

Dopant and defect energetics: Si in GaAs

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We calculate the formation energy of Si donors, acceptors, and defect complexes in GaAs. From these energies we obtain the equilibrium concentrations of native defects and Si-defect complexes as well as the total solubility of Si in GaAs. The calculated equilibrium solubility limit of Si is in good agreement with experiment. The $(\text{Si}_{\text{Ga}}-\text{V}_{\text{Ga}})^{2-}$ complex occurs in relatively high concentrations under As-rich conditions and may therefore mediate Si and Ga diffusion. The donor-vacancy complex is found to be an important mechanism for compensation in heavily doped GaAs.

Interest in the behavior of Si as an impurity in GaAs is centered on the nature of compensation in highly doped material^{1,2} and on the mechanism for Si diffusion.³⁻¹⁰ Diffusion of Si is technologically important since it causes impurity-induced layer disordering of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum-well laser structures.³ Because Si diffusion is mediated by defects and occurs in a temperature regime where an equilibrium population of defects may be assumed, the equilibrium concentrations of Si-induced defects in GaAs are of considerable interest. In this paper we report calculations of the formation energies and concentrations for Si_{Ga}^+ donors, Si_{As}^- acceptors, Si-Si pairs, and the complexes formed by Si with the native defects. The calculations are performed using density-functional theory and the first-principles pseudopotential method. We find that in equilibrium, under As-rich conditions, the compensation of Si_{Ga}^+ donors occurs primarily by incorporating Si_{As}^- acceptors and donor-vacancy complexes $(\text{Si}_{\text{Ga}}-\text{V}_{\text{Ga}})^{2-}$. The calculations predict a high equilibrium concentration of $(\text{Si}_{\text{Ga}}-\text{V}_{\text{Ga}})^{2-}$, and therefore provide theoretical support for the proposal⁶⁻⁸ that the donor-vacancy complex mediates Si diffusion in GaAs in As-rich conditions.

The calculations indicate that in equilibrium Si is an amphoteric dopant in GaAs. That is, Si occupies the Ga and As sites with comparable frequencies with the predominantly occupied site determined by the As and Ga chemical potentials. The calculations predict Si solubilities which are in agreement with experiment and show that for high Si concentrations a significant fraction (more than 10%) of the Si occurs in the form of Si-Si nearest-neighbor pairs.

In previous work we calculated formation energies of the native defects in GaAs as a function of the atomic chemical potentials.¹⁰ We now extend this approach to include dopants and the possibility of dopant-defect complex formation. The defect formation energies depend on the atomic chemical potentials of Si, Ga, and As as well as the electron chemical potential (Fermi energy). The formation energy of a defect or a defect complex may be written as

$$\Omega_D(\mu_e, \mu_{\text{Ga}}, \mu_{\text{As}}, \mu_{\text{Si}}) = E_D + Q_D \mu_e - n_{\text{Ga}} \mu_{\text{Ga}} - n_{\text{As}} \mu_{\text{As}} - n_{\text{Si}} \mu_{\text{Si}}, \quad (1)$$

where E_D is the total energy of a supercell containing one defect in charge state Q_D , μ_e is the electron chemical potential relative to the bulk valence-band maximum, the n 's are the numbers of atoms in the cell, and the μ 's are the corresponding atomic chemical potentials. We make use of the constraint $\mu_{\text{Ga}} + \mu_{\text{As}} = \mu_{\text{GaAs}(\text{bulk})}$, which holds under equilibrium conditions, to write

$$\Omega_D(\mu_e, \Delta\mu, \mu_{\text{Si}}) = E_D' + Q_D \mu_e - \frac{1}{2}(n_{\text{Ga}} - n_{\text{As}}) \Delta\mu - n_{\text{Si}}(\mu_{\text{Si}} - \mu_{\text{Si}(\text{bulk})}), \quad (2)$$

where

$$E_D' = E_D - \frac{1}{2}(n_{\text{Ga}} + n_{\text{As}}) \mu_{\text{GaAs}(\text{bulk})} - \frac{1}{2}(n_{\text{Ga}} - n_{\text{As}}) (\mu_{\text{Ga}(\text{bulk})} - \mu_{\text{As}(\text{bulk})}) - n_{\text{Si}} \mu_{\text{Si}(\text{bulk})},$$

