defect, located at site 0, is written as

$$\Delta V = V_{00} + \sum_{i=1}^{4} (V_{0i} + V_{i0}), \tag{4}$$

where the subscript i runs over the sites near-neighbor to the defect site. In the TB formulation with sp^3 local orbital basis, the inter-and intra-atomic potentials are 4×4 matrices and can be written in terms of a finite number of interatomic parameters.[22] It can be shown that the full wave function, ψ, at the defect energy E_t, will satisfy the equation

$$[1 - G_0(E_t)\Delta V]\psi(E_t) = 0, \tag{5}$$

where G_0 is the unperturbed Green's function (GF). When ΔV as given in Eq. (5) takes the local form, both G_0 and ΔV can be cast as 20×20 matrices. The interatomic parameters are systematically varied so that one of the eigenvalues of the matrix $(1 - G_0\Delta V)$ is zero at a chosen E_t. The corresponding eigenvector yields a set of expansion coefficients required for the calculation of the defect state wave function. Once the wave functions are obtained, the dipole interaction mediated rate of electron transfer from an initial and final state is calculated from Fermi's golden rule.

The transition rate from the initial state $|c\rangle$ (in CB) to a defect state $|d\rangle$ and that from $|d\rangle$ to $|v\rangle$ are calculated from Fermi's golden rule as

$$R_{cd}(\mathbf{k}) = R_0 M_{cd}^2,$$
$$R_{dv}(\mathbf{k}) = R_0 M_{dv}^2,$$
$$M_{cd}^2 = \left[\sum_{j=1}^{3} |\langle \psi_d | p_j | \psi_c(\mathbf{k})\rangle|^2\right] \frac{1}{|\nabla_{\mathbf{k}} E_{\mathbf{k}}^c|(E_{\mathbf{k}}^c - E_t)}, \tag{6}$$
$$M_{dv}^2 = \left[\sum_{j=1}^{3} |\langle \psi_v(\mathbf{k}) | p_j | \psi_d\rangle|^2\right] \frac{1}{|\nabla_{\mathbf{k}} E_{\mathbf{k}}^v|(E_t - E_{\mathbf{k}}^v)},$$
$$R_0 = \left[\frac{2\pi e}{m_0}\right]^2 \frac{2\hbar n_t}{3}.$$

First let us consider the case of an electron in heavily p-doped material. The lifetime of this electron (τ_{n0}) is the sum of transition time from CB to defect state (τ_{n1}) and that from defect state to the VB state (τ_{n2}). For the known probability that a given $\mathbf{k}$ in the CB is occupied and the defect state at energy E_t is empty, τ_{n1} and τ_{n2} can be written as

$$\tau_{n1} = \frac{\Sigma_{\mathbf{k}} f_c(\mathbf{k}) R_{cd}(\mathbf{k})[1 - f_d(E_t)]}{\Sigma_{\mathbf{k}} f_c(\mathbf{k})},$$
$$\tau_{n2} = \sum_{\mathbf{k}} R_{dv}(\mathbf{k}), \tag{7}$$
$$\tau_{n0} = \tau_{n1} + \tau_{n2}.$$

Similarly we can get the expressions for the case of a single hole in heavily p-doped material as

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TABLE I. Native point defect density (n_t) and defect energy level (E_t) in InAs at room temperature. We assumed perfect quench of the defects from equilibration at the melt temperature of 1215 K with a monomeric arsenic partial pressure of 10^{-7} atm. E_c and E_v are energies at conduction and valance band edges, respectively.

Defect	n_t (cm^{-3})	E_t (eV)
V_{In}	0.72×10^{13}	E_v
V_{As}	0.58×10^{12}	$E_c-0.04$
$\mathrm{As}_{\mathrm{In}}$	0.25×10^{18}	$E_c-0.20$
$\mathrm{In}_{\mathrm{As}}$	0.95×10^{13}	$E_v+0.23$
As_I	0.71×10^{09}	$E_c-0.18$
In_I	0.45×10^{11}	$E_c-0.26$

$$\tau_{p1}=\sum_{\mathbf{k}} R_{cd}(\mathbf{k}),$$

$$\tau_{p2}=\frac{\Sigma_{\mathbf{k}}[1-f_v(\mathbf{k})]R_{dv}(\mathbf{k})f_d(E_t)}{\Sigma_{\mathbf{k}}f_c(\mathbf{k})}, \tag{8}$$

$$\tau_{p0}=\tau_{p1}+\tau_{p2}.$$

The values of τ_{n0} and τ_{p0} in Eqs. (7) and (8) are used Eq. (1) to obtain the SRH-limited minority carrier lifetimes.

