I. INTRODUCTION

Whether a GaAs crystal doped by Si is $n$ type or $p$ type depends on the chemical composition of the crystal, as indicated during crystal growth or annealing by the ambient pressure of the vapor phase As$_4$ which coexists with the crystal. Under As-rich conditions, $n$-type GaAs crystals are obtained, while under Ga-rich conditions at lower temperatures $p$-type crystals are obtained. On the other hand, Si has been used as the main $n$-type dopant in GaAs for which it is well known that the maximally attainable electron concentrations saturate at high Si concentrations, independent of whether Si is introduced during crystal growth or by indiffusion from an external source material. This kind of electrical behavior of Si in GaAs is due to its amphoteric nature: Si can exist in GaAs on both Ga and As sublattice sites. By occupying a Ga sublattice site, a Si atom constitutes a shallow donor while it constitutes a shallow acceptor by occupying an As sublattice site. The amphoteric nature of Si in GaAs, which contains only fundamental constants of the materials. The concentrations of the two ionized Si species are expressed by the concentrations of the appropriate neutral species, as well as the GaAs crystal Fermi level, and hence, the carrier concentration and the band gap energy level positions. The thermal equilibrium concentrations of the two neutral species are expressed by the relevant Gibbs free energies of formation and the As$_4$ vapor phase pressure in the ambient. Using these equations, the long observed relations between the carrier and Si concentrations in different experiments involving both $n$- and $p$-type Si doping produced GaAs are quantitatively explained. A difference of $\sim 1.55$ eV in the effective formation enthalpy between the neutral Si atoms occupying the As and Ga sublattice sites has been identified. Moreover, at high temperatures, the GaAs intrinsic Fermi level energy $E_f$ appears to be higher than the midgap energy $E_g/2$ by $\sim 20–80$ meV. © 1999 American Institute of Physics. [S0021-8979(99)00622-2]
degeneracy factor $g_a$ has a value of four. For Si in GaAs, designate the donor species as $Si_{Ga}^d$ and $Si_{Ga}^{0}$, and the acceptor species as $Si_{As}^a$ and $Si_{As}^{0}$, Eqs. (1) and (2) yield, under thermal equilibrium conditions,
\[ C_{Si_{Ga}^d}^{eq} = \frac{1}{g_d} C_{Si_{Ga}^{0}}^{eq} \frac{n_i}{n} \exp \left( \frac{E_c - E_d}{k_B T} \right), \]
\[ C_{Si_{As}^{0}}^{eq} = \frac{1}{g_a} C_{Si_{As}^{0}}^{eq} \frac{n_i}{p} \exp \left( \frac{E_i - E_v}{k_B T} \right). \]

In obtaining Eq. (3), the relations $E_d \approx E_c$, $n_i = N_e \exp \left( (E_i - E_d)/k_B T \right)$, and $N_e = N_c \exp \left( (E_F - E_c)/k_B T \right)$ have been used. Here $n_i$ is the intrinsic carrier concentration, $n$ is the electron concentration, $N_c$ is the effective density of states of the conduction band, $E_c$ is the conduction band edge position, and $E_d$ is the intrinsic Fermi-level position. In obtaining Eq. (4), the relations $E_a \approx E_v$, $n_i = N_v \exp \left( (E_v - E_a)/k_B T \right)$, and $p = N_v \exp \left( (E_a - E_F)/k_B T \right)$ have been used. Here $p$ is the hole concentration, $N_v$ is the effective valence band density of states, and $E_v$ is the valence band edge position.

It is desirable to express the thermal equilibrium concentrations of the neutral native point defect species and impurity species in GaAs in terms of the involved fundamental physical constants. In this context, there was no satisfactory treatment for a long time in the past. It is only fairly recently that the thermal equilibrium concentrations of the neutral native point defect species in GaAs have been satisfactorily treated using a Gibbs free energy formulation method.17,18 In this article, we follow the same general method to treat the thermal equilibrium concentrations of the neutral Si species in GaAs, $C_{Si_{Ga}^d}^{eq}$ and $C_{Si_{As}^{0}}^{eq}$. At a given temperature, these quantities are defined for the thermal equilibrium coexistence of a GaAs crystal and an unique source material composed of only Si, Ga, and As atoms.

