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First-Principles Calculation of Alloy Scattering in Ge_xSi_{1-x}

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First-principles electronic structure methods are used to find the rates of intravalley and intervalley n-type carrier scattering due to alloy disorder in $Si_{1-x}Ge_x$ alloys. The required alloy scattering matrix elements are calculated from the energy splitting of nearly degenerate Bloch states which arises when one average host atom is replaced by a Ge or Si atom in supercells containing up to 128 atoms. Scattering parameters for all relevant Δ and L intravalley and intervalley alloy scattering are calculated. Atomic relaxation is found to have a substantial effect on the scattering parameters. f-type intervalley scattering between Δ valleys is found to be comparable to other scattering channels. The n-type carrier mobility, calculated from the scattering rate using the Boltzmann transport equation in the relaxation time approximation, is in excellent agreement with experiments on bulk, unstrained alloys.

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Alloying is widely used as a method of engineering the electronic, mechanical, and optical properties of semiconductors. $Si_{1-x}Ge_x$ alloys, in particular, are of increasing importance in strained heterostructure devices, where carrier mobility is a key physical property [1]. The theory of carrier scattering in alloys has been qualitatively understood since the early work of Nordheim [2], expressing all quantities phenomenologically in terms of matrix elements for scattering of Bloch states by the constituent atoms of the alloy. Extensive work since that time greatly increased our understanding of the role of disorder scattering and led to well-developed formal methods for the calculation of scattering rates [notably, the coherent potential approximation (CPA)] in terms of the scattering by individual alloy constituents [3,4]. By and large, these developments have treated the interaction of individual atoms with the carrier states on a phenomenological basis. However, the determination of the relevant matrix elements from experimentally measured quantities proves difficult in a number of important cases. In particular, the role of alloy disorder in intravalley and intervalley scattering for $Si_{1-x}Ge_x$ alloys has not been well determined.

Calculations relating the band structure and the transport properties of $Si_{x-1}Ge_x$ alloys have so far been performed with empirical methods [5–8], where the effects of inelastic phonon and elastic alloy scattering have been considered. Alloy intervalley scattering has been either deemed negligible [5] or calculated together with intravalley scattering from the difference of the conduction band energies of Si and Ge [6,8–11]. The relative strength of intravalley and intervalley scattering is of particular importance in understanding mobility in strained $Si_{1-x}Ge_x$ alloys.

In this Letter, we calculate for the first time the scattering matrix elements due to alloy disorder, using first-principles electronic structure methods. We demonstrate how standard supercell methods, of a type similar to those used in studying the properties of point defects, can be used to extract the relevant scattering matrix elements from the single-particle wave functions and energies. The methods developed are applicable to a wide range of semiconductor alloys. We apply this approach to random $Si_{1-x}Ge_x$ alloys and calculate the individual matrix elements for intravalley Δ and L scattering, for f- and g-type Δ intervalley scattering, and for L intravalley and intervalley scattering. We then calculate the n-type carrier scattering rate and use the Boltzmann transport equation, in the relaxation time approximation, to calculate the carrier mobility. We find excellent agreement with the measured mobility in bulk, unstrained alloys. Notably, the strength of f-type intervalley scattering is found to be comparable to g-type scattering—an important correction to previous phenomenological models, which assumed f-type alloy scattering to be negligible [5]—and both are comparable to intravalley scattering. L intervalley scattering is found to be much stronger than L intravalley scattering.

The scattering rate for carriers of valley α due to alloy disorder in the random binary substitutional alloy is given by

$$R_A^\alpha(E) = \frac{2\pi}{\hbar} x(1-x)\frac{a_0^3}{8}\sum_\beta |\langle V_{\alpha\beta}\rangle|^2 \rho^\beta(E), \qquad (1)$$

where x is the Ge content, a_0 is the cubic lattice constant, β labels the valley into which scattering occurs, $\rho^\beta(E)$ is the density of states per spin in the final valley β at the carrier energy E, and the scattering matrix

$$\begin{aligned}\langle V_{\alpha\beta}\rangle &= \langle V_{\alpha\beta}^{\mathrm{Ge}}\rangle - \langle V_{\alpha\beta}^{\mathrm{Si}}\rangle \\ &= N\langle\psi_\alpha|\Delta V^{\mathrm{Ge}}|\phi_\beta\rangle - N\langle\psi_\alpha|\Delta V^{\mathrm{Si}}|\phi_\beta\rangle. \qquad (2)\end{aligned}$$

