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The advertisement for the Lake Shore CRYOTRONICS Model PS-100 Preconfigured Tabletop Probe Station features a photograph of the device. The device is a complex, black, mechanical probe station with various components, including a probe head, a sample stage, and a base. The background of the advertisement is a gradient of blue and white. The text "NEW" is in orange, and "Model PS-100" is in large, bold, blue letters. Below it, "Preconfigured Tabletop Probe Station" is in smaller, blue letters. The Lake Shore CRYOTRONICS logo is on the right, with the tagline "An affordable solution for a wide range of research" in white, italicized font.

Antisites and anisotropic diffusion in GaAs and GaSb

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The significant diffusion of Ga under Ga-rich conditions in GaAs and GaSb is counter intuitive as the concentration of Ga vacancies should be depressed although Ga vacancies are necessary to interpret the experimental evidence for Ga transport. To reconcile the existence of Ga vacancies under Ga-rich conditions, transformation reactions have been proposed. Here, density functional theory is employed to calculate the formation energies of vacancies on both sublattices and the migration energy barriers to overcome the formation of the vacancy-antisite defect. Transformation reactions enhance the vacancy concentration in both materials and migration energy barriers indicate that Ga vacancies will dominate. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824126>]

A number of binary III–V compound semiconductors have high electron mobility, narrow direct band gap and can be lattice matched with ternary or quaternary III–V compounds.^{1–5} These properties make them technologically important for microelectronic applications, diodes, photovoltaics, and solar cells.¹ For example, GaAs is being considered for advanced nanoelectronic devices as the recent trend is to replace silicon (Si) in devices with substrates that exhibit higher electron mobility.^{6,7} Interestingly, theoretical studies can provide a fundamental insight in the defect processes of group III–V compounds (such as growth in GaAs).⁵

Interestingly, Bracht *et al.*^{8,9} 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. Furthermore, Ga self-diffusion is more significant than Sb even under Ga-rich conditions. Ga-diffusion is mainly vacancy-mediated in GaSb so one needs to understand the large disparity between the diffusion coefficients of Ga and Sb and the role of Ga vacancies (V_{Ga}) even under Ga-rich conditions.

Bracht and Brotzmann⁶ explain the diffusion of Zn in GaAs via the kick-out mechanism that involves neutral and single positively charged self-interstitials. In addition, V_{Ga} contributes to Zn diffusion via the dissociative mechanism.⁶ Zn diffusion in GaAs is effectively a probe to determine the individual contributions of charged Ga interstitials (Ga_i) and V_{Ga} to the total Ga self-diffusion coefficient. For Zn diffusion under As-rich conditions, Bracht and Brotzmann⁶ fitted the experimental Zn profiles data for the individual contribution of Ga_i and V_{Ga} to Ga self-diffusion in GaAs, which are consistent with the total self-diffusion coefficient. That is, the individual contributions are lower than the total Ga self-diffusion. However, the situation is very different under Ga-rich conditions. Although

the same diffusion mechanisms (see Eqs. (2)–(4) of Ref. 6) describe the experimental Zn profiles and even the Ga profiles, the individual contributions of neutral and positive charged V_{Ga} reduced to standard conditions (electronically intrinsic and to an As pressure of 1 atm), exceed the total Ga self-diffusion coefficient.¹⁰ It is striking that the same model that works for As-rich conditions also accurately reproduces Zn profiles obtained under Ga-rich conditions. One counter intuitive idea that may nevertheless explain the situation is that significant concentrations of V_{Ga} exist and can evolve from V_{As} even under Ga-rich conditions.

Apart from the investigation of vacancies, the present study will also focus on the associations of antisites defects with vacancies. Using density functional theory (DFT), we present a detailed investigation of the point defects under different compositional conditions (stoichiometric, Ga-rich, and As/Sb-rich) and Fermi levels. To gain a complete understanding of the processes, we also consider the kinetics of the transformation reactions.

The results were generated using density functional theory as implemented in the VASP code.¹¹ Exchange and correlation were described according to the formulation of Perdew *et al.*¹² Pseudopotentials were generated using the projector-augmented method¹³ in which the 3 electrons of the group III atoms and 5 electrons of the group IV atoms were treated as valence. Wavefunctions were expanded to a kinetic energy cut-off of 400 eV.

The calculations were carried out in 216 atom supercells. Integration over the Brillouin zone was performed using a $2 \times 2 \times 2$ grid generated according to Monkhorst and Pack.¹⁴ Energies and forces were iterated up to tolerances of 1×10^{-5} eV and 1×10^{-2} eV/Å, respectively. Defect formation energies were calculated according to

$$E^f = E_{\text{tot}}(D, q) - E_{\text{tot}}(\text{perfect}) + \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q \mu_e + E_{\text{corr}} \quad (1)$$

where $E_{\text{tot}}(D, q)$ and $E_{\text{tot}}(\text{perfect})$ are the total energies of the defective and perfect cells, respectively. n_{α} represents the