The GaAs phase diagram is shown in Fig. 1(a), wherein the allowed GaAs crystal chemical composition range is greatly exaggerated. Actually this range is so small that measured data are not available at any temperature. In thermal equilibrium coexistence with a GaAs crystal, there are four host-crystal-atom vapor phases: $Ga_1$, $As_1$, $As_2$, and $As_4$. Since all vapor phase materials are in thermal equilibrium among themselves, it is sufficient to consider the role of only one of them, e.g., that of $As_4$.17 The thermal equilibrium pressure values of these four vapor phases are shown in Fig. 1(b), from which it is also seen that, at temperatures sufficiently lower than the GaAs melting point of $T_m = 1238 \, ^\circ C$, the $As_4$ phase pressure $p_{As_4}$ spans a range of orders of magnitude for GaAs crystals with compositions between the allowed As-rich and Ga-rich limits.

In principle, the case of a growing GaAs crystal can be regarded as the case of having a small perturbation occurring to the thermal equilibrium coexistence of a source material and a GaAs crystal which is neither growing nor shrinking. This allows to regard the source material and the GaAs crystal as in thermal equilibrium with the Ga and As vapor phases. Incorporating a $Si_{Ga}^{0}$ atom in the GaAs crystal displaces an As atom from the crystal to the As ambient vapor phases, while the reverse holds for incorporating a $Si_{As}^{0}$ atom in the crystal. Because thermal equilibrium conditions are maintained for Si atoms in the source material and in the GaAs crystal, and for As atoms in the $As_4$ ambient, the GaAs crystal, and the GaAs source material, the equilibrium chemical reactions
\[ Si_{sor} + \frac{1}{2}As_4 \rightleftharpoons Si_{Ga}^{0} + As_{As}, \]
\[ Si_{sor} + As_{As} \rightleftharpoons Si_{As}^{0} + \frac{1}{2}As_4, \]
hold. In Eqs. (5) and (6), $Si_{sor}$ is a Si atom in the source material, and $As_{As}$ is an As atom on an As sublattice site of the GaAs crystal. Reactions (5) and (6) do not apply directly to also charged Si species, since all the involved species are neutral and the role of electrons or holes are not involved.
The Gibbs free energy density of the GaAs crystal containing either the Si$_{As}$ or the Si$_{Ga}$ atoms is written as

$$G_{Si}^{0} = g_{Si}^{0} + C_{As}^{0} g_{As}^{f} + C_{Ga}^{0} g_{Ga}^{f} + C_{Si}^{0} g_{Si}^{f} - T S_{Si}^{0},$$

where $\gamma$ stands for either the As or Ga sublattice site, $g_{Si}^{f}$ is the Gibbs free energy of incorporating a Si atom onto such a site, $g_{Si}^{0}$ is the Gibbs free energy of incorporating an As atom on an As sublattice site, $g_{Si}^{eff}$ is 1/4 of the Gibbs free energy of forming an As$_4$ molecule, $g_{Si}^{eff}$ is the additional Gibbs free energy of an As$_4$ molecule due to its translational thermal motion, and $S_{Si}^{max}$ is the entropy of mixing of the GaAs crystal due to the presence of Si$_{Si}^{0}$ atoms. In writing down Eq. (7), the absolute zero of energy, to which all other energy quantities are referenced, is defined to be that of an As atom existing alone in vacuum. The relative positions of these energies are schematically shown in Fig. 2. The quantity $S_{Si}^{max}$ is given by

$$S_{Si}^{max} = -k_B \ln \left( \frac{C_{o}^{0}}{C_{Si}^{0} \left( C_{o}^{0} - C_{Si}^{0} \right)^{1/4}} \right),$$

where $C_{o}$ is the Ga or As sublattice site density of 2.21 $\times 10^{22}$ cm$^{-3}$. Regarding As$_4$ as an ideal gas, the quantity $g_{As}^{f}$ is given by

$$g_{As}^{f} = -k_B T \ln \left( \frac{B_{As}}{P_{As}} \right),$$

where $P_{As}$ is the ambient As$_4$ vapor pressure, and $B_{As}$ is the associated ideal gas pressure constant given by $B_{As} = \left( 2 \pi m_{As} / h^2 \right)^{3/2} (k_B T)^{5/2}$, with $m_{As}$ being the mass of an As$_4$ molecule and $h$ the Plank constant. The value of $B_{As}$ is $\sim 135.1 T^{5/2}$ atm.$^{17}$

