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ABSTRACT

The thermodynamics of Bi incorporation into bulk and epitaxial GaAs was studied using density functional theory (DFT) and anharmonic elasticity calculations. The equilibrium concentration of Bi was determined as a function of epitaxial strain state, temperature, and growth conditions. For a bulk, unstrained system, Bi in GaAs under typical growth conditions (Ga-rich and Bi-metal-rich at 400° C) has a dilute heat of solution of 572 meV/Bi and a solubility of $x = 5.2 \times 10^{-5}$ in $GaAs_{1-x}Bi_x$. However, epitaxial strain can greatly enhance this solubility, and under the same conditions an epitaxial film of $GaAs_{1-x}Bi_x$ with 5% in-plane tensile strain is predicted to have a Bi solubility of $x = 7.3 \times 10^{-3}$, representing approximately a hundred times increase in solubility over the unstrained bulk case. Despite these potentially large increases in solubility, the equilibrium solubility is still very low compared to values that have been achieved experimentally through non-equilibrium growth. These values of solubility are also sensitive to choice of the Bi reference state. If the primary route for phase separation is the formation of GaBi within the same structure, rather than Bi metal, GaBi would serve as the source/sink for Bi. If GaBi is used as the Bi reference state, the epitaxial formation energy on a bulk unstrained GaAs substrate is reduced dramatically to 144 meV/Bi, yielding a Bi solubility of $x = 0.083$ in $GaAs_{1-x}Bi_x$. These calculations suggest that Bi solubility could be greatly enhanced if Bi metal formation is inhibited and the system is forced to remain constrained to the $GaAs_{1-x}Bi_x$ structure. Although GaBi is not a naturally stable compound, it could potentially be stabilized through a combination of kinetic limitations and alloying.

I. INTRODUCTION

Adding even small amounts of Bi to GaAs causes a large decrease in the band gap[1-6], an increase in the spin-orbit splitting energy[2, 3, 6], and creates a relatively temperature-insensitive band gap[1, 6-11]. These properties make GaAs$_{1-x}$Bi$_x$ potentially useful for optical, electronic, and spintronic applications. As a result, isoelectronic doping of GaAs using bismuth to form the ternary GaAs$_{1-x}$Bi$_x$ has attracted a considerable amount of attention in recent years.

Due to its large size, bismuth does not easily incorporate into the GaAs matrix[12]. Unless the GaAs$_{1-x}$Bi$_x$ growth occurs using non-equilibrium growth methods and a very narrow set of growth conditions[4, 7-10, 13], Bi tends to surface segregate. The growth of GaAs$_{1-x}$Bi$_x$ up to $x = 0.037$ has been achieved using metalorganic vapor-phase epitaxy (MOVPE)[1, 3, 7-10, 12, 14-16] and, more recently, up to $x = 0.11$ using molecular beam epitaxy (MBE)[4, 6, 11, 13, 17-22]. For both MOVPE and MBE growth, the temperature must be relatively low, usually in the range of 350-400° C[8-10], and the V/III, the cation-to-anion, ratio at the growth front must be relatively low. Most successful GaAs$_{1-x}$Bi$_x$ growths using MOVPE have been done at a gas phase V/III ratio of about 10[7-10]. Typically, the V/III ratio for GaAs-based alloys are at least 20 when growing at atmospheric pressure and as high as 80 at lower pressures to avoid carbon contamination from the alkyl gallium and bismuth sources when using AsH$_3$ as an anion source[23].

Most GaAs$_{1-x}$Bi$_x$ studies to date, both experimental and theoretical, have focused on the optical and electronic properties of the compound[1, 3, 7-10, 12, 24, 25] and the thermodynamics of GaAs$_{1-x}$Bi$_x$ growth have not yet been investigated thoroughly[24-27]. This work uses *ab initio* calculations to better understand the thermodynamics GaAs$_{1-x}$Bi$_x$ growth to both better understand the thermodynamic limits and how the driving forces for Bi incorporation, which impact equilibrium and non-equilibrium growth, depend on the Bi reference state and the strain state of the system. These results provide guidance to future experiments on routes to enhance levels of Bi incorporation or incorporate Bi more easily through altered growth conditions.