and $\Delta\mu = (\mu_{\text{Ga}} - \mu_{\text{As}}) - (\mu_{\text{Ga}(\text{bulk})} - \mu_{\text{As}(\text{bulk})})$. The chemical potential difference $\Delta\mu$ varies over a range limited by the inequalities $\mu_{\text{Ga}} \leq \mu_{\text{Ga}(\text{bulk})}$ and $\mu_{\text{As}} \leq \mu_{\text{As}(\text{bulk})}$. These constraints together with calculations of the heat of formation¹¹ of GaAs, which is defined as $\Delta H = \mu_{\text{Ga}(\text{bulk})} + \mu_{\text{As}(\text{bulk})} - \mu_{\text{GaAs}(\text{bulk})}$, determine the allowed range of $\Delta\mu$: $-\Delta H \leq \Delta\mu \leq \Delta H$.

The calculation of defect energies is performed within the local-density approximation¹² using scalar-relativistic pseudopotentials^{13,14} and a supercell containing 32 atoms. Kinetic energies up to 8 Ry were included in the expansion of the wave functions in a plane-wave basis.¹⁵ Atomic relaxations around the defect were determined by force calculations.

Formation energies for the native defects were calculated previously¹⁰ and values for E_D' are listed in Table I. The energies of the defects which contain Si atoms are given in Table II. Binding energies and transition levels may also be determined from these results. For example, the binding energy of the Si-Si nearest-neighbor pair is 0.4 eV with respect to isolated Si_{Ga}^+ and Si_{As}^- . We will see below that the pair configuration makes a substantial contribution to the Si solubility limit. The formation energy of the $(\text{Si}_{\text{Ga}}-\text{V}_{\text{Ga}})^{2-}$ donor-vacancy complex drops below 1 eV in As-rich, n -type conditions and may therefore be expected to play an important role both in compensation of Si-doped GaAs and in the diffusion of Si in GaAs. The binding energy predicted for the $(\text{Si}_{\text{Ga}}-$

TABLE I. Calculated formation energies $\Omega(\mu_e, \Delta\mu)$ for native defects in GaAs. The allowed ranges of chemical potentials correspond to $0 < \mu_e < E_g$ and $-\Delta H < \Delta\mu < \Delta H$.

Defect	E'_D (eV)
V_{Ga}^0	4.55 $+\Delta\mu/2$
V_{Ga}^-	4.74 $-\mu_e + \Delta\mu/2$
V_{Ga}^{2-}	4.94 $-2\mu_e + \Delta\mu/2$
V_{Ga}^{3-}	5.26 $-3\mu_e + \Delta\mu/2$
V_{As}^+	2.97 $+\mu_e - \Delta\mu/2$
Ga_{As}^0	2.74 $-\Delta\mu$
Ga_{As}^{1-}	3.29 $-\mu_e - \Delta\mu$
Ga_{As}^{2-}	3.50 $-2\mu_e - \Delta\mu$
As_{Ga}^0	2.50 $+\Delta\mu$
As_{Ga}^{1+}	1.74 $+\mu_e + \Delta\mu$
As_{Ga}^{2+}	0.93 $+2\mu_e + \Delta\mu$
Ga_{i1}^+	2.14 $+\mu_e - \Delta\mu/2$
Ga_{i1}^{2+}	1.59 $+2\mu_e - \Delta\mu/2$
Ga_{i1}^{3+}	1.07 $+3\mu_e - \Delta\mu/2$
Ga_{i2}^+	2.00 $+\mu_e - \Delta\mu/2$
As_{i1}^0	6.14 $+\Delta\mu/2$
As_{i1}^+	5.09 $+\mu_e + \Delta\mu/2$
As_{i1}^{2+}	4.13 $+2\mu_e + \Delta\mu/2$
As_{i1}^{3+}	3.15 $+3\mu_e + \Delta\mu/2$

V_{Ga}^{2-} complex is 0.77 eV and is consistent with simple estimates of the screened Coulomb attraction between Si_{Ga}^+ and V_{Ga}^{3-} at the second-nearest-neighbor separation of 4 Å. Table II also contains the calculated formation energies of the acceptor-antisite complex ($Si_{As}-As_{Ga}$)⁻, the donor-antisite complex ($Si_{Ga}-Ga_{As}$)⁺, and the Chadi-Chang¹⁶ model for the DX^- center (denoted Si_{Ga}^- in Table II). It may be worthwhile to note that the Chadi-Chang structure is 0.21 eV lower in energy than ($Si_{As}-As_{Ga}$)⁻. This latter complex was recently proposed¹⁷ as a competing candidate for DX^- . Under equi-

