

## Chemical Potential Dependence of Defect Formation Energies in GaAs: Application to Ga Self-Diffusion

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We calculate absolute formation energies of native defects in GaAs. The formation energy and hence the equilibrium concentration of the defects depends strongly on the atomic chemical potentials of As and Ga as well as the electron chemical potential. For example, the Ga vacancy concentration changes by more than 10 orders of magnitude as the chemical potentials of As and Ga vary over the thermodynamically allowed range. This result indicates that the rate of self-diffusion depends strongly on the surface-annealing conditions.

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Defects play a very important role in mediating self-diffusion and the diffusion of substitutional impurities in semiconductors. Although the defect concentration is often determined by kinetics, there are important processes, such as during prolonged anneals at high temperatures, where the concentration is governed primarily by defect formation energies. Thus the formation energies of individual native defects are quantities of central importance. It is known that the formation energy and hence the concentration of charged defects depends on the electron chemical potential [1-4]. More generally, the formation energy is dependent on the chemical potentials of the atomic constituents as well as the electron chemical potential. In this Letter we present first-principles calculations of the absolute formation energies of individual native defects in GaAs as a function of the atomic chemical potentials of As and Ga. The chemical potentials are allowed to vary over a restricted range determined by equilibrium thermodynamics [5]. Experimentally, the atomic chemical potentials can be controlled by annealing the system in a sealed ampoule containing varying amounts of elemental Ga or As.

Our results, together with the requirement of charge neutrality, provide a basis for calculating the equilibrium concentration of defects and allow us to understand the observed strong dependence of self-diffusion rates in GaAs on surface-annealing conditions: With *n*-type dopants self-diffusion is enhanced by As-rich conditions and is suppressed by Ga-rich conditions [6]. Conversely, with *p*-type dopants self-diffusion is enhanced by Ga-rich conditions and is suppressed by As-rich conditions [6]. In *n*-type GaAs, self-diffusion is thought to be mediated by the triply charged Ga vacancy [7]. Our calculations indicate that the concentration of such vacancies can change by ~10 orders of magnitude depending on whether the system reaches equilibrium in As-rich or Ga-rich conditions. Thus the atomic chemical potentials play a crucial role in the theory and phenomenology of defect formation.

Previous theoretical studies due to Baraff and Schluter [1,8] yielded important insight into the defect energetics

in GaAs. These authors focused mainly on the Fermi-level dependence of the defect energies and on the energies of defect reactions; the calculation of absolute formation energies of individual defects was not attempted. More recent calculations of defect formation energies in GaAs by Jansen and Sankey [9] are based on the assumption that the formation energies of neutral Ga and As vacancies are the same. This assumption is equivalent to fixing the Ga and As chemical potentials at unknown values which may or may not be physically allowed.

The formalism we have adopted for the calculation of defect formation energies is similar to that employed in calculations of surface energies [5,10]. In equilibrium the same restrictions on the chemical potentials at the surface apply to defects in the bulk. If the system contains an excess of As, the excess As may form a bulk As precipitate. Consequently, the chemical potential of As may not exceed the chemical potential of bulk As;  $\mu_{\text{As}} \leq \mu_{\text{As}(\text{bulk})}$ . Similarly, the chemical potential of Ga may not exceed that of bulk Ga;  $\mu_{\text{Ga}} \leq \mu_{\text{Ga}(\text{bulk})}$ . In addition, the sum of the As and Ga chemical potentials is required to equal the chemical potential (per pair) of bulk GaAs;  $\mu_{\text{Ga}} + \mu_{\text{As}} = \mu_{\text{GaAs}}$ . These conditions limit the difference in chemical potentials,  $\mu_{\text{Ga}} - \mu_{\text{As}}$ , to a range determined by the heat of formation of bulk GaAs from elemental As and Ga.