The equilibrium composition of GaAs$_{1-x}$Bi$_x$ is a function of the Gibbs free energy of formation, and can be written in the dilute limit as[28]

$$x_{Bi}^{eq} = \exp\left(-\frac{\Delta G_f}{k_B T}\right) \tag{1}$$

where ΔG_f is the Gibbs free energy of adding a Bi atom into GaAs (without the configurational entropy contributions), k_B is the Boltzmann constant, and T is the temperature[28]. If vibrational free energy effects are negligible, the Gibbs free energy of formation can be calculated from *ab initio* supercell calculations using[29]

$$\Delta G_f = \Delta E^{bulk} - \Delta n_i \mu_i - \sigma_{\alpha\beta} V_{\alpha\beta}^f + \Delta q \mu_F \tag{2}$$

where ΔE^{bulk} is the energy difference between a defected cell and a pure, undefected cell, Δn_i is the number of species i added to or removed from the original GaAs cell (+1 for a single interstitial, -1 for a single vacancy), μ_i is the chemical potential of species i, $\sigma_{\alpha\beta}$ is the stress state of the GaAs, $V_{\alpha\beta}^f$ is the relaxation volume (the change in cell dimensions associated with the change in composition), Δq is the number of electrons removed from the defected cell (+1 for the removal of a single electron, -1 for the addition of a single electron) and μ_F is the Fermi energy. Generally, it is not expected that isoelectronic dopants such as Bi in GaAs would have a charge state. However, shallow bound states are known to form at isoelectronic dopants when they are of sufficient size and core potential difference from the host atoms, which may be the case for Bi in GaAs[27]. The α and β represent the direction of the stress. In this equation, repeated indices imply a summation, i.e., one should sum over the variables, i, α and β. For this work, $n = 1$ and ΔE^{bulk} is the difference between $Ga_N As_{N-1} Bi$ and $Ga_N As_N$, which means that the overall expression gives the Gibbs free energy per Bi added.

The effects of vibration free energy are not considered explicitly in this study. At relevant temperatures for growth the dominant term in the change in vibrational free energy is the vibrational entropy. For some ternary semiconductor systems, such as GaP-InP[30], AlN-GaN, GaN-InN, and AlN-InN[31], vibrational entropy terms have a relatively mild effect on the overall shape and scale of the miscibility gap[30-32]. However, it has been shown that in some systems the solubility of a dilute species can be altered by over an order of magnitude by vibrational contributions[33]. Including the vibrational effects are expected to reduce the Bi solubility from the Bi reference state as the Bi is being forced into a compressed state and will therefore tend to have less vibrational entropy. While the vibrational effects may scale the reported solubility values significantly, including vibrational energy terms is not expected to change the qualitative trends identified in this work.

Since the formation enthalpy and the relaxation volume are properties of the bismuth defect and cannot be varied, potential pathways for increasing the solubility of Bi involve engineering a favorable stress state in the GaAs, varying the chemical potentials by changing the growth conditions, i.e. reactant ratios or fluxes, or engineering the Fermi level (if Bi were present as a charged impurity).