TABLE II. Calculated formation energies $\Omega(\mu_e, \Delta\mu, \mu_{Si})$ for Si impurities and Si-defect complexes. The ranges of the chemical potentials are $-\Delta H < \Delta\mu < \Delta H$ and $\mu_{Si} < \mu_{Si(bulk)}$. To obtain the formation energies for Si_{Ga}^0 and Si_{As}^0 we use the fact that the (+|0) transition level for Si_{Ga} is approximately equal to the conduction-band minimum ($\mu_e = 1.5$ eV) and that the (0|-) transition level for Si_{As} is approximately equal to the valence-band maximum ($\mu_e = 0$).

Defect	E'_D (eV)
Si_{Ga}^+	0.01 $+\mu_e + \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
Si_{Ga}^-	3.18 $-\mu_e + \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
Si_{As}^-	1.30 $-\mu_e - \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{Ga}-V_{Ga})^{2-}$	4.51 $-2\mu_e + \Delta\mu - (\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{As}-Ga_{i1})^{2+}$	1.94 $+2\mu_e - \Delta\mu - (\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{Ga}-Si_{As})^0$	0.91 $-2(\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{Ga}-Ga_{As})^{1-}$	2.44 $-\mu_e - \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{As}-As_{Ga})^{1+}$	1.69 $+\mu_e + \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
$(Si_{As}-As_{Ga})^{1-}$	3.39 $-\mu_e + \Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
Si_{Ga}^0	1.51 $+\Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$
Si_{As}^0	1.30 $-\Delta\mu/2 - (\mu_{Si} - \mu_{Si(bulk)})$

librium conditions the antisite complexes and Si_{Ga}^- do not play an appreciable role in the self-compensation of Si in GaAs.

In thermodynamic equilibrium, the concentration of a defect D is given by

$$C_D = z_D N_s \exp[-\Omega_D(\mu_e, \Delta\mu, \mu_{Si})/k_B T], \quad (3)$$

where z_D is the number of distinct configurations per sublattice site for a defect complex¹⁸ and $N_s = 2.2 \times 10^{22} \text{ cm}^{-3}$ is the number of sublattice sites per unit volume. For a given $\Delta\mu$ and μ_{Si} the Fermi level μ_e is determined by the requirement of charge neutrality:

$$\sum Q_D C_D - N_{\text{electrons}} + N_{\text{holes}} = 0. \quad (4)$$

This equation may be cast in the form $P(x) = 0$ where P is a polynomial in $x = \exp(\mu_e/k_B T)$. In this work we have considered defects with charge states from -3 to $+3$ and so $P(x)$ is a seventh-degree polynomial. The number of electrons and holes is determined by the effective conduction-band and valence-band densities of states.¹⁹ Of necessity we neglect the temperature dependence of both the defect formation energies and the electronic excitation energies.

From Eqs. (3) and (4) and the calculated defect energies we may obtain defect concentrations as a function of temperature and $\Delta\mu$. As a test of this approach we have calculated the solubility limit of Si as a function of temperature and compared to experimental values in Fig. 1. The maximum concentration of Si, $Si_{\text{max}}(\Delta\mu, T)$, is obtained when the Si chemical potential reaches its maximum value: $\mu_{Si} = \mu_{Si(bulk)}$. $Si_{\text{max}}(\Delta\mu, T)$ turns out to be nearly independent of $\Delta\mu$. This is a consequence of the charge neutrality constraint. For high Si concentrations, changes in $\Delta\mu$ are offset by changes in μ_e so the formation energy of Si_{Ga}^+ remains approximately equal to that of Si_{As}^- . Approximately equal concentrations of donors and acceptors are required to maintain charge neutrality. The solubility limit may be expressed in terms of an Arrhenius equation: $Si_{\text{max}}(T) = 1.1 \times 10^{23} \exp(-0.73 \text{ eV}/k_B T)$. This result may be understood within a simple model in which we neglect all the channels for Si incor-