In Eq. (2), ΔV^A is the perturbing potential caused by the substitution of one atom in the periodic host by a type-A atom, ψ is the Bloch state of the periodic host lattice, and ϕ is the exact eigenstate in the presence of the perturbing

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potential, with the boundary condition $\phi_k(\vec{r}) = \psi_k(\vec{r})$, when $\vec{r}$ is far from the type-A atom. The wave functions ψ and ϕ are normalized in a (very large) region, containing N host atoms. Both intravalley ($\beta = \alpha$) and intervalley ($\beta \neq \alpha$) terms are included in the total scattering rate. We assume that the scattering matrix element is independent of $\mathbf{k}$ and $\mathbf{k}'$, where $\mathbf{k}$ is the initial Bloch state wave vector near the α valley band edge and $\mathbf{k}'$ is the final state wave vector near the β valley band edge. We also assume that each atom scatters independently of others, an approximation that can be verified directly in our calculations (see below). Finally, no preferential ordering or clustering of Si or Ge in the alloy is included; i.e., we assume a truly random substitutional alloy.

The periodic host is represented in the virtual crystal approximation (VCA), taking the ionic potential at each atomic site to be $V_x^{\mathrm{VCA}} = (1-x)V^{\mathrm{Si}} + xV^{\mathrm{Ge}}$. (We calculate the CPA correction to the VCA band dispersion, below, and verify that it is small [12].) The potential ΔV^A (with A = Si or Ge) is found by placing one A-type atom as a substitutional defect in a supercell of $N-1$ VCA host atoms. Structural relaxation around the defect atom and the supercell single-particle electronic states $|\phi\rangle$ are calculated in density functional theory (DFT).

Two technical complications arise in finding the appropriate matrix element $\langle\psi_\alpha|\Delta V|\phi_\beta\rangle$ from a finite supercell. (a) The zero of the potential is arbitrary in a supercell, and a physically well-defined way must be developed to compare the potential in the supercell with N host atoms and that with one type-A atom and $N-1$ host atoms. (b) The A-type defect breaks the translational symmetry of the host, mixing band states which are degenerate or nearly degenerate in the host supercell. Thus, no eigenstate of the Hamiltonian satisfies the boundary condition $\phi_\beta(\vec{r}) = \psi_\beta(\vec{r})$ for r far from the impurity atom; we must define which linear combination of the nearly degenerate energy eigenstates $|\phi_i\rangle$ corresponds to the state $|\phi_\beta\rangle$.

To compare the potentials in different supercells, we take the average of the local DFT potential over points in the supercell far from the type-A atom and compare with the same average in the periodic host. The difference in these averages gives the required reference shift in the potentials and allows us to compare potentials and energy eigenvalues obtained in the two supercells. For supercells with greater than 16 atoms, we can choose the distance from the type-A atom to be sufficiently large that the average difference in potentials is well-defined. We define the state $|\phi_\beta\rangle$ as that linear combination of the M nearly degenerate states $|\phi_i\rangle$ (with energies E_i, $i = 1, M$) which has maximum overlap with the Bloch state $|\psi_\beta\rangle$ (with energy $E_0 \approx E_i$ in the periodic host). Then

$$|\phi_\beta\rangle = \sum_{i=1}^{M} |\phi_i\rangle\langle\phi_i|\psi_\beta\rangle, \tag{3}$$

and the scattering matrix elements are

$$\langle\psi_\alpha|\Delta V|\phi_\beta\rangle = \langle\psi_\alpha|dV^{\mathrm{red}}|\psi_\beta\rangle, \tag{4}$$

where the "reduced Hamiltonian" is given by

$$dV^{\mathrm{red}} = \sum_{i=1}^{M} dE_i|\phi_i\rangle\langle\phi_i|, \tag{5}$$

with $dE_i = E_i - E_0$ [13].