By reaction (5), $\partial C_{As} / \partial C_{Si}^{0} = 1$, and $\partial C_{As} / \partial C_{Si}^{0} = -1/4$, hold for the case of Si$_{Ga}$. Using these conditions and Eqs. (8) and (9), Eq. (7) yields the chemical potential of a Si$_{Ga}^{0}$ atom as

$$\mu_{Si}^{0} = g_{Si}^{0}^{f} + g_{Si}^{eff} + 1/k_B T \ln \frac{P_{As}}{B_{As}} + \mu_{Si}^{eff},$$

where $C_{Si}^{0}$ holds. In thermal equilibrium coexistence with a specific source material, $\mu_{Si}^{0}$ is equal to the source material Si atom chemical potential $\mu_{Si}^{eff}$, which we regarded as constant by assuming that consumption of the source material Si atoms is insignificant. Hence, we obtain

$$\frac{C_{Si}^{eq}}{C_{o}} = \left( \frac{P_{As}}{B_{As}} \right)^{1/4} \exp \left( -\frac{g_{Si}^{eff}}{k_B T} \right),$$

where $g_{Si}^{eff}$ is the effective formation Gibbs free energy of Si$_{Si}^{0}$ Ga given by

$$g_{Si}^{eff} = g_{Si}^{0}^{f} + g_{As}^{eff} - g_{As}^{f} - \mu_{Si}^{eff}.$$

Similarly.

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**TABLE I.** The experimental data of Green$^{a}$ and Brozel$^{a,b}$ the used materials energy constants, and the calculated results based on the present model. All concentration values are in the unit of cm$^{-1}$, and all energies are in the unit of eV.

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<th>X'tal</th>
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<th>$C_{Si}^{eq}$ (10$^{15}$)</th>
<th>$C_{Si}^{eq}$ (10$^{15}$)</th>
<th>$C_{Si}^{eq}$ (10$^{15}$)</th>
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<td>1.6</td>
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</table>

*aSee Ref. 1.

*bSee Ref. 2.
\[
\frac{C_{\text{eq}}}{{C_0}} = \left( \frac{P_{\text{As}4}}{B_{\text{As}4}} \right)^{-1/4} \exp \left( -\frac{g^{\text{eff}}_{\text{As}4}}{k_B T} \right),
\]

where \( g^{\text{eff}}_{\text{As}4} \) is the effective formation Gibbs free energy of \( \text{Si}^{0}_{\text{As}} \) given by

\[
g^{\text{eff}}_{\text{As}4} = g^{f}_{\text{As}4} - g^{f}_{\text{As}_{\text{As}4}} + g^{f}_{\text{As}_{\text{4As}}} - \mu_{\text{As}_{\text{As}4}}.
\]

It is important to note that a source material may be prepared to a given strength with a specific \( \mu_{\text{Si}_{\text{As}}} \) value. The thermal equilibrium concentration expressions of the \( \text{Si}^{0} \) species, Eqs. (11) and (13), apply at a given temperature for a source material with any strength. A special source material, the saturated source, gives rise to the \( \text{Si}^{0} \) solubilities at a given temperature, which we shall denote as \( (C_{\text{eq}}^{\text{Si}^{0}_{\text{Ga}}})^{\text{g}} \) and \( (C_{\text{eq}}^{\text{Si}^{0}_{\text{As}}})^{\text{g}} \).

If the source material strength exceeded that of the saturated source, then in thermal equilibrium \( \text{Si}^{0} \) solubilities will result together with \( \text{Si} \) precipitation in \( \text{GaAs} \).

III. ANALYSIS OF EXPERIMENTAL RESULTS

A. Method of analysis

Using the following procedure, experimental results on total \( \text{Si} \) concentrations together with charge carrier concentrations have been analyzed to obtain quantitative knowledge on the \( \text{Si} \) thermal equilibrium concentrations in \( \text{GaAs} \). First note that, the mass conservation relation

\[
(C_{\text{Si}^{0}_{\text{Ga}}} + C_{\text{Si}^{0}_{\text{As}}}^{\text{eq}}) + (C_{\text{RT}}^{\text{Si}^{0}_{\text{As}}} + C_{\text{RT}}^{\text{Si}^{0}_{\text{As}}}^{\text{eq}}) = C_{\text{Si}}^{\text{eq}}
\]

holds at the experimental temperature. In experiments, the RT carrier concentration \( n^{\text{RT}} \) or \( p^{\text{RT}} \) is measured. Since the shallow donors \( \text{Si}_{\text{Ga}} \) and shallow acceptors \( \text{Si}_{\text{As}} \) are practically all ionized at RT, we have

\[
(C_{\text{Si}^{0}_{\text{Ga}}}^{\text{eq}} + C_{\text{Si}^{0}_{\text{As}}}^{\text{eq}}) - (C_{\text{Si}^{0}_{\text{As}}}^{\text{RT}} + C_{\text{Si}^{0}_{\text{As}}}^{\text{RT}}) = n^{\text{RT}},
\]

