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Concentration of intrinsic defects and self-diffusion in GaSb

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Early experiments have determined that the gallium and antimony diffusivities in gallium antimonide are similar, whereas recent more precise studies demonstrate that gallium diffuses up to three orders of magnitude faster than antimony. In the present study using electronic structure calculations we predict the concentrations and migration enthalpy barriers of important defects in gallium antimonide. It is predicted that the asymmetric self-diffusion in gallium antimonide is due to the insufficient concentration of the point defects that can facilitate the antimony transport. The results are in excellent agreement with the recent experimental evidence and theoretical studies in gallium antimonide and related materials. © 2008 American Institute of Physics.

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I. INTRODUCTION

Gallium antimonide (GaSb) is a compound semiconductor with high electron mobility, narrow direct band gap, and can be lattice matched with ternary or quaternary III–V compounds.¹ These properties constitute GaSb as a technologically important material for diodes, photovoltaics, and solar cells.¹ GaSb can also be considered for advanced nanoelectronic devices as the recent trend is to replace silicon (Si) in devices with substrates of higher mobility of electrons (e.g., III–V compounds) and higher mobility of holes [e.g., germanium (Ge)].^{2,3} Catalytic in that direction is the idea to replace silicon dioxide (SiO₂) as a gate dielectric in complementary metal oxide semiconductor transistors with high dielectric constant (high-*k*) materials to reduce gate leakage currents.^{4,5}

The interest in GaSb does not stem only from its technological applications, which until now are limited compared to other materials such as Si or gallium arsenide (GaAs). Bracht *et al.*^{6,7} have determined that self-diffusion in GaSb is asymmetric with Ga diffusing more rapidly than Sb by over three orders of magnitude near the melting temperature. This is of scientific interest as it implies that a myriad of radiotracer studies, which determined that self-diffusion in compound semiconductors is similar, may not be necessarily valid. As it was mentioned by Gösele,⁸ there is a need for electronic structure calculations to study the self-diffusion in compound semiconductors at the atomic level.

Electronic structure calculations have been used to study the properties of native defects of GaSb and related materials such as GaAs.^{9,10} The density functional theory (DFT) study of Hakala *et al.*⁹ was consistent with the conclusions of Bracht *et al.*^{6,7} in that the dominant native defects are the Ga interstitial (Ga_i), the Ga vacancy (V_{Ga}), and Ga antisite (Ga_{Sb}).

A recent experimental study by Sunder *et al.*¹¹ on the extrinsic diffusion of zinc (Zn) in GaSb supports the V_{Ga}-mediated Ga diffusion via the V_{Sb} ↔ V_{Ga}Ga_{Sb} transfor-

mation reaction leading to the formation of V_{Ga}. The study by Sunder *et al.*¹¹ does not provide evidence for the existence of the defect clusters proposed by Shaw.¹² Another suggestion by Shaw¹² is that the differences between the self-diffusion coefficients reported by Weiler and Mehrer¹³ and those determined by Bracht *et al.*^{6,7} are related to the presence of hydrogen (H) as an impurity. This hypothesis stems from the fact that the experiments by Weiler and Mehrer¹³ were performed in H atmosphere. Attempting to resolve the issue, Sunder and Bracht¹⁴ performed self-diffusion experiments with GaSb isotope heterostructures under ²H₂ atmosphere. The limited annealing time used in that study did not provide clear evidence on the impact of H on self-diffusion in GaSb.

GaSb is a stoichiometric ordered binary compound with the zinc-blende structure (*F* $\bar{4}3m$, space group No. 216). The zinc-blende structure includes two sublattices, with each sublattice being occupied, ideally, by atoms of one kind. The four nearest neighbor sites of every lattice site lie on the other sublattice. Therefore, the large disparity between the diffusion coefficients of Ga and Sb is very unusual. The aim of this study is to calculate the concentrations of the defects that affect self-diffusion in GaSb. DFT is used to predict the association and migration enthalpies of self-diffusion in GaSb.