Depending on alloy composition, the conduction band minimum in $Si_{1-x}Ge_x$ is either at the L point or the Δ point, $\mathbf{k} = (2\pi/a_0)(\xi, 0, 0)$, with $\xi = 0.83$. If the alloy contains less than 85% Ge, the conduction band minimum is at the Δ valley; otherwise, it is at the L valley. Near Ge content $x \simeq 0.85$, scattering between the nearly degenerate Δ and L valleys becomes important. The Δ band has 6 equivalent valleys in the [001], [00$\bar{1}$], [010], [0$\bar{1}$0], [100], and [$\bar{1}$00] crystallographic directions, while the L band has 4 equivalent valleys along the [111], [$\bar{1}$11], [1$\bar{1}$1], and [$\overline{11}$1] directions. Two distinct parameters characterize Δ intervalley scattering: [001] $\rightarrow$ [00$\bar{1}$] is g-type and [001] $\rightarrow$ [100] is f-type.

Total energy calculations are performed with the ABINIT code [14,15]. We use the local density approximation for exchange and correlation. Hartwigsen-Goedecker-Hutter pseudopotentials [16] were used for all DFT calculations. The supercell used to calculate the scattering rate must be sufficiently large to contain important structural relaxation of the host around the substitutional Si or Ge atom. Moreover, we use periodic boundary conditions on the supercell single-particle wave functions, which limits the Bloch state wave vectors considered. The scattering matrices dV^{red} between degenerate Bloch states were calculated in supercells of sizes N = 16, 54, 64, and 128 atoms, as shown in Table I. The k-point grids used for Brillouin zone integration are also given in Table I. Results were well converged with respect to plane-wave expansions at an energy cutoff of 18 hartree. Changes in scattering parameters $\langle V_{\alpha\beta}\rangle$ from the 16-atom to the 64-atom supercell were minor and further changes to the 128-atom supercell negligible. The scattering amplitudes at the minimum of the

TABLE I. Details of the supercells used for the calculation of scattering parameters, giving the number N of atoms in the supercell, the k-point grid dimensions for Brillouin zone (BZ) integrations, and the sets of degenerate k points for which the scattering matrix dV^{red} are calculated. The Δ points are $(2\pi/a_0)(\xi, 0, 0)$.

N	BZ grid	dV^{red}
16	$4\times4\times4$	X, L
54	$2\times2\times2$	Δ ($\xi = \frac{2}{3}, \frac{4}{3}$)
64	$2\times2\times2$	X, L, Δ ($\xi = \frac{1}{2}$)
128	$2\times2\times2$	X, L, Δ ($\xi = \frac{1}{2}$)

conduction band along the Δ line ($\xi = 0.83$) were calculated by interpolating the amplitudes at different points along the k-space Δ line, namely, at the X point ($\xi = 1$), $\xi = \frac{1}{2}$, $\xi = \frac{2}{3}$, and $\xi = \frac{4}{3}$ (see Fig. 1).

We have calculated the scattering matrices from first principles with the method described above at Ge compositions of $x = 0, 0.25, 0.5, 0.75$, and 1. Results are shown in Table II, interpolated as functions of x. The intravalley scattering elements at the Δ and L valleys are denoted by V_Δ and V_L, respectively. The intervalley g-type scattering matrix element between Δ valleys is denoted by $V_{\Delta g}$, the f-type element by $V_{\Delta f}$. The intervalley element between L valleys is V_{LL} and the interband element between the Δ and L valleys $V_{\Delta L}$.