where the superscript RT refers to RT values, while the equilibrium quantities are those at the experimental temperature. For cases \( p^{\text{RT}} \) is measured instead, the relation \( n^{\text{RT}}p^{\text{RT}} = (n^{\text{RT}})^{2} \) applies. Equations (15) and (16) yield

\[
C_{\text{Si}^{0}_{\text{Ga}}}^{\text{eq}} + C_{\text{Si}^{0}_{\text{As}}}^{\text{eq}} = \frac{C_{\text{Si}}^{\text{eq}} + n^{\text{RT}}}{2},
\]

\[
C_{\text{Si}^{0}_{\text{As}}}^{\text{eq}} + C_{\text{Si}^{0}_{\text{As}}}^{\text{eq}} = \frac{C_{\text{Si}}^{\text{eq}} - n^{\text{RT}}}{2}.
\]

Moreover, at the experimental temperature, the charge neutrality condition

\[
\frac{n}{n^{\text{RT}}} + C_{\text{Si}_{\text{Ga}}}^{\text{eq}} = n + C_{\text{Si}_{\text{As}}}^{\text{eq}}
\]

holds. In writing down Eq. (19), it is assumed that charge compensation results only from Si distribution on the Ga and As sublattices. There are two kinds of charged point defects which may also participate in the charge compensation process: (i) the deep donor EL2, which is most likely the charged As antisite defect \( \text{As}^{\text{As}_{\text{Ga}}} \); and (ii) the triply-negatively-charged Ga sublattice vacancies \( \text{Ga}^{3}_{\text{Ga}} \), which is a deep acceptor. The effects of \( \text{As}_{\text{Ga}} \) and \( \text{Ga}^{3}_{\text{Ga}} \) are ignored because of their mutual compensation and because of their small concentrations. EL2 may reach a maximum concentra-
tion of $\sim 10^{17}$ cm$^{-3}$, attained only in As-rich GaAs.\textsuperscript{19} This is much smaller than the $C_{Si}^{Ga}$ and $C_{Ga}^{Si}$ concentrations of $\sim 10^{19} - 10^{20}$ cm$^{-3}$ reached in experiments. There is no measured $V_{Ga}^{c}$ concentration values. Under the condition that the maximally attainable n value is a few times of $10^{18}$ cm$^{-3}$ in experiments due to Si doping, one calculated result\textsuperscript{20} indicated that the $V_{Ga}^{c}$ concentration is less than $\sim 10^{17}$ cm$^{-3}$, which is also small.

The set of five equations, Eqs. (3), (4), and (17)–(19) are used to solve for the five unknown experimental temperature quantities $C_{Si}^{eq, Ga}$, $C_{Ga}^{eq, Ga}$, $C_{Si}^{eq, As}$, $C_{Ga}^{eq, As}$, and n or p. To perform the analysis, the needed materials constants are $n_i$, $E_c - E_i$, $E_i - E_x$, $g_{Si}^{eff}$ and $g_{Ga}^{eff}$. The usual $n_i$ values will be used, and all energy quantities will be used as adjustable parameters. The quantities $E_x - E_i$ and $E_i - E_x$ are subjected to two restrictive conditions. First, the used $E_x$ values will be those of Panish and Casey\textsuperscript{21} extrapolated to the appropriate experimental temperatures. Base on experimental data between 0 and 973 K, they have given

$$ E_x \approx 1.52 - 5.8 \times 10^{-4} T^2, $$

where $T$ is in Kelvin. The GaAs band narrows as $T$ increases because of the thermal expansion effect, electron-phonon and electron-hole interactions, etc.\textsuperscript{22,23} Second, the $E_i$ position will be allowed to deviate only slightly from that of $E_x/2$. Here it is assumed that the highly satisfactory RT approximation $E_i \approx E_x/2$ does not hold at high temperatures. However, $E_x$ cannot be too close to either $E_c$ or $E_x$. Among the experimental results, only in one case Si solubility values appear to have been attained.\textsuperscript{3} The other cases are either unclear,\textsuperscript{3,4,8} or the Si thermal equilibrium concentrations reached are below the corresponding solubility values.\textsuperscript{1,2}

Thus, in fitting the experimental results according to Eqs. (11) and (13), the used $g_{Si}^{eff}$ and $g_{Ga}^{eff}$ values for the different cases should not be the same, because the source material Si chemical potentials $\mu_{Si}^{As}$ should not be the same. However, the concentration ratio of the two neutral species is given by

$$ \frac{C_{Si}\left(\frac{Ga}{As}\right)}{C_{Si}^{eq}} = \frac{P_{As}^{1/2}}{B_{As}^{1/2}} \exp \left( \frac{g_{Si}^{eff} - g_{Ga}^{eff}}{k_B T} \right), $$

wherein the quantity $g_{Si}^{eff} - g_{Ga}^{eff}$ is not dependent on $\mu_{Si}^{As}$ and is, hence, independent of the Si concentrations and almost independent of temperature.