II. METHODOLOGY

A. Details of calculations

Within the DFT framework, GaSb was simulated using a plane-wave basis with an energy cutoff of 350 eV and the generalized gradient approximation using the Perdew–Burke–Ernzerhof¹⁵ exchange–correlation functional combined with ultrasoft pseudopotentials.¹⁶ The calculations were performed using the CASTEP code^{17,18} with a 64 site supercell and Brillouin-zone sampling using a Monkhorst–Pack¹⁹ grid of 2³ *k* points. The atomic coordinates were allowed to relax using energy minimization under constant volume conditions. The adequate convergence of

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the present computational approach was demonstrated in previous studies on related systems.^{20–22}

Migration and association enthalpy barriers were predicted using the linear synchronous transit (LST) method,²³ as developed by Halgren and Lipscomb.²⁴ In this method, geometric interpolation between a reactant and a product is used to generate a reaction pathway (constant volume configuration). The structures that connect the reactant to the product configuration are generated by interpolating distances between pairs of atoms in the reactant and product. In synergy with single point energy calculations the LST method can be used to study transition states. The efficacy of the approach used in the present study has been recently established by comparing with experimental results.^{25–29}

B. Formation energy definition

The concentrations of native defects are important as they are required to facilitate self-diffusion. For GaSb the formation energy of a defect in a charge state q is given by³⁰

$$\begin{aligned} \Delta E_D = E_D - \frac{1}{2}(n_{\text{Ga}} + n_{\text{Sb}})\mu_{\text{GaSb}}^{\text{bulk}} - \frac{1}{2}(n_{\text{Ga}} - n_{\text{Sb}}) \\ \times (\mu_{\text{Ga}}^{\text{bulk}} - \mu_{\text{Sb}}^{\text{bulk}}) - \frac{1}{2}(n_{\text{Ga}} - n_{\text{Sb}})\Delta\mu + q(E_v + \mu_e), \end{aligned} \quad (1)$$

where E_D is the total energy of the defective supercell, n_j is the number of atoms of species j in the supercell, μ_j^{bulk} is the chemical potential of j in its reference state (calculated from the elemental bulk phases), $\Delta\mu$ describes the variation in the chemical potentials under different conditions, q is the charge (electrons or holes) transferred to the defect from a reservoir, μ_e is the electron chemical potential, and E_v is the valence band maximum. If we neglect the entropic contributions the chemical potentials of the reference phases can be replaced by their cohesive energies. The limits of $\Delta\mu$ are given by the heat of formation (ΔH_f), which has been experimentally determined to be 0.43 eV.³¹

In the present study we consider intrinsic conditions to compare with previous experiments. Under intrinsic conditions μ_e is approximated by one-half of the energy of the band gap (E_g). The temperature (T) dependence of the band gap is given by³²

$$E_g(T) = 0.813 \text{ eV} - \frac{(0.000378 \text{ eV K}^{-1})T^2}{T + 94 \text{ K}} \text{ eV}. \quad (2)$$

III. RESULTS AND DISCUSSION

A. Formation and concentration of defects

Table I represents the Hakala *et al.*⁹ formation energies of native defects in GaSb for Ga-rich ($\Delta\mu = \Delta H_f = 0.43$ eV) and Sb-rich ($\Delta\mu = \Delta H_f = -0.43$ eV) conditions under intrinsic conditions ($\mu_e = E_g/2$). To quantify the temperature dependence of the concentration of isolated defects [D], we used the relation $[D] = N_s \exp(-E_f/k_B T)$, where N_s is the density of sublattice sites ($1.75 \times 10^{22} \text{ cm}^{-3}$), E_f is the formation energy of the defect, and k_B is Boltzmann's constant. To facilitate comparison with previous experiments^{6,11} the temperature dependence of the native defects was considered

TABLE I. The Hakala *et al.* (Ref. 9) formation energies (eV) of native defects in GaSb under Ga-rich ($\Delta\mu = \Delta H_f = 0.43$ eV) and Sb-rich ($\Delta\mu = \Delta H_f = -0.43$ eV) conditions for electronically intrinsic conditions ($\mu_e = E_g/2$ eV).