The formation energy  $\Omega$  of a defect may be written as

$$\Omega = E_D - n_e \mu_e - n_{\text{Ga}} \mu_{\text{Ga}} - n_{\text{As}} \mu_{\text{As}}, \quad (1)$$

where  $E_D$  is the energy of a supercell containing  $n_{\text{Ga}}$  Ga atoms,  $n_{\text{As}}$  As atoms, and one defect.  $n_e$  is the number of electrons transferred from an electron reservoir with a chemical potential  $\mu_e$  to the defect for a given charge state. By defining

$$\Delta\mu = (\mu_{\text{Ga}} - \mu_{\text{As}}) - (\mu_{\text{Ga}(\text{bulk})} - \mu_{\text{As}(\text{bulk})}),$$

Eq. (1) may be rewritten as

$$\Omega = E'_D - n_e \mu_e - \frac{1}{2} (n_{\text{Ga}} - n_{\text{As}}) \Delta\mu, \quad (2)$$

where  $E'_D$  is independent of  $\Delta\mu$  and  $\mu_e$ . For a perfect

crystal  $E_D^0=0$ , and the formation energy vanishes. The restrictions on the chemical potentials are

$$0 \leq \mu_e \leq E_g \text{ and } -\Delta H \leq \Delta\mu \leq \Delta H,$$

where  $E_g$  is the energy gap, and  $\Delta H = -(\mu_{\text{GaAs}} - \mu_{\text{Ga(bulk)}} - \mu_{\text{As(bulk)}})$  is the heat of formation of GaAs [11]. In our calculations we have neglected the temperature dependence of  $E_D^0$ ,  $E_g$ , and  $\Delta H$ . We recognize, however, that this dependence may be important in obtaining accurate defect concentrations for high temperatures.

The calculation of the defect energy ( $E_D$ ) employed the local-density approximation [12], scalar-relativistic pseudopotentials [13,14], and a supercell containing 32 atoms. Plane waves with kinetic energies up to 8 Ry were included in the expansion of the wave functions [15]. The atomic relaxations associated with the defect were determined by force calculations, and the associated relaxation energies can be substantial ( $\sim 0.8$  eV). While  $\Omega$  varies typically by several eV over the allowed range of  $\mu_e$  and  $\Delta\mu$ , the error in  $\Omega$  is not expected to be larger than  $\pm 0.3$  eV.

The thermodynamic transition levels for the defects are shown in Fig. 1. These results are in qualitative agreement with those obtained by Jansen and Sankey [9]. The transition levels for the Ga vacancy are clustered in a rather narrow energy range between 0.19 and 0.32 eV above the valence-band maximum corresponding to a positive correlation energy. The effective Coulomb interaction is not large for  $V_{\text{Ga}}^{3-}$  because the added electrons are distributed over the four spatially separated As dangling bonds. For the Ga interstitial, formation of the  $3+$

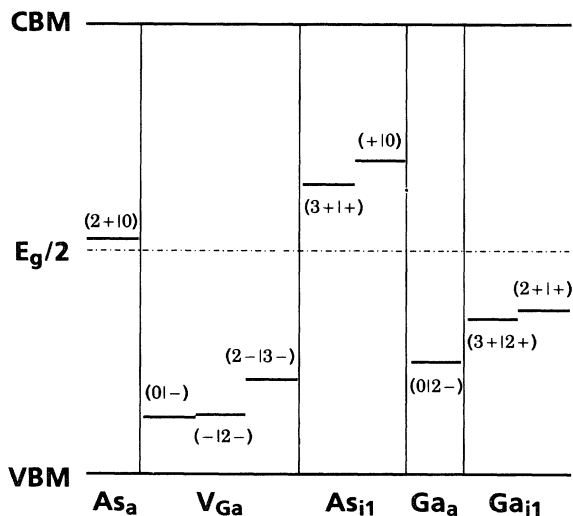


FIG. 1. Thermodynamic transition energy levels for native defects having levels in the gap.  $V$  denotes vacancies. The subscripts  $a$  and  $i$  are used for antisites and interstitials, respectively, and the subscript 1 (2) labels interstitials with four As (Ga) nearest neighbors.  $V_{\text{As}}$  and  $Ga_{i2}$  are singly positively charged defects for all values of  $\mu_e$ .

charge state requires that electrons are removed from an orbital which has weight not only on the interstitial but also in four neighboring As-Ga bonding regions. The positive charge is therefore distributed over an extended volume and this reduces the effective correlation energy.