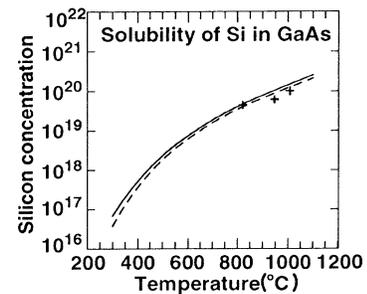


FIG. 1. Solubility limit of Si in GaAs. The solid line is the calculated solubility limit. The dashed line corresponds to the Arrhenius equation $[Si] = P \exp(-Q/k_B T)$, with $P = 1.1 \times 10^{23} \text{ cm}^{-3}$ and $Q = 0.73 \text{ eV}$. Experimental values from Deppe *et al.* (Ref. 7) and Kavanagh *et al.* (Ref. 5) are indicated by crosses.

poration except Si_{Ga}^+ and Si_{As}^- . In this model charge neutrality requires equal numbers of donors and acceptors and hence equal formation energies: $\Omega(\text{Si}_{\text{Ga}}^+) = \Omega(\text{Si}_{\text{As}}^-) = 0.65$ eV. Therefore, this model predicts $\text{Si}_{\text{max}}(T) = 4.4 \times 10^{22} \exp(-0.65 \text{ eV}/k_B T)$ which is close to the result calculated including all channels for Si incorporation. The most important additional channel for Si incorporation is the Si-Si pair: $N_{\text{pairs}}(T) = 8.8 \times 10^{22} \exp(-0.91 \text{ eV}/k_B T)$. Our results for the solubility are in agreement with experimental values,^{4,5,7} which are typically of order 10^{20} cm^{-3} at $T = 1000^\circ\text{C}$.

Figure 2 shows the equilibrium defect concentrations as a function of the Si concentration up to the Si solubility limit. The results shown there are for As-rich conditions and a temperature of 940°C . This is a typical set of conditions under which Si is diffused into GaAs.⁵ At low Si concentrations almost all of the Si occurs in the form of Si_{Ga} donors. However, as the Si concentration increases the number of Si_{As} acceptors increases rapidly until at high concentrations the donors are heavily compensated by Si_{As} acceptors. The Fermi level (Fig. 3) rises as the Si concentration is increased, and this leads to a reduction in the formation energy of the compensating acceptors until a balance is achieved: $\Omega(\text{Si}_{\text{As}}^-) \approx \Omega(\text{Si}_{\text{Ga}}^+)$. For very low Si concentrations the dominant compensating defect is the triply charged Ga vacancy. The concentration of V_{Ga}^{3-} depends on the Si concentration indirectly through the Fermi level. As the Si concentration increases, the Fermi level rises as shown in Fig. 3 and the formation energy of the vacancy is reduced. This reduction in turn leads to an increase in the vacancy concentration. The concentration of the $(\text{Si}_{\text{Ga}}-V_{\text{Ga}})^{2-}$ complex increases rapidly with Si concentration and reaches a value of $5 \times 10^{18} \text{ cm}^{-3}$ at the solubility limit. Because this complex occurs in such high concentrations, and is expected to be very mobile,^{6,7} it should be an important mechanism for the diffusion of Si in GaAs. The Si-Si nearest-neighbor pair concentration increases roughly as the square of the total Si concentration, and makes a substantial contribution (25% in this case) to the solubility limit. However, an isolated Si-Si pair is expect-

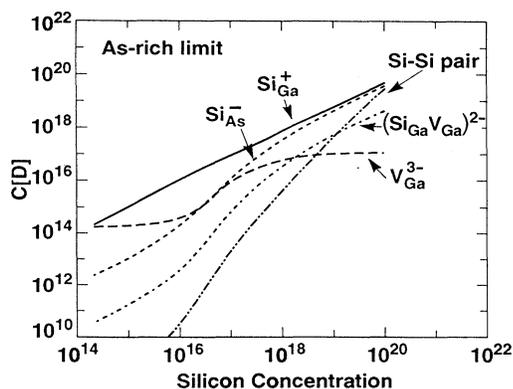


FIG. 2. Concentrations of Si-induced defects in GaAs plotted as a function of the total Si concentration for the As-rich limit ($\Delta\mu = -\Delta H$) and $T = 940^\circ\text{C}$.