| Defect | Ga-rich | Sb-rich |
|---|-----------------|-----------------|
| V_{Ga}^{3-} | $2.84 - 3/2E_g$ | $2.41 - 3/2E_g$ |
| V_{Ga}^{2-} | $2.29 - E_g$ | $1.86 - E_g$ |
| V_{Ga}^{1-} | $1.98 - 1/2E_g$ | $1.55 - 1/2E_g$ |
| V_{Sb}^{1-} | $2.10 - 1/2E_g$ | $2.53 - 1/2E_g$ |
| V_{Sb}^0 | 0.90 | 1.33 |
| V_{Sb}^{1+} | $1.72 + 1/2E_g$ | $2.15 + 1/2E_g$ |
| $\text{Ga}_{\text{Sb}}^{2-}$ | $1.00 - E_g$ | $1.86 - E_g$ |
| $\text{Ga}_{\text{Sb}}^{1-}$ | $0.74 - 1/2E_g$ | $1.60 - 1/2E_g$ |
| Ga_{Sb}^0 | 0.70 | 1.56 |
| Sb_{Ga}^0 | 1.76 | 0.90 |
| Ga_i^{1+} | $0.56 + 1/2E_g$ | $0.99 + 1/2E_g$ |
| Sb_i^{3+} | $3.99 + 3/2E_g$ | $3.56 + 3/2E_g$ |
| Sb_i^{1+} | $3.02 + 1/2E_g$ | $2.59 + 1/2E_g$ |
| $(V_{\text{Ga}}\text{Ga}_{\text{Sb}})^{3-}$ | $2.49 - 3/2E_g$ | $2.92 - 3/2E_g$ |
| $(V_{\text{Ga}}\text{Ga}_{\text{Sb}})^{2-}$ | $1.97 - E_g$ | $2.40 - E_g$ |
| $(V_{\text{Ga}}\text{Ga}_{\text{Sb}})^{1-}$ | $1.69 - 1/2E_g$ | $2.12 - 1/2E_g$ |
| $(V_{\text{Sb}}\text{Sb}_{\text{Ga}})^{1+}$ | $2.57 + 1/2E_g$ | $2.14 + 1/2E_g$ |
| $(V_{\text{Ga}}\text{Sb}_i)^0$ | 1.99 | 1.13 |

under both Ga-rich conditions [Fig. 1(a)] and Sb-rich conditions [Fig. 1(b)] over the temperature range 600–1000 K.

As it can be observed from Fig. 1(a) under Ga-rich conditions the dominant species are the Ga_{Sb} antisites (with $\text{Ga}_{\text{Sb}}^{2-}$ and $\text{Ga}_{\text{Sb}}^{1-}$ more significant) and the Ga_i interstitials. There is also a significant concentration of V_{Sb} that even though it is not important for Sb transport (group V elements migrate via interstitials in III–V compounds) it can be facilitating the Ga self-diffusion. In particular under Ga-rich conditions the formation of V_{Ga} has been previously explained by the transformation reaction $V_{\text{Sb}} \leftrightarrow V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ that also leads to the suppression of V_{Sb} .^{6,11} Notably, the V_{Ga} (mainly V_{Ga}^{1-} but also V_{Ga}^{2-}) are calculated to have relatively low concentrations (about $3.9 \times 10^{13} \text{ cm}^{-3}$ at 1000 K). Therefore, for the observed high self-diffusivity of the Ga even under Ga-rich conditions the $V_{\text{Sb}} \leftrightarrow V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ reaction is necessary.^{6,11} This is compatible with the present results [see Fig. 1(a)], where a significant concentration of $V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ (about $1.3 \times 10^{15} \text{ cm}^{-3}$ at 1000 K) is predicted to form. Considering the high formation enthalpy of Sb_i^{1+} and Sb_i^{3+} interstitials (see Table I), it is concluded that the diffusion of Sb under Ga-rich conditions will be insignificant as the vehicles for its migration will have very low concentrations (concentration of Sb_i only $7 \times 10^5 \text{ cm}^{-3}$ at 1000 K). This is in agreement with experiment, where under Ga-rich conditions it was impossible to determine the Sb self-diffusion due to insufficient Sb motion.⁶ Sb_{Ga} antisites [see Fig. 1(a)] have very low concentrations, whereas all other defects considered in Table I have practically negligible concentrations. Overall these results are also in agreement with the recent DFT study of Åberg *et al.*³³ that predicted equivalent defects to be dominant under aluminum-rich conditions in aluminum antimonide (AlSb).