III. LIFETIMES IN INAS

The method described in previous sections for calculating the defect densities, defect levels, τ_{n0}, and τ_{p0} is applied to study the SRH-limited minority carrier lifetimes in InAs. First, we calculate densities and energies of a number of points defects: In vacancy (V_{In}), As vacancy (V_{As}), In antisite ($\mathrm{In}_{\mathrm{As}}$), As antisite ($\mathrm{As}_{\mathrm{In}}$), In interstitial ($\mathrm{In}_I$), and As interstitial ($\mathrm{As}_I$). The calculated values of n_t and E_t depend on the processing conditions of the InAs sample. We assume that bulk is grown from its melt at 1215 K. Table I gives the calculated values of n_t and E_t, assuming that the bulk is grown from the melt. Note that the impact on the native defect concentrations is negligible if the doping density of the material is less than the intrinsic carrier concentration at the equilibrium temperature.

Of the defects considered, only In antisite and As antisite were found be dominant. Although the first-principles calculations predict As antisites to be the most dominant defect with energy level at the midgap, we found no TB solution that gave a state in the gap. A solution was possible only when the state is moved into the conduction band. The LDA is well known to underestimate the band gap, and accuracy of the prediction of the energy levels associated with donor state derived from the conduction band is uncertain.[23] One possibility is that donor level associated with As antisite is resonant in the conduction band, and in that case the defect does not contribute to SRH scattering. Hence we consider only the In-antisite defect in the calculation of minority carrier lifetimes. We use the hybrid pseudopotential TB Hamiltonian, which includes all long range interactions.[24] The change in site-term values, bond angle, and bond length distortions in the presence of a defect are included within the TB approximation. Interatomic interaction between the defect and the host neighbor is varied to obtain a zero eigenvalue, Eq. (5), at the predicted defect energy level.

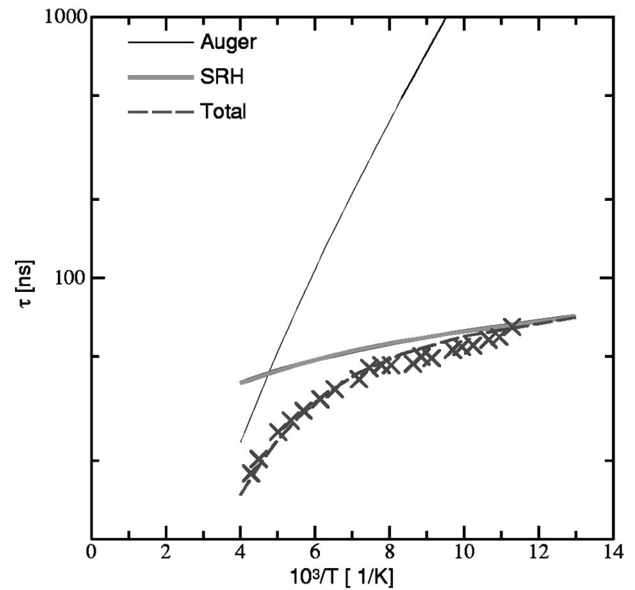

FIG. 1. The calculated Auger (thin solid line), SRH (thick solid line), and the total (dotted line) lifetimes in $3.5\times10^{16}\,\mathrm{cm}^{-3}$ n-doped InAs are compared with experimental (see Ref. 7) values (crosses).

We found that the calculated lifetimes did not depend appreciably on the method chosen to vary the interatomic interactions. When the zero eigenvalue is identified, the real-space wave function at the defect level is obtained. Since the basis atomic orbitals are expanded in plane waves, the calculation of the dipole matrix element, Eq. (6), is tedious, but straightforward. Thus calculated matrix elements are substituted first in Eqs. (7) and (8) and then in Eq. (1). We calculated the lifetimes in $3.5\times10^{16}\,\mathrm{cm}^{-3}$ n-doped InAs as a function of temperature. Full band structures are used in calculating both Fermi energy and lifetimes.