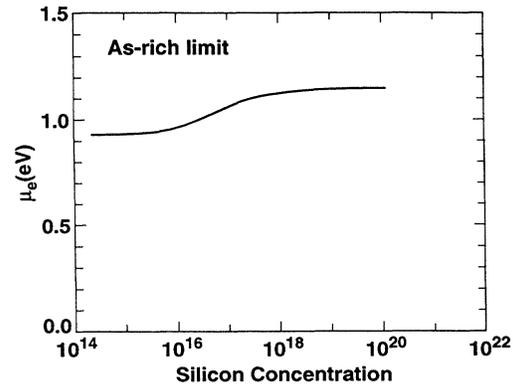


FIG. 3. Position of the electron chemical potential in GaAs as a function of Si concentration for As-rich conditions and $T = 940^\circ\text{C}$.

ed to be relatively immobile; it probably requires the presence of a vacancy to migrate at an appreciable rate.⁴

There are several charge compensation mechanisms which limit n -type doping levels obtainable with Si in GaAs. For As-rich conditions we find (see Table II) that the conversion of Si_{Ga}^+ to Si_{As}^- is exothermic for $\mu_e > 1.17$ eV. Conversion of Si_{Ga}^+ to $(\text{Si}_{\text{Ga}}-V_{\text{Ga}})^{2-}$ is exothermic for $\mu_e > 1.33$ eV, and DX formation, $\text{Si}_{\text{Ga}}^+ \rightarrow \text{Si}_{\text{Ga}}^-$, is exothermic for $\mu_e > 1.58$ eV. Under equilibrium conditions the first two processes would prevent the Fermi level from rising to the conduction-band minimum, $E_{\text{cbm}} = 1.5$ eV. The implication is that room-temperature degenerate doping of GaAs results from the quenching of nonequilibrium concentrations of Si_{Ga} and Si_{As} . In other words, doping is a consequence of kinetic barriers for the reactions $\text{Si}_{\text{Ga}}^+ \rightarrow \text{Si}_{\text{As}}^-$ and $\text{Si}_{\text{Ga}}^+ \rightarrow (\text{Si}_{\text{Ga}}-V_{\text{Ga}})^{2-}$. This is not surprising since both processes require extensive atomic migration. The DX reaction does not require atomic transport, and may be important in limiting the free carrier density under conditions where site switching and vacancy formation are kinetically limited.^{16,21}

Typical molecular-beam epitaxy (MBE) growth conditions for Si-doped GaAs result in heavily compensated n -type material.^{1,2} An open question is the origin of the compensation. Under equilibrium conditions the principal mechanism for the compensation of Si_{Ga}^+ donors is the formation of Si_{As}^- acceptors. However, the defect and dopant concentrations resulting from MBE growth do not necessarily correspond to the bulk equilibrium concentrations. For example, Pashley and Haberer²⁰ have shown experimentally that growth may result in a very high nonequilibrium concentration of Si donors within the depletion region, but that outside the depletion region the material is compensated. They suggested that the compensation occurring outside the depletion region during growth resulted from a site-switching process. For example, one may achieve site switching by the reaction $\text{Ga}_{\text{int}} + \text{Si}_{\text{Ga}} \rightarrow \text{Si}_{\text{As}} + \text{As}_{\text{int}}$. This reaction requires migration of both As and Ga atoms across the depletion region and will occur readily if the surface acts as a source

for Ga interstitials and a sink for the As interstitials. However, when the growth is performed under As-rich conditions, the surface is not an effective source of Ga interstitials or a sink for As interstitials, and so the site exchange reaction may be inhibited. We note, therefore, that compensation may also occur via the generation of V_{Ga}^{3-} , and the subsequent formation of $(\text{Si}_{\text{Ga}}-V_{\text{Ga}})^{2-}$ complexes. The Ga interstitials created concurrently diffuse to the As-rich surface.

In conclusion we have calculated formation energies

for Si-related defects and dopants in GaAs. From these energies we obtain a total Si solubility which agrees with experimental values. The formation energy of the donor-vacancy complex is found to be very low in As-rich conditions. This result provides theoretical support for the proposal that $(\text{Si}_{\text{Ga}}-V_{\text{Ga}})^{2-}$ is the dominant mechanism for diffusion of Si in GaAs.

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