Under Sb-rich conditions about three orders of magnitude more Sb_i^{1+} interstitials will form as their formation enthalpy ($2.59 + E_g/2$ eV) is lower by 0.43 eV compared to the

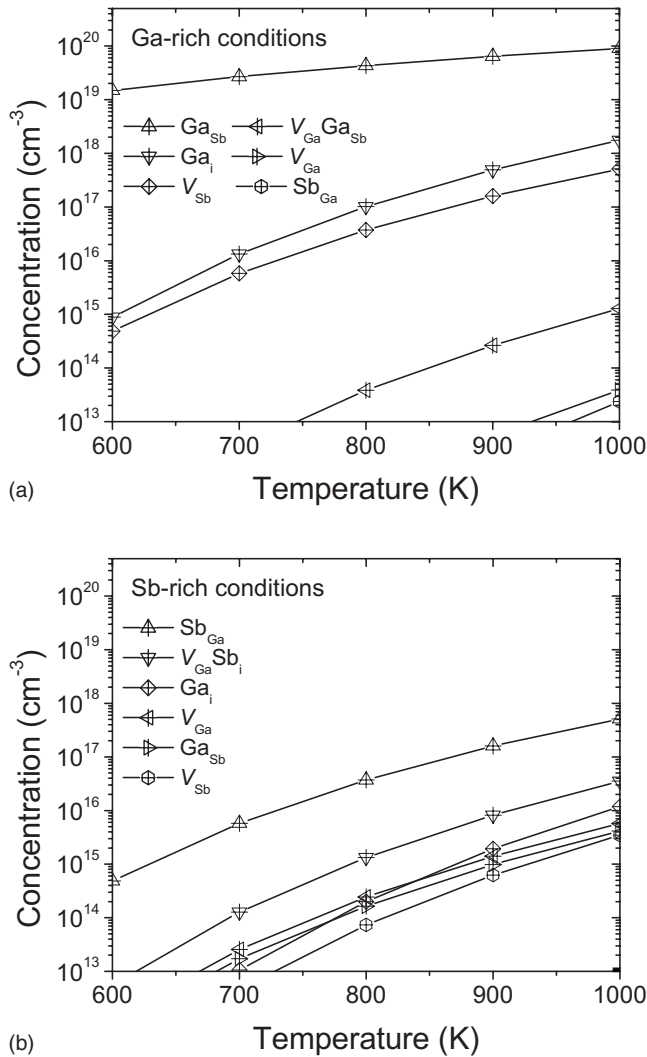


FIG. 1. Intrinsic defect concentrations for GaSb for temperatures in the range 600–1000 K for (a) Ga-rich and (b) Sb-rich conditions.

Ga-rich conditions (see Table I). Nevertheless, the concentration of Sb_i^{1+} will still be insignificant in comparison with other intrinsic defects. From Fig. 1(b) it is evident that there is a significant concentration of $V_{\text{Ga}}\text{Sb}_i$ pairs. It is expected that most of these will not enhance the Sb_i concentration. This is because $V_{\text{Ga}}\text{Sb}_i$ have been previously reported to be metastable forming neutral Sb_{Ga} antisites via the reaction $V_{\text{Ga}}\text{Sb}_i \leftrightarrow \text{Sb}_{\text{Ga}}$ (see for example Ref. 9). Notably, in the present study it is predicted that the neutral Sb_{Ga} antisite is the dominant intrinsic disorder species under Sb-rich conditions [see Fig. 1(b)]. The present results are consistent with the more recent experimental studies that predict that under Sb-rich conditions Sb migration is more significant compared to Ga-rich conditions but still far lower than Ga migration.^{6,11} The V_{Ga} (mainly V_{Ga}^{1-} and V_{Ga}^{2-}) have significant concentrations under Sb-rich conditions (for example about $5.75 \times 10^{15} \text{ cm}^{-3}$ at 1000 K) and dominate the V -mediated migration of Ga atoms (see Sec. II below). The Ga_{Sb} antisites (mainly $\text{Ga}_{\text{Sb}}^{1-}$, $\text{Ga}_{\text{Sb}}^{2-}$ and to a lesser extent Ga_{Sb}^0) have a significant concentration. For Sb-rich conditions the concentration of V_{Sb} (predominantly V_{Sb}^0) is lower by more than two orders of magnitude compared to Ga-rich conditions. All