The stress state engineering of the epitaxial film is of particular interest since the phase equilibria in epitaxial systems can be entirely different than in bulk. Liu *et al.*[34, 35], have shown that $GaAs_{1-x}Sb_x$ ordered phases are stable in the entire region $0 < x < 1$ under epitaxial conditions. This is a result of the increased energy of the epitaxially strained GaSb that makes the phase separation unfavorable. The incorporation of Bi into GaAs might be expected to follow similar trends to Sb incorporated into GaAs. Both are large group V elements, significantly larger than Ga or As, making them difficult to incorporate under normal growth conditions, with a tendency to surface segregate[4, 14, 16]. However, unlike GaSb, GaBi is not a naturally stable compound[7, 13, 25] and therefore may never form even in epitaxial systems, although it might be possible for GaBi to be stabilized through some combination of kinetic inhibition and alloying[3, 26]. However, the analogy to GaSb raises the possibility that by using growth conditions that prevent the segregation of Bi to Bi metal, and instead force Bi to either incorporate into GaAs or form an epitaxial GaBi compound, the chemical potential of Bi might

be raised enough to significantly increase its solubility into GaAs. To explore the potential of this approach, the range of Bi chemical potentials ranging from Bi in Bi metal to Bi in epitaxial GaBi has been considered. While it is interesting to consider the possibility of enhancing Bi solubility through the stabilization of a GaBi or doped GaBi phase, we reiterate that such a stabilization has not been achieved to date and that the solubility limit of Bi is generally controlled by the formation of Bi metal under typical growth conditions.

In this work, both the bulk and epitaxial formation energy of Bi in GaAs are calculated using VASP energies and elasticity calculations. The equilibrium solubility of Bi in GaAs is determined using these energies and Eq. (1). The effects on Bi solubility of expanding the lattice parameter of the GaAs substrate are examined, as well as the theoretical limits of Bi incorporation.

II.   METHOD

Ab initio calculations were performed using density functional theory (DFT) and the projector augmented wave method (PAW)[36] with the Vienna Ab-Initio Simulation Package (VASP)[37-40]. All calculations were performed using the local density approximation (LDA) exchange correlation functional[41]. The PAW potentials used had electronic configurations of Ga (4s2 4p1), As (4s2 4p3), and Bi (6s2 5d10 6p3). The energy cut-off was set to 313 eV for all of the calculations except GaBi. For GaBi, a series of many calculations of epitaxially-strained structures was needed to find the elastic coefficients. To complete these calculations faster they were all run at a lower energy cutoff of 202 eV. Using a lower energy cutoff for the strained GaBi calculations was shown to cause ~1 meV/Bi difference in the formation energy of GaAs$_{1-x}$Bi$_x$ using the GaBi reference state, which has a negligible effect on the results in this work.

It has been shown[42] that interactions of periodic defect images take the form

$$E_f^{sc}(L) = E_f + a\frac{1}{L} + b\frac{1}{L^3}$$
(3)

where E_f is the formation energy in the dilute limit, E_f^{sc} is the formation energy for a finite size supercell, L is the length of the supercell (distance between periodic images), and a and b are constants related to the defect charge, the dielectric and elastic response of the material, and the supercell shape[42]. For this fit, it is important that the smallest cell is large enough that no other interactions are introduced[43, 44]. Figure 1 shows the supercell convergence using three different supercell sizes: 54, 128, and 250-atom cells. Each Ga$_N$As$_{N-1}$Bi supercell was a zincblende Ga$_N$As$_N$ structure with one As atom replaced by a Bi atom, and the energy difference between the defected and undefected cell was determined for every supercell size. Fitting Eq. (3) to these values, then, gives the difference between Ga$_N$As$_{N-1}$Bi and Ga$_N$As$_N$ for an infinite supercell size, or as $\frac{1}{L^3} \rightarrow 0$, which is found to be 1441 meV/Bi. This value is the dilute Bi relaxation energy, $\Delta E_{dilute}^{Bi,bulk}$, used in subsequent equations. The k-point mesh size was scaled relative to the cell size. A 4 x 4 x 4 Γ-centered k-point mesh was used for the 54 atom cell, and

a 3 x 3 x 3 Γ-centered k-point mesh for the 128 atom cell, and a 2 x 2 x 2 Γ-centered k-point mesh for the 250 atom cell.