In the present formulation of the problem, appropriate Gibbs free energy quantities have been used and in the consequent method of analysis. In practice, only values of enthalpy contributions, i.e., $h_{Si}^{eff}$ and $h_{Ga}^{eff}$, will be obtained in the form of used parameters for fitting the experimental results. These enthalpies constitute close approximations to the corresponding Gibbs free energy quantities. The experimental results are not sufficiently accurate to also warrant an identification of the corresponding entropy values.

### B. Analytical findings from experimental data

The first group of experimental results to be analyzed consists of those obtained by Green\textsuperscript{1} and Brozel et al.\textsuperscript{2} with Si introduced into GaAs crystals during growth at the GaAs melting temperature of $T_m = 1238 \, ^\circ C$ under an As$_4$ pressure of 1 atm. By including different amount of Si in the GaAs melt, P. D. Green\textsuperscript{1} has grown a number of GaAs crystals yielding different $n$ values. The total Si concentration ($C_{Si}$) in these crystals has been physically measured by Brozel et al.\textsuperscript{2} Clearly, these thermal equilibrium Si concentrations were under the appropriate Si solubility value. The measured $n$ values and $C_{Si}$ values are listed in Table I. To analyze

### Table II. The experimental data of Fewster and Willoughby,\textsuperscript{4} the used materials energy constants, and the calculated results based on the present model. All concentration values are in the unit of cm$^{-3}$, and all energies are in the unit of eV.

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<th>$C_{Si}^{eq, As}$ ($10^{15}$)</th>
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\textsuperscript{4}See Ref. 8.
values of $n$, $C_{SiGa}^{eq}$, $C_{Sis}^{eq}$, $C_{SiAs}^{eq}$, and $C_{SiAs}^{eq}$. Figure 3(a) shows the experimental and the calculated electron concentrations at RT, obtained using the averaged $h_{SiAs}^{\text{eff}}$ and $h_{SiGa}^{\text{eff}}$ values of the three crystals listed in Table I. For comparison, the calculated $n$ values at 1273 °C are also shown in Fig. 3(a). From the calculated values it is seen that $n$ values at $T_m$ are larger than the corresponding $n^R_T$ values at smaller total Si concentrations, because the $n_i$ value at $T_m$ is much larger than that at RT. However, at a total Si concentration much larger than the $n_i$ value at $T_m$, $n^R_T$ can become larger than the corresponding high temperature $n$ value, because a sizable portion of Si is neutral at $T_m$ (or at other high temperatures). For these crystals, almost all Si atoms are occupying Ga sublattice sites as donors, see Figs. 3(b) and 3(c) for the calculated neutral, ionized, and total Si concentrations on both sublattices as a function of $C_{Si}$ at $T_m$. Also plotted in Figs. 3(b) and 3(c) are the total Si concentrations on each sublattice deduced by Green, and by Brozel et al.

The second group of experimental results is that of Fewster and Willoughby. The samples are Si-doped $p$-type epitaxial GaAs layers grown using the liquid-phase-epitaxy method under Ga-rich conditions at 700–750 °C. Since no actual As vapor phase pressure value was given, we assume that the As$_4$ pressure values are those at the Ga-rich limit as shown in Fig. 1. The measured $p^R_T$ and $C_{Si}$ values of their samples are listed in Table II, together with the used values of the GaAs energy constants as well as the calculated results. The used $n_i$ value is $2 \times 10^{16}$ cm$^{-3}$. Figure 4(a) shows the calculated hole concentrations at room temperature and at 725 °C, which is the mean experimental temperature. These calculated results are obtained using the averaged $h_{SiAs}^{\text{eff}}$ and $h_{SiGa}^{\text{eff}}$ values of the six crystals. For comparison, the measured $p^R_T$ values of Fewster and Willoughby are also shown in Fig. 4(a). Figures 4(b) and 4(c) show the calculated neutral and ionized Si concentrations on the As and Ga sublattices, respectively, and the experimental data deduced by Fewster and Willoughby. It is seen in Fig. 4(b) that at high temperatures the neutral Si atoms on the As sublattice reached $\sim 10\%$ of the total Si atoms on that sublattice.