other intrinsic defects considered are predicted to have comparably negligible concentrations under Sb-rich conditions.

B. Self-diffusion mechanisms

Van Vechten³⁴ pointed out that a V , which migrates by nearest-neighbor jumps, needs a ten-jump process to move just one place in its sublattice without leaving a trail of antisite disorder. In previous studies, (for example Ref. 13 and references therein) the ten-jump process was criticized on the grounds of too great departure from order for just one jump. Here we predict that the ten-jump process³⁴ requires a migration enthalpy of 3.35 eV and is therefore not energetically favorable. This result is consistent with the predictions of El-Mellouhi and Mousseau³⁵ in GaAs as they concluded that a complete diffusion process via such a mechanism was not feasible. Nevertheless, a modified mechanism proposed by Van Vechten³⁴ cannot be ruled out. If for example the antisite-vacancy pairs created by the moving V recombine, this will lead to the reduction in the energy of the migration process. In that respect, Bockstedte and Scheffler³⁶ predicted by means of *ab initio* molecular dynamics that arsenic antisite-vacancy ($\text{As}_{\text{Ga}}V_{\text{As}}$) pairs in GaAs quickly recombine, however similar calculations have not yet been performed in GaSb. Bockstedte and Scheffler³⁶ also predicted in their study that the dominant self-diffusion mechanism for Ga in GaAs is the plane-passing mechanism (see below) and not a modified Van Vechten³⁴ mechanism.

Weiler and Mehrer¹³ proposed the triple-defect mechanism in which the Ga (or Sb) atoms migrate in their own sublattice via a divacancy ($V_{\text{Ga}}V_{\text{Sb}}$). Essentially, the attractiveness of the triple defect mechanism (see Figs. 8 and 9 of Ref. 13) is that self-diffusion can be mediated without the need to create antisite disorder. Their assumptions are that self-diffusion for Ga and Sb in GaSb occurs via a single mechanism and that $V_{\text{Ga}}V_{\text{Sb}}$ pairs form in adequate concentrations (see below). The implications of these assumptions are that Ga and Sb self-diffusion are of the same order. Therefore the triple-defect mechanism is not compatible with recent experimental results.^{6,7}

In the plane-passing mechanism proposed by Bockstedte and Scheffler³⁶ (for Ga diffusion in GaAs) a Ga atom at a second nearest neighbor position with respect to a V_{Ga} moves toward it leaving its own site vacant. In more detail, the Ga atom moves at the interstitial region along the diffusion plane that is perpendicular to the 110 direction (see also Fig. 3 in Ref. 36). The advantage of the plane-passing mechanism is that it does not necessitate the formation of defect complexes (such as the $V_{\text{Sb}}V_{\text{Ga}}$ in the triple-defect mechanism¹³) or the creation of antisite disorder (such as in the ten-jump process³⁴). In recent DFT studies El-Mellouhi and Mousseau^{35,37} considered other possible mechanisms for Ga self-diffusion in GaAs but predicted that the plane-passing mechanism is the most energetically favorable for V_{Ga}^0 and V_{Ga}^{1-} (both diffusion barriers 1.7 eV) but also for V_{Ga}^{2-} (diffusion barrier 1.85 eV).