To obtain the chemical potential terms, the energies of the reference states GaBi, Ga metal, As metal and Bi metal were calculated. A 5 x 5 x 5 Γ-centered k-point mesh was used for GaBi, which was a 16-atom zincblende cell, as it has been shown using *ab initio* calculations that GaBi is more stable in the zincblende phase than the wurtzite phase[45, 46]. A 20 x 20 x 20 Γ-centered k-point mesh was used for Ga, which has a complex unit cell consisting of 8 atoms[47]. A 15 x 15 x 15 Γ-centered k-point mesh was used for both Bi and As, which have the same trigonal unit cell structure consisting of 6 atoms[48].

To compare with the results of elasticity calculations, epitaxial calculations in VASP were carried out using 16-atom cells for GaAs$_{1-x}$Bi$_x$, GaAs and GaBi. For GaAs$_{1-x}$Bi$_x$, the concentration was 1 Bi atom, or 12.5%, leading to a cell composition of Ga$_8$As$_7$Bi. Bi was always placed on the As sublattice, although some authors have proposed a small concentration of Bi on Ga may occur[49]. The bulk metal reference states as listed above were also used for epitaxial calculations. Epitaxial calculations were performed using constant volume supercells which were strained up to 10.5% of the calculated GaAs lattice parameter in increments of 0.5% in the transverse x and y directions. For each value of the transverse strain, the lattice parameter in the z direction was set to that which gave the minimum total energy for the cell as determined by interpolating the energy obtained for 3-5 calculations of varying z lattice parameter. The energy of the strained GaAs substrate was not included in these calculations but served only to adjust the substrate lattice parameter.

Ab initio calculations using hybrid functionals can provide higher accuracy by including a fraction of exact nonlocal exchange in the exchange-correlation potential[50]. Initially, hybrids were considered for use in this work because they have been shown to produce more accurate results than semi-local calculations when applied to a variety of semiconductors and insulators[50, 51]. However, hybrid calculations for GaAs$_{1-x}$Bi$_x$ gave questionable results, showing a negative formation energy for GaBi from Ga and Bi metal, although it is known experimentally that GaBi is not a stable compound. Therefore, LDA calculations were used for this work. A comparison of alternate energy methods is presented in Appendix A.

The Gibbs free energy of formation at a particular supercell size is obtained from Eq. 2 with the enthalpy change, $\Delta E^{bulk} = E_{VASP}^{def} - E_{VASP}^{undef}$, calculated from the change in the calculated total energy upon introducing a defect. In the dilute limit then, $\Delta E^{bulk} = \Delta E_{dilute}^{Bi,bulk}$. When calculating the formation energy of dilute GaAs$_{1-x}$Bi$_x$, a range of limiting cases was considered based on possible reaction conditions. The following reactions were considered:

Bulk:

As-rich: *Ga$_n$As$_n$ + Bi → Ga$_n$As$_{n-1}$Bi + As*

Ga-rich: *Ga$_{n-1}$As$_{n-1}$ + Bi + Ga → Ga$_n$As$_{n-1}$Bi*

As-rich (stabilized GaBi):   *Ga$_n$As$_n$ + GaBi → Ga$_n$As$_{n-1}$Bi + Ga + As*

Ga-rich (stabilized GaBi):   *Ga$_{n-1}$As$_{n-1}$ + GaBi → Ga$_n$As$_{n-1}$Bi*

Epitaxial:

As-rich: *Ga$_n$As$_n$(epi) + Bi → Ga$_n$As$_{n-1}$Bi(epi) + As*

Ga-rich: *Ga$_{n-1}$As$_{n-1}$(epi) + Bi + Ga → Ga$_n$As$_{n-1}$Bi(epi)*

As-rich (stabilized GaBi):   *Ga_nAs_n(epi) + GaBi(epi) → Ga_nAs_{n-1}Bi(epi) + Ga + As*
Ga-rich (stabilized GaBi):   *Ga_{n-1}As_{n-1}(epi) + GaBi(epi) → Ga_nAs_{n-1}Bi(epi)*