The third group of experimental results consists of Si-doped $n$-type GaAs epitaxial layers grown at different temperatures, due to Kung and Spitzer. In these experiments, $n^R_T$ and $C_{Si}$ values were measured, but not the Si concentration on each sublattice. Table III lists the layer growth temperatures and the values of $n^R_T$ and $C_{Si}$, the used materials constants, and the corresponding calculated results. The fittings of $n^R_T$ as functions of $C_{Si}$ are as satisfactory as the previous cases, and will not be further plotted.

Kolm, Kulkin, and Averbach reported that the Si solubility value in GaAs is $2 \times 10^{20}$ cm$^{-3}$ at 1200 °C for $P_{As_4} = 10$ atm, as evidenced by Si precipitation at still higher concentrations. On the other hand, Kung and Spitzer mentioned that the highest achievable $n^R_T$ values are in the range of $4 - 5.5 \times 10^{18}$ cm$^{-3}$ under fairly similar experimental conditions. An analysis has been carried out based on these information, for which four $n^R_T$ values were chosen in the achievable $n^R_T$ value range. The experimental data, the used

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**Figure 4.** Experimental results of Fewster and Willoughby and the calculated fits. (a) Hole concentrations at RT and at 725 °C. (b) Concentrations of neutral and ionized Si species at 725 °C on the As sublattice. (c) Concentrations of neutral and ionized Si species at 725 °C on the Ga sublattice. The averaged $h_{SiAs}^{\text{eff}}$ and $h_{SiGa}^{\text{eff}}$ values of the six crystals listed in Table II have been used.
energy values, and the calculated results, are summarized in Table IV.

IV. DISCUSSION

There exist two previous theoretical efforts addressing the problem of Si concentrations in GaAs. In both cases, effects of the Fermi level and $P_{\text{As}}$ on the ionized Si species occupying both Ga and As sublattices appear to have been given in the correct form. However, in the work of Brebrick the assignment of the concentrations of neutral Si species as independent of $P_{\text{As}}$ is erroneous. Moreover, there is no quantitative calculation of the concentrations of these neutral Si species.

Hurle applied his analysis to the $P_{\text{As}}=1$ atm cases of Green and Brozel et al., and it can be readily extended to cases with other $P_{\text{As}}$ values. He has given concentration expressions of the neutral Si species in terms of the concentrations of the GaAs crystal vacancy species ($V_{\text{Ga}}$ and $V_{\text{As}}$), which are correct in form. It is clear that Hurle considered the exchange reactions

$$\text{Si}_{\text{sc}} + V_{\text{As}} \leftrightarrow \text{Si}_{\text{As}}^0,$$  

$$\text{Si}_{\text{sc}} + V_{\text{Ga}} \leftrightarrow \text{Si}_{\text{Ga}}^0,$$  

respectively for incorporating a neutral Si atom onto an As and a Ga site. Hurle’s expressions of the thermal equilibrium concentrations of the neutral Si species in GaAs contain the thermal equilibrium concentrations of vacancies, or equivalently the formation energies of the vacancies. In our opinion, the usefulness of these expressions is in doubt, for two reasons. First, these expressions would be useful if the vacancy related parameters are known, but they are not. Second, in thermal equilibrium, concentrations of vacancies and

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### Table IV

The experimental data of Kung and Spitzer, a the used materials constants, and the calculated results. All concentration values are in the unit of $10^{18}$ cm$^{-3}$, and all energy constants are in the unit of eV.

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<th>$n RT$</th>
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<th>$n_1$</th>
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<th>$E_i - E_e$ (eV)</th>
<th>$h eff_{\text{Si Ga}}$</th>
<th>$h eff_{\text{Ga Sc}}$</th>
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<td>$4.0 \times 10^{19}$</td>
<td>1.0 $\times 10^{14}$</td>
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<td>0.69</td>
<td>1.23</td>
<td>1.23</td>
<td>1.23</td>
<td>1.23</td>
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</tbody>
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### Table III

The experimental data of Kolm, Kulin, and Averbach a and four chosen values in the saturation $n RT$ data range of $4 - 5.5 \times 10^{17}$ cm$^{-3}$ under $T = 1200^\circ$C and $P_{\text{As}}=10$ atm conditions, as mentioned by Kung and Spitzer. Also listed are the materials energy constants used and the calculated results based on the present model. All concentration values are in the unit of $10^{18}$ cm$^{-3}$, and all energy constants are in the unit of eV.