The values of n_t depend critically on the growth conditions. The typical values of In antisite density are 10^{14} to $10^{15}\,\mathrm{cm}^{-3}$. All other defects either have low densities or we speculate that the energy levels are resonant in the conduction band, as in the case of the As antisite, and thus do not contribute to SRH scattering. The limiting lifetimes calculated with these values of n_t and E_t vary in the range of 1–10 ns for electrons and 2–100 ns for holes. When we use the value of 0.23 eV for E_t and $5\times10^{14}\,\mathrm{cm}^{-3}$ for In antisite density, n_t, we obtain τ_{n0} and τ_{p0} to be 2 and 71 ns, respectively. Although the energy difference between defect levels and the bands is small, the calculated radiative recombination lifetimes are very small owing to the relaxation of momentum conservation condition in the presence of defects.

Figures 1 and 2 plot the SRH lifetimes calculated with these values of parameters and compare them with published experimental values in 3.5×10^{16} and $2.0\times10^{16}\,\mathrm{cm}^{-3}$ doped InAs respectively.[7] We see that the calculated values are consistently higher than the observed values. Noting that recombination through the Auger process will also play a role, we performed the full band-structure calculation of Auger limited lifetime[25] in InAs, as shown (thin line) in Figs. 1 and 2. As expected, the Auger rate is more important at higher tem-

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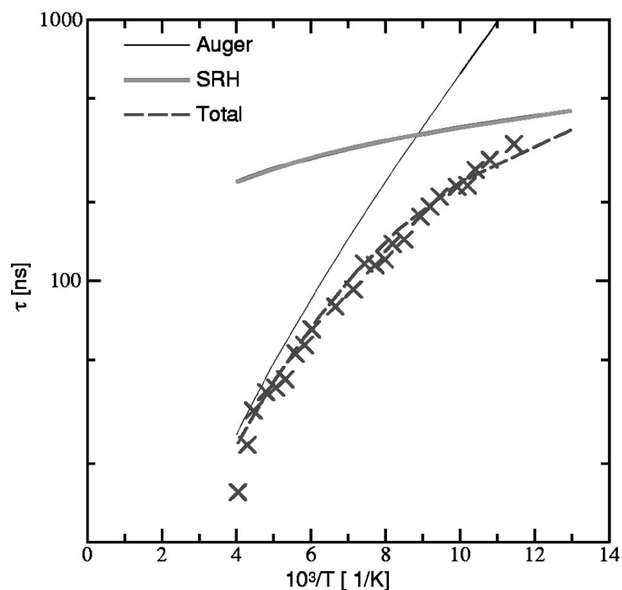

FIG. 2. The calculated Auger (thin solid line), SRH (thick solid line), and the total (dotted line) lifetimes in $2.0\times10^{16}\,\mathrm{cm}^{-3}$ n-doped InAs are compared with experimental (see Ref. 7) values (crosses).

peratures, owing to larger carrier densities. We see that the resultant lifetime, $(\tau_{\mathrm{SRH}}^{-1}+\tau_{\mathrm{AR}}^{-1})^{-1}$ (shown by a dotted line) agrees well with experiment. We see that near perfect agreement could be achieved with the choice of n_t within the range predicted by the first-principles calculations. For more accurate comparison, reliable information about bulk growth conditions is required.

The results clearly shows that the lifetime in InAs samples is limited by defects at low temperatures. Since the growth conditions can be changed to lower In antisites by an order of magnitude,[21] this offers the possibility of considerably longer lifetimes in InAs. When the defect density is very low, the lifetimes will be limited by the Auger recombination process.

IV. CONCLUSIONS

We have developed a method for calculating the defect-state-assisted electron–hole radiative recombination lifetime in semiconductors. Using the defect densities and energy levels obtained from first-principles calculation, we calculated the SRH-limited minority carrier lifetimes in n-doped InAs. The calculated values of n_t, E_t, τ_{p0}, and τ_{n0} are within the range required to explain the observed lifetimes in InAs. We find that SRH is dominant at low temperatures. Although this apparent agreement could be fortuitous in the absence of any information about the processing conditions of the samples used in this experiment, the method developed here offers a nearly parameter-free approach to quantifying the SRH mechanism. For accurate comparison and prediction, reliable information about pressure and temperature during the bulk growth is essential.

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