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number of atoms added or removed and μ_x is the corresponding chemical potential. Charged defect-defect interactions were accounted for using the recent technique due to Freysoldt *et al.*,¹⁵ which has been applied in several previous studies and appears in the equation above as E_{corr} . To calculate the migration barriers, we employed the nudged elastic band technique with the climbing image functionality (CI-NEB).¹⁶

It is important to consider how V_{Ga} is relevant in GaAs and GaSb. When III–V compounds are stoichiometric, they are ordered binary compounds with the zinc-blende structure ($F\bar{4}3m$, space group No. 216). The zinc-blende structure has 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, whereas the second neighbour sites lie on the same sublattice. In the plane-passing mechanism proposed by Bockstedte and Scheffler¹⁷ (for Ga diffusion in GaAs), a Ga atom at a second nearest neighbor position with respect to a V_{Ga} moves towards it leaving its own site vacant. Thus, the Ga atom moves towards the interstitial region along the diffusion plane that is perpendicular to the (110) plane (see also Fig. 3 in Ref. 17). The advantage of the plane-passing mechanism is that it does not necessitate the formation of defect complexes (such as $V_{\text{Sb}}V_{\text{Ga}}$ in the triple-defect mechanism¹⁸) or the creation of antisite disorder (such as in the ten-jump process¹⁹). This is because Ga self-diffusion is taking place on the Ga-sublattice and As self-diffusion on the As sublattice. In recent DFT studies, El-Mellouhi and Mousseau^{20,21} 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 with diffusion barriers of 1.7 eV) but also for V_{Ga}^{2-} (diffusion barrier 1.85 eV).

Results presented in Fig. 1(a) show that in GaSb, irrespective of the composition conditions (i.e., Ga or Sb rich)

or Fermi level, the isolated V_{Ga} defect has a lower formation energy than the antimony vacancy (V_{Sb}). Fig. 1(b) shows that for GaAs, the V_{As} is more favorable than the V_{Ga} only for some *p*-type conditions in stoichiometric and Ga-rich compositions, although, it is always most favorable in As-rich compositions.

Bracht *et al.*⁸ have proposed the transformation reaction $V_{\text{As}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{As}}$ as a way to produce V_{Ga} from V_{As} in GaAs under Ga-rich conditions. In essence, Bracht *et al.*⁸ considered the formation of two isolated species, however, as an intermediate process the vacancy-antisite pair is formed. Formally, the dissociation energy required to break up the pair defect also needs to be calculated to gain a full understanding of the defect processes. This will involve the V_{Ga} migrating away from the pair via the plane-passing mechanism,¹⁷ effectively with a Ga atom at a second nearest neighbor position (with respect to a V_{Ga}) moving towards it, leaving its own site vacant. Here, we assume that under experimental conditions, all the vacancies will contribute to diffusion at their sublattice. For such conditions, our calculations, illustrated in Fig. 1(b), reveal that it is energetically favourable to form isolated vacancies. In addition, we calculated the transformation reaction to form antisite-vacancy pairs for both materials to assess the impact on the V_{Ga} concentration, as was proposed experimentally. Fig. 1 reports the antisite-vacancy pair formation energies for the most stable charge states as a function of the Fermi level for stoichiometric, III-rich, and V-rich conditions in both GaSb and GaAs. The most stable cluster configuration is predominantly the nearest neighbour $\text{Ga}_{\text{As}}V_{\text{Ga}}$ in GaAs and $\text{Sb}_{\text{Ga}}V_{\text{Sb}}$ in GaSb regardless of composition. Considering first GaSb under Ga-rich conditions, the $\text{Ga}_{\text{Sb}}V_{\text{Ga}}$ cluster has a low formation energy under *n*-type conditions supporting the transformation reaction $V_{\text{Sb}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{Sb}}$ that was previously proposed to explain the V_{Ga} mediated diffusion of Ga in

FIG. 1. Lowest energy vacancy and antisite-vacancy pair formation energies assuming the most stable charge state as a function of the Fermi level for stoichiometric, III-rich and V-rich conditions for (a) GaSb and (b) GaAs. Numbers in the figures represent the charge state of the respective defects.

FIG. 2. The migration energy barriers for (a) $V_{\text{As}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{As}}$ and (b) $V_{\text{Ga}} \rightarrow V_{\text{As}} + \text{As}_{\text{Ga}}$ transformation reactions in GaAs. On the top of the figure is the initial and final state of the transformation reaction. Cubes represent the vacant site, red spheres the As atoms and purple spheres the Ga atoms. The reaction coordinates represent the distance between the images along the path of the diffusing species. Numbers in the figures represent the charge state of the respective defects.

GaSb under Ga-rich conditions.⁸ The present study, however, also supports the view that isolated V_{Ga} is produced even under Ga-rich conditions and is prevalent over V_{Sb} (Fig. 1(a)). Again, this is consistent with the experimental evidence of significantly higher Ga self-diffusion compared with Sb self-diffusion in GaSb. At any rate, the transformation reaction can add complementary V_{Ga} to the system.