<table>
<thead>
<tr>
<th>X'tal</th>
<th>$n RT$ (10$^{18}$)</th>
<th>$(C_{\text{Si Ga}}^0)'$ (10$^{18}$)</th>
<th>$E_i$</th>
<th>$E_e - E_i$</th>
<th>$E_i - E_e$</th>
<th>$h eff_{\text{Si Ga}}$</th>
<th>$h eff_{\text{Ga Sc}}$</th>
<th>$h eff_{\text{Si As}}$</th>
<th>$h eff_{\text{Ga Sc}} - h eff_{\text{Si As}}$</th>
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<tr>
<td>1</td>
<td>4.0</td>
<td>2.0</td>
<td>0.812</td>
<td>0.374</td>
<td>0.44</td>
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<td>0.473</td>
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<td>1.50</td>
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<tr>
<td>2</td>
<td>4.5</td>
<td>2.0</td>
<td>0.812</td>
<td>0.374</td>
<td>0.44</td>
<td>1.98</td>
<td>0.471</td>
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<td>5.0</td>
<td>2.0</td>
<td>0.812</td>
<td>0.374</td>
<td>0.44</td>
<td>1.98</td>
<td>0.471</td>
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<td>4</td>
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<td>2.0</td>
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<td>1.981</td>
<td>0.47</td>
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$^4$See Refs. 4 and 7.
Si in GaAs are not directly related, but are both the consequences of the crystal’s effort of minimizing its Gibbs free energy. In principle, the thermal equilibrium concentration of the neutral Ga sublattice vacancies $V_{\text{Ga}}^0$ in GaAs is given by

$$C_{V_{\text{Ga}}}^0 = \left( \frac{P_{\text{As}}}{B_{\text{As}}} \right)^{1/4} \exp \left( \frac{g_{V_{\text{Ga}}}^0}{k_B T} \right),$$

(23)

with

$$g_{V_{\text{Ga}}}^0 = g_{V_{\text{Ga}}}^f + g_{\text{As}}^f - g_{\text{As}}^f,$$

(24)

and two analogous expressions for the neutral As sublattice vacancies $V_{\text{As}}$ in GaAs. In Eq. (24) $g_{V_{\text{Ga}}}^0$ is the standard Gibbs free energy of formation of $V_{\text{Ga}}^0$ which is the Gibbs free energy increase of replacing a Ga atom by a $V_{\text{Ga}}^0$ without considering further the fate of the removed Ga atom. The quantity $g_{V_{\text{Ga}}}^f$ as given by Eq. (23) is a constant, and hence, $C_{V_{\text{Ga}}}^0$ as given by Eq. (23) is also the $V_{\text{Ga}}^0$ solubility value at a given temperature. Equation (23) is identical to Eq. (11) and Eq. (24) is identical to Eq. (12), except for the absence of a term analogous to $\mu_{\text{Si}}^\text{sol}$.

In our expressions of the thermal equilibrium concentrations of the neutral Si species, Eqs. (11) and (13), the involved constants of the materials are $P_{\text{As}}$, $B_{\text{As}}$, as well as $g_{\text{Si}}^0$, $g_{\text{As}}^0$, $g_{\text{As}}^f$, $g_{\text{Si}}^f$, and $\mu_{\text{Si}}^\text{sol}$, with the two latter quantities further given by Eqs. (12) and (14) in terms of the more fundamental constants $g_{\text{Si}}^0$, $g_{\text{As}}^0$, $g_{\text{As}}^f$, $g_{\text{Si}}^f$, and $\mu_{\text{Si}}^\text{sol}$. In our analysis, the value of $P_{\text{As}}$ is that appropriate for the experiment, the value of $B_{\text{As}}$, $\sim 135.17^{50}$ atm is a physical constant based on statistical mechanics, and the other energy quantities are in principle well defined materials constants. In the form of used parameters for obtaining satisfactory fits to experimental results, values of some of these constants are obtained, which constitute meaningful findings.

From Tables I–IV, it is seen that our presently used band gap-related values indicate that $E_i$, is lower than $E_g/2$ by $\sim 20–80$ meV, see also Fig. 5. For the GaAs band gap energy levels, it is well known that at RT the approximation $E_g = E_c - E_v$ is highly satisfactory, but this may not be the case at high temperatures. It appears that the GaAs $E_i$ positions at high temperatures have been estimated.

Because in experiments different Si source strengths are involved, the obtained values of $h_{\text{Si}}^\text{eff}$ and $h_{\text{Si}}^\text{eff}$ in the present study are in principle not constants. However, the $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ value should be a constant independent of the Si concentration and the experimental temperature. These quantities are plotted in Fig. 6 as a function of $C_{\text{Si}}$. It is seen that the scattering of the $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ values is much narrower than those of the values of $h_{\text{Si}}^\text{eff}$ and $h_{\text{Ga}}^\text{eff}$, which is indicative that $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ is a constant. The average value

$$h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff} = 1.55 \pm 0.1 \text{ eV}$$

(25)

fits the $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ data in Fig. 6 well. We have further found that the value of $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ has a practical upper limit of $\sim 1.8$ eV, above which p-type GaAs cannot be obtained at the temperature range of around 700 °C, irrespective of whether the crystal is rich in Ga or in As. It also has a lower limit of $\sim 1.2$ eV, below which only p-type materials can be obtained from Si doping at around 700 °C. Our present finding of $h_{\text{Si}}^\text{eff} - h_{\text{Ga}}^\text{eff}$ of $\sim 1.55$ eV is between these two limiting values.