We note that the matrix elements $\langle V_{\alpha\beta}\rangle$ have only a weak x dependence and, to a first approximation, could be considered as approximately independent of the host lattice. Atomic relaxation near the Si or Ge atom in the supercell is found to have an important effect on the scattering factors; in some cases, the scattering intensity is twice as large as that calculated, keeping all atoms in their ideal diamond lattice positions. Note the comparable magnitudes of the Δ intravalley and intervalley (both f- and g-type) scattering, in contrast to the assumptions of previous, phenomenological models [5]. Note also that intervalley scattering is much larger than intravalley scattering at the L point.

We have verified the assumption that each site contributes independently to the scattering amplitude by calculating the scattering matrix [Eq. (4)] with two nearest-neighbor Ge atoms substituted in a Si host. The sum of the scattering matrices for atom 1 [$V_{\alpha\beta}(1)$] and atom 2 [$V_{\alpha\beta}(2)$] separately is approximately equal to that of the two scattering together [$V_{\alpha\beta}(1+2)$]. The scattering intensity is proportional to $\mathrm{Tr}\{[V_{\alpha\beta}]^2\}$ and we find $\mathrm{Tr}\{[V_{\alpha\beta}(1+2)]^2\} = 0.96\ \mathrm{Tr}\{[V_{\alpha\beta}(1) + V_{\alpha\beta}(2)]^2\}$. In each case, the scattering matrices were calculated for the relaxed atomic positions.

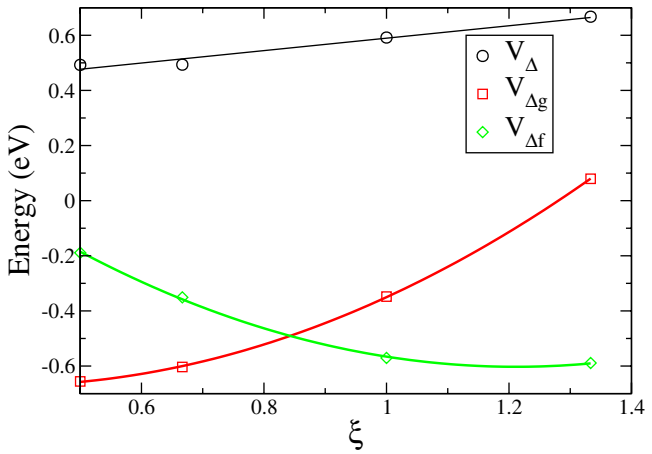


FIG. 1 (color online). The intravalley, intervalley f-type, and intervalley g-type scattering matrix elements between the six equivalent k points, $\mathbf{k} = (2\pi/a_0)(\xi 00)$, etc., as functions of crystallographic momentum ξ along the Δ line in the Brillouin zone, for Ge content $x = 0$.

To calculate the scattering rate, we also need the density of states near the band minima. We use an ellipsoidal approximation for the density of states per spin in valley β at the carrier energy E:

$$\rho^\beta(E) = \frac{\sqrt{m_l^\beta m_t^\beta}\sqrt{E - E_c^\beta}}{\sqrt{2}\pi^2\hbar^3}\Theta(E - E_c^\beta), \qquad (6)$$

where $\Theta(a)$ is a unit step function (0 if $a < 0$, 1 otherwise), E_c^β is the conduction band minimum energy, and m_l^β and m_t^β are the longitudinal and transverse effective masses, respectively, for valley β.

The effective masses m_l and m_t, as functions of the Ge mole fraction, are calculated from the DFT energy bands of the VCA crystal [17]. We use a diamond primitive unit cell, a $10 \times 10 \times 10$ k-point grid (110 k points in the irreducible zone), and a plane-wave energy cutoff of 30 hartree. The effective masses and lattice constants are in excellent agreement with experimental and previously calculated values. To find the conduction band energy differences between the Δ and L band minima more accurately than in the DFT bands, we calculated the energy bands for the VCA crystal using the GW approximation [18–20], which yields the correct $\Delta - L$ splitting in both Si and Ge. This method gives the correct crossover of the bands at $x = 0.85$. Since the GW and DFT single-particle wave functions are very similar [18] and since the change ΔV^A in the potential on substituting atom A into the lattice is dominated by the change in the ionic potential, we expect the matrix element in Eq. (2), calculated in DFT, to be very similar to that for a full GW quasiparticle calculation. Finally, we have added the CPA correction $\Delta E_\alpha^{\mathrm{CPA}} = (1 - x)\langle V_{\alpha\alpha}^{\mathrm{Si}}\rangle + x\langle V_{\alpha\alpha}^{\mathrm{Ge}}\rangle$ to the VCA band energies for the Δ and L minima. The correction $\Delta E^{\mathrm{CPA}} \approx Ax(1 - x)$, where $A = -0.39$ eV for the Δ valley and $A = -0.31$ eV for the L valley. This gives a very small further shift of the crossover where $E_\Delta = E_L$ to $x = 0.87$.