In GaAs under Ga-rich conditions, $\text{Ga}_{\text{As}}V_{\text{Ga}}$ has low formation energies especially for low Fermi levels where V_{As} have lower formation energies than V_{Ga} (see Fig. 1(b)). Accordingly, we expect through the transformation reaction that additional V_{Ga} is added to the system. Therefore, GaAs and GaSb are similar under Ga-rich conditions. Where the two materials behave differently is that under all conditions the $\text{Sb}_{\text{Ga}}V_{\text{Sb}}$ pair exhibits a lower formation energy than the V_{Ga} , the analogous pair in GaAs (i.e., the $\text{As}_{\text{Ga}}V_{\text{As}}$ pair) exhibits significantly higher formation energy under Ga rich conditions. The lower formation energies of the $\text{Sb}_{\text{Ga}}V_{\text{Sb}}$ pair suggest that the transformation reaction $V_{\text{Ga}} \rightarrow V_{\text{Sb}} + \text{Sb}_{\text{Ga}}$ would form V_{Sb} even under Sb-rich conditions, something that was not observed experimentally.⁸ Hence to understand the absence of these thermodynamically favourable species, the kinetics of the transformation reactions are considered next by calculating the migration energies for these processes.

While the formation of V_{Ga} via transformation reactions may increase the V_{Ga} concentration one has to consider the migration energy barrier that must be overcome to form the

defect pair. A schematic representation of the transformation reaction $V_{\text{As}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{As}}$ in GaAs is provided at the top of Fig. 2(a). In essence, a nearest neighbour Ga atom moves into the vacant As site. This leads to the formation of the Ga antisite and a vacant Ga site. Analogous mechanisms were also considered for $V_{\text{Ga}} \rightarrow V_{\text{As}} + \text{As}_{\text{Ga}}$, $V_{\text{Sb}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{Sb}}$, and $V_{\text{Ga}} \rightarrow V_{\text{Sb}} + \text{Sb}_{\text{Ga}}$ in Figs. 2(b), 3(a), and 3(b).

Figs. 2 and 3 report the energies along the path defined on the top of the figures for GaAs and GaSb, respectively. The charge states considered correspond to the dominant values of the vacancy-antisite pair identified in Fig. 1. It can be observed by comparing Figs. 2(a) and 2(b) and Figs. 3(a) and 3(b) that the lowest energy barriers, irrespective of the charge states, are for the production of V_{Ga} via the respective transformation reactions. For example, considering GaAs (see Fig. 2), the barrier to form doubly negatively charged $V_{\text{As}} + \text{As}_{\text{Ga}}$ pairs (via $V_{\text{Ga}} \rightarrow V_{\text{As}} + \text{As}_{\text{Ga}}$, Fig. 2(a)) is more than 1.3 eV higher compared with the barrier to form the doubly negatively charged $V_{\text{Ga}} + \text{Ga}_{\text{As}}$ pairs (via $V_{\text{As}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{As}}$, Fig. 2(b)).

It is evident that the transformation reactions leading to the production of V_{Ga} are energetically favourable over the analogous reactions for all conditions in both materials (Figs. 2 and 3). For GaSb this supports the model proposed by Bracht *et al.*,⁸ namely, that under Ga-rich conditions transformation reactions ($V_{\text{Sb}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{Sb}}$) lead to the formation of Ga vacancies (Fig. 3). At high Fermi levels, the energy of this

FIG. 3. The migration energy barriers for (a) $V_{\text{Sb}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{Sb}}$ and (b) $V_{\text{Ga}} \rightarrow V_{\text{Sb}} + \text{Sb}_{\text{Ga}}$ transformation reactions in GaSb. On the top of the figure is the initial and final state of the transformation reaction. Cubes represent the vacant site, red spheres the Sb atoms and purple spheres the Ga atoms. The reaction coordinates represent the distance between the images along the path of the diffusing species. Numbers in the figures represent the charge state of the respective defects.

process is very low leading to the transformation of V_{Sb} to additional V_{Ga} . Conversely, the process $V_{\text{Ga}} \rightarrow V_{\text{Sb}} + \text{Sb}_{\text{Ga}}$ in GaSb (which appears favourable at high Fermi energies in terms of formation energies in Fig. 1(a)) is hindered by the high migration energy barriers (refer to Fig. 3(b)). The picture in GaAs is very similar, that is, the migration energy barriers for the production of V_{Ga} via the transformation reactions are lower as compared with the production of the V_{As} .

The results of the present study lead to counterintuitive conclusions as it is predicted that the concentration of V_{Ga} or $\text{Ga}_{\text{As}}V_{\text{Ga}}$ pairs is significant and dominant over group-V vacancies even under Ga-rich conditions for both GaSb and GaAs. They are consistent though with the experimentally observed diffusion behavior in both materials. Transformation reactions under Ga-rich conditions can provide complementary V_{Ga} but these reactions are not necessary to explain the existence of V_{Ga} as they exhibit formation energies that are compatible with high Ga diffusion. The kinetics of the processes are, however, necessary to explain the suppression of V_{Sb} as the migration energies of the transformation reaction establish the dominance of the V_{Ga} over V_{As} or V_{Sb} for GaAs and GaSb.

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