With the values $h_{\text{As}}^\text{eff} = -3.5$ eV and $h_{\text{As}}^\text{eff} = -2.76$ eV, Eqs. (12) and (14) allow the values of $h_{\text{Si}}^\text{eff} - h_{\text{As}}^\text{eff}$ and $h_{\text{Si}}^\text{eff} - h_{\text{As}}^\text{eff}$ to be deduced from the tabulated $h_{\text{Si}}^\text{eff}$ and $h_{\text{Si}}^\text{eff}$.
values, see Table V. The quantities $h^f_{Si,a} - \mu_{Si_{As}}$ and $h^f_{Si,a} - \mu_{Si_{Ga}}$ are respectively the enthalpy of formation of a neutral Si atom on a Ga and on an As site from a given Si source material without considering the thermal equilibrium requirement among the displaced As atoms in the GaAs crystal and in the $As_4$ vapor phase. It is seen from Table V that, within each group of experiments and in particular for each crystal, the values of $h^f_{Si,a} - \mu_{Si_{As}}$ and $h^f_{Si,a} - \mu_{Si_{Ga}}$ are close (some are nearly identical!), which is indicative of two related points. First, this means that the energy increase in the GaAs crystal due to the incorporation of a neutral Si atom on a Ga site and on an As site is about the same. This energy increase consists of the bond energy increase and a long range elastic energy. Since Ga and As atoms are of about the same size, it is reasonable to expect that the elastic energy increase due to the incorporation of a Si atom on either sublattice site be of the same magnitude. It is also reasonable to expect that the bond energy increases should be about the same for these two cases, discussed as follows. A neutral Si atom on a Ga site possesses an additional electron after forming four bonds with four neighboring As atoms, so that there is one dangling bond associated with this neutral Si atom. On the other hand, a neutral Si atom on an As site lacks one electron to form four covalent bonds with four neighboring Ga atoms so that there is one dangling bond associated with the Ga atoms. It seems reasonable to assume that the bond energies in the two cases will be essentially the same, since in either case the energy is associated with one dangling bond. Second, it follows that, the net effective enthalpies of incorporating neutral Si atoms on Ga and As sites, respectively $h^f_{Si,a} - \mu_{Si_{As}}$, are very different, because the enthalpy values of an As atom in the GaAs crystal or in the $As_4$ ambient are very different. Note also that this enthalpy effect due to the As atoms is balanced by the $As_4$ pressure effect, which results from the entropy associated with the translational motion of the $As_4$ molecules.

V. CONCLUSIONS

In this article, expressions for the thermal equilibrium concentrations of the amphoteric shallow dopant species Si in GaAs have been presented. The thermal equilibrium concentration of each neutral species is determined by the $As_4$ vapor phase pressure in the ambient and by a well defined effective Gibbs free energy of formation. Based on these expressions, the experimentally observed relations between Si concentrations and carrier concentrations are satisfactorily explained on a quantitative basis, for both $n$- and $p$-type Si doped GaAs materials. A difference of $\sim 1.55$ eV in the effective formation enthalpy between the neutral Si atoms occupying the As and Ga sublattice sites has been identified. Moreover, at high temperatures, the GaAs intrinsic Fermi level energy $E_F$ appears to be higher than its midgap energy $E_g/2$ by $\sim 20$–$80$ meV.

References


Table V. Values of $h^f_{Si,a} - \mu_{Si_{As}}$ and $h^f_{Si,a} - \mu_{Si_{Ga}}$ deduced from the $h^f_{Si,a}$ and $h^f_{Si,a}$ values for each case listed in Tables I–IV.

<table>
<thead>
<tr>
<th>X’/ul</th>
<th>Green and Brozel et al.</th>
<th>Fewster and Willoughby</th>
<th>Kung and Spitzer</th>
<th>Kolm, Kulin, and Averback</th>
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<td>$h^f_{Si,a} - \mu_{Si_{As}}$</td>
<td>$h^f_{Si,a} - \mu_{Si_{Ga}}$</td>
<td>$h^f_{Si,a} - \mu_{Si_{As}}$</td>
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