Figure 2 shows the defect formation energy  $\Omega$  as a function of  $\Delta\mu$  for three characteristic values of the electron chemical potential. The formation energies of the defects can be changed significantly depending on whether  $\Delta\mu = -\Delta H$  (As-rich limit) or  $\Delta\mu = \Delta H$  (Ga-rich limit). For example, when  $\mu_e$  is at the conduction-band minimum the formation energy of the Ga vacancy is in-

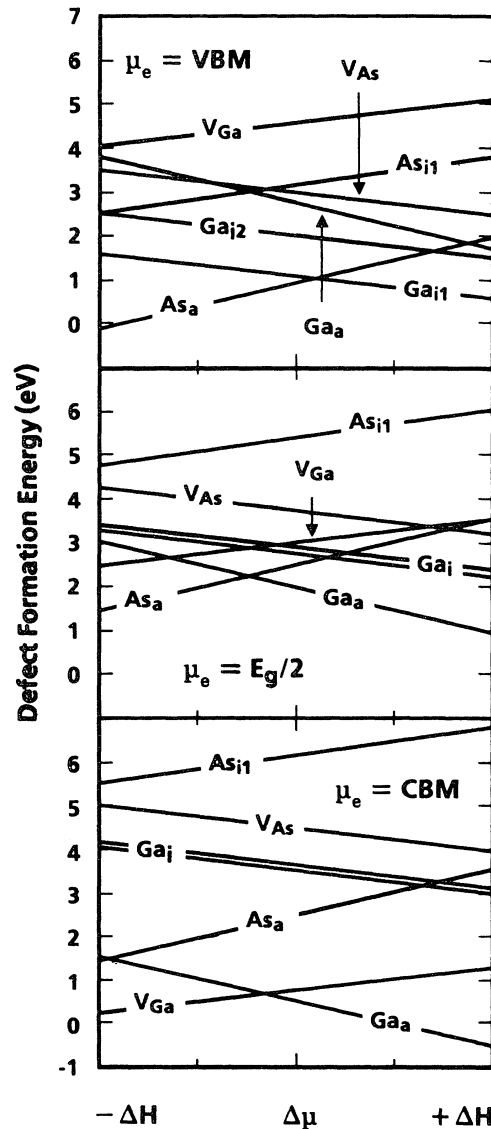


FIG. 2. Defect formation energies as a function of  $\Delta\mu$  are shown for three different  $\mu_e$ .  $\Delta\mu$  varies from the As-rich limit ( $-\Delta H$ ) to the Ga-rich limit ( $\Delta H$ ). The charge state of the defects depends upon  $\mu_e$  and can be determined from Fig. 1.

creased from 0.25 eV in the As-rich limit to over 1 eV in the Ga-rich limit. In certain extreme conditions the *charged* Ga and As antisite defects have negative formation energies. However, such extreme values for  $\Delta\mu$  and  $\mu_e$  cannot be obtained simultaneously because of charge neutrality requirements. Over the whole range of allowed  $\Delta\mu$ , the energies for the As vacancies and interstitials remain high.

The equilibrium concentration  $C_i$  of a defect is  $N_s \exp(-\Omega_i/\tau)$ , where  $\tau = k_B T$  and  $N_s$  is the concentration of sublattice sites ( $2.2 \times 10^{22}/\text{cm}^3$  for GaAs). Given  $\Delta\mu$ ,  $\mu_e$ , and  $T$  we may calculate the defect concentrations. However,  $\mu_e$  itself depends on the defect concentrations and the effective doping level through the requirement of charge neutrality. This consistency requirement renders the concentration of the dominant defect much less sensitive to uncertainties in the formation energies than might otherwise be anticipated. Given an effective doping level,  $N_d = N_D^+ - N_A^-$ , where  $N_D^+$  and  $N_A^-$  are the concentrations of ionized donor and acceptor impurities,  $\mu_e$  is determined as a function of  $\Delta\mu$  and the temperature. Specifically,

$$\sum n_e C_i + N_c \exp[-(E_g - \mu_e)/\tau] - N_v \exp(-\mu_e/\tau) = N_d \quad (3)$$