TABLE II. Calculated scattering matrix elements for the intravalley, intervalley, and interband scattering at the Δ and L valleys in $Si_{1-x}Ge_x$ as functions of alloy composition x. All quantities are in eV.

Symbol	Function
V_Δ	$0.1691x^2 - 0.0644x + 0.5418$
$V_{\Delta g}$	$0.0457x - 0.5267$
$V_{\Delta f}$	$-0.0415x - 0.4641$
V_L	$0.1848x^2 - 0.1274x - 0.1918$
V_{LL}	$0.102x - 0.9739$
$V_{\Delta L}$	0.58

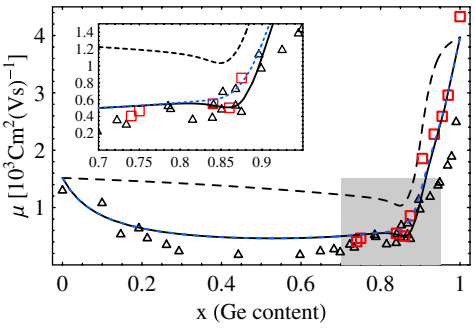


FIG. 2 (color online). Calculated n-type carrier mobility in $Si_{1-x}Ge_x$ at 300 K (solid line), mobility without Δ-L alloy scattering (clear dashed line), phonon limited mobility only (dashed line), and experimental data from Refs. [23] (triangles) and [9,24] (squares).

In order to calculate the mobility from the Boltzmann transport equation, we must also know the phonon scattering rate, which we have calculated following Fischetti and Laux [5], using the deformation potential method. They have calculated the acoustic deformation potentials for pure Si and Ge, using empirical potentials and comparison to experiment, extracted the optical and intervalley deformation potentials and phonon energies from Ref. [21], and then interpolated them in x. We note that our calculated contribution to the mobility from acoustic phonon scattering coincides with that calculated by Herring and Vogt [22].

The calculated alloy scattering rates were used, together with empirical phonon scattering rates from Ref. [5], to calculate the room temperature mobility, shown in Fig. 2 in comparison to experimental measurements [9,23,24]. The agreement is excellent with the measurements of Glicksmann, where they have used single-crystal samples and have corrected for ionized impurity scattering, while our values are somewhat higher than those of Busch and Vogt, indicating the presence of other types of scattering, possibly ionized impurity and grain boundary scattering, since they have used polycrystalline samples. The importance of scattering between the Δ and L band is clear in the region around $x \sim 0.85$ (see inset in Fig. 2), as has been observed before [6,9,23], due to the crossing of the two bands.

In summary, we have presented the first *ab initio* calculation of n-type intravalley and intervalley scattering parameters for $Si_{1-x}Ge_x$ alloys as a function of alloy composition, using supercell methods to numerically represent the alloy scattering problem. We find f-type Δ intervalley scattering and L intervalley scattering to be comparable to other scattering channels, contrary to previous assumptions based on simple phenomenological models. We have used our calculated alloy scattering parameters and previously calculated phonon scattering rates in the Boltzmann transport equation to find the n-type mobility at room temperature. The resulting mobilities are in excellent agreement with experiment, in particular, near the Δ-L band crossing region. The *ab initio* methods developed are broadly applicable to a wide range of semiconductor alloys.

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