Figure 2 compares the migration enthalpy barriers of Ga via the mechanism proposed by Bockstedte and Scheffler³⁶ (plane-passing) and the triple-defect mechanism of Weiler

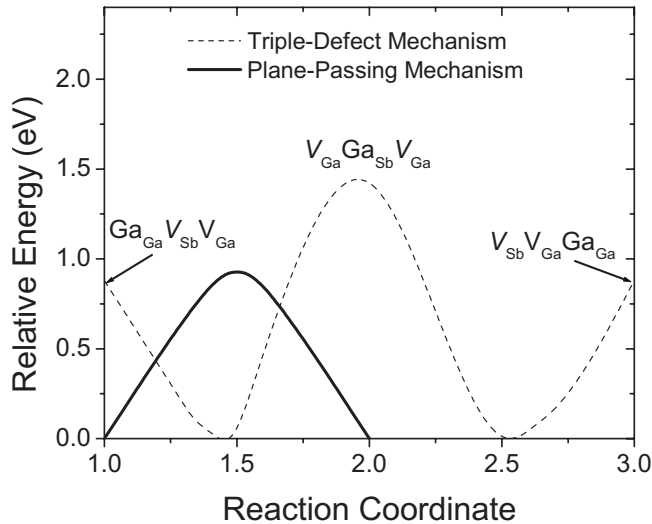


FIG. 2. The migration enthalpy barriers for Ga self-diffusion in GaSb via the plane-passing mechanism proposed by Bockstedte and Scheffler (Ref. 36) and the triple-defect mechanism of Weiler and Mehrer (Ref. 13).

and Mehrer.¹³ It is evident from Fig. 2 that the plane-passing mechanism has a lower migration enthalpy (0.94 eV) compared to the triple-defect mechanism (1.42 eV). Additionally, the triple defect mechanism¹³ is insignificant for self-diffusion as it necessitates the formation of $V_{\text{Ga}}V_{\text{Sb}}$ pairs, which are of negligible concentration because of the low V_{Ga} concentration under Ga-rich conditions and the low V_{Sb} concentration under Sb-rich conditions.

The activation energy for the V -mediated Ga self-diffusion is the sum of the formation energy of the V_{Ga}^{1-} and the migration energy via the plane passing mechanism. This is $2.92 - E_g/2$ eV for Ga-rich and $2.49 - E_g/2$ eV for Sb-rich conditions. The energy for Ga-rich conditions may be lowered to $2.63 - E_g/2$ eV if we consider that the $(V_{\text{Ga}}\text{Ga}_{\text{Sb}})^{1-}$ formation contributes to a V_{Ga}^{1-} -mediated diffusion process. The predicted energies are about 1 eV lower compared to the experimentally determined activation energies for Ga self-diffusion.^{6,11} This energy difference can be attributed mainly to the underestimation (due to the lack of exact exchange) of the formation energies of defects in the DFT approach. This has been noted in previous studies of group IV semiconductors (see for example Refs. 38 and 39). With the use of more advanced computational techniques such as quantum Monte Carlo, this problem can be overcome.⁴⁰ Notably, these techniques predict for Si formation energies of defects that are about 1 eV higher than the normal DFT predictions.⁴⁰ Therefore, taking into account the discrepancy of the formation energy of the defects in GaSb, the predicted activation energies are in good agreement with the recent experimental studies.^{6,11}

IV. CONCLUSIONS

The stability, concentration, and migration enthalpies of intrinsic defects in GaSb were investigated using atomic scale computer simulation. The high formation energies of the intrinsic defects, which could mediate Sb self-diffusion under both Ga-rich and Sb-rich conditions, lead to its insignificant movement. The plane-passing mechanism is pre-

dicted to be energetically favorable with a migration enthalpy barrier of 0.94 eV for Ga. It is found that under Ga-rich conditions most V_{Ga} form via the transformation reaction $V_{\text{Sb}} \leftrightarrow V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ providing additional evidence to the previous studies.^{6,11} The predicted activation energies for Ga self-diffusion are consistent with the experimental data^{6,11} if we consider the errors in the calculated formation energies. Finally, the present work provides additional theoretical support for the previous experimental studies,^{6,7} which determined that the slow Sb diffusion in GaSb is due to a suppressed concentration of native defects that are required for Sb diffusion and that Ga migrates significantly faster.

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