The three terms on the left are, respectively, the sum of defect charge densities, the electron concentration, and the hole concentration.  $N_c$  and  $N_v$  are the effective conduction-band and valence-band density of states [16]. The usage of Boltzmann rather than Fermi-Dirac statistics in Eq. (3) is adequate to determine the defect concentrations for the doping levels and temperatures considered here. Shown in Fig. 3 is the calculated dependence of  $\mu_e$  on  $\Delta\mu$  at  $T = 580^\circ\text{C}$  for three different doping levels:  $N_d = 10^{18}/\text{cm}^3$  (excess of donors),  $N_d = 0$  (impurity compensated or undoped), and  $N_d = -10^{18}/\text{cm}^3$  (excess of acceptors). The variations in  $\mu_e$  as a function

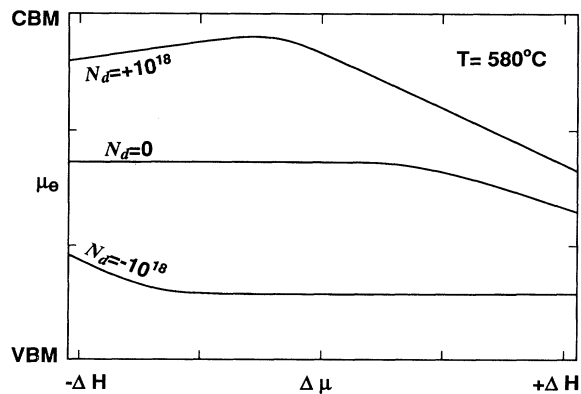


FIG. 3. The electron chemical potential  $\mu_e$  is shown as a function of  $\Delta\mu$  for three different doping levels for a temperature of  $580^\circ\text{C}$ . The structure in these curves results from compensation by the defects.

of  $\Delta\mu$  result from charge compensation by the native defects.

We are now in a position to obtain equilibrium defect concentrations as a function of temperature, doping level, and  $\Delta\mu$ . For example, we may determine the deviation from ideal stoichiometry ( $S$ ) arising from native defects. Thermodynamics places well-defined limits on the equilibrium value of  $S$ . For a given temperature, the most As-rich material will be obtained when  $\Delta\mu = -\Delta H$  and the most Ga-rich material when  $\Delta\mu = \Delta H$ . In equilibrium, the contribution to  $S$  arising from native defect formation in undoped material is very small. For example,  $S_{\text{max}} \sim 10^{16}/\text{cm}^3$  in the Ga-rich limit and  $10^{14}/\text{cm}^3$  in the As-rich limit for a typical molecular-beam-epitaxy growth temperature ( $T = 580^\circ\text{C}$ ). The low values of  $S_{\text{max}}$  are a consequence of two facts: (1) The neutral defects in GaAs are high in energy, and (2) there are no pairs of low-energy charged defects which can compensate each other and both contribute to  $S$  in the same sense. In doped material deviations from stoichiometry occur through the formation of charged defects and  $S_{\text{max}}$  is limited by the effective doping level.

We now turn to the question of the concentration of individual defects. We are specifically interested in the mobile defects (vacancies and interstitials) which mediate self-diffusion. Figure 4 shows the calculated equilibrium concentration of  $V_{\text{Ga}}^{3-}$  in GaAs for an effective doping level of  $10^{18}/\text{cm}^3$  and a temperature of  $827^\circ\text{C}$ . This doping level can be achieved readily by Si diffusion into GaAs [6]. For this doping level we find that  $V_{\text{Ga}}^{3-}$  is the dominant defect in the As-rich limit and that its concentration approaches a limiting value  $\sim \frac{1}{3}$  of the effective doping level. Under these conditions the formation energy of

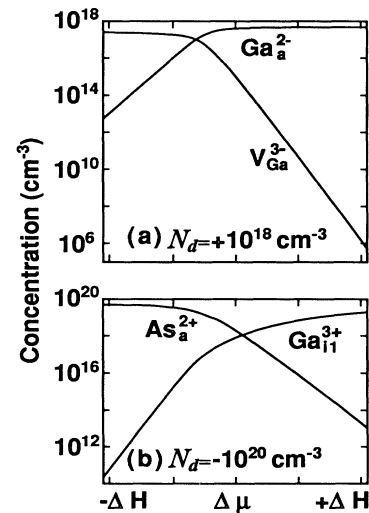


FIG. 4. (a) Concentration of the Ga vacancy and Ga antisite as a function of  $\Delta\mu$  at  $T = 827^\circ\text{C}$  for  $n$ -type doping. (b) Concentration of the Ga interstitial and As antisite under  $p$ -type conditions.

the vacancy is sufficiently low that on the order of one  $V_{\text{Ga}}^{3-}$  is formed for every three electrons introduced by doping. On the other hand, in the Ga-rich limit the relatively immobile  $\text{Ga}_a^{2-}$  is the dominant defect and the concentration of  $V_{\text{Ga}}^{3-}$  is negligible. This result explains why impurity-enhanced diffusion employing  $n$ -type dopants is most effective in As-rich conditions [6,17,18]. The strong dependence of the  $V_{\text{Ga}}^{3-}$  concentration on  $\Delta\mu$  occurs for two reasons: (1) As-rich conditions provide a low-energy sink for the removed Ga atoms; and (2)  $\mu_e$  tends to increase (see Fig. 3) as  $\Delta\mu$  approaches the As-rich limit and this further lowers the formation energy of  $V_{\text{Ga}}^{3-}$ . Experimentally, As-rich conditions are obtained by annealing the GaAs under a high As overpressure. The surface then provides an effective sink for Ga interstitials thus suppressing their equilibrium concentration. This leads, by the law of mass action, to an enhanced concentration of vacancies.

Experimental evidence that self-diffusion in  $n$ -type GaAs occurs via diffusion of  $V_{\text{Ga}}^{3-}$  is the observation that the diffusion rate is proportional to the third power of the free-electron concentration [7]. This dependence is observed over a wide range of doping levels and implies that the Ga vacancy is triply charged even for very low doping levels. Our calculations strongly support this result. Because the  $(2-|3-)$  transition level of the Ga vacancy is well below midgap in our calculations we find that the dominant charge state of the vacancy is  $3-$  even for undoped GaAs.

Self-diffusion in GaAs may also be enhanced by the in-diffusion of group-II  $p$ -type dopants such as Be, Mg, and Zn. Under conditions of heavy  $p$ -type doping ( $N_d = -10^{20}/\text{cm}^3$ ) we find that the  $\text{Ga}_{i1}^{3+}$  is the dominant native defect in Ga-rich conditions (see Fig. 4). This defect has a negligible concentration under As-rich conditions (where the  $\text{As}_a^{2+}$  has the highest concentration). The contribution to Ga self-diffusion arising from interstitials therefore depends strongly on annealing conditions at the surface. This result is in agreement with experiments [6,17]. We find that the charge state of the Ga interstitial depends on the level of  $p$ -type doping. For  $p$ -type doping less than  $10^{17}/\text{cm}^3$  the interstitial occurs predominantly in the singly charged state. Thus the diffusion rate will not necessarily exhibit a simple power-

law dependence on the hole concentration.

In summary, we calculated the formation energies of native defects in GaAs as a function of electronic and atomic chemical potentials over their allowed range. These results indicate that impurity-enhanced self-diffusion in GaAs is mediated by  $V_{\text{Ga}}^{3-}$  under As-rich,  $n$ -type conditions and by  $\text{Ga}_{i1}^{3+}$  under Ga-rich,  $p$ -type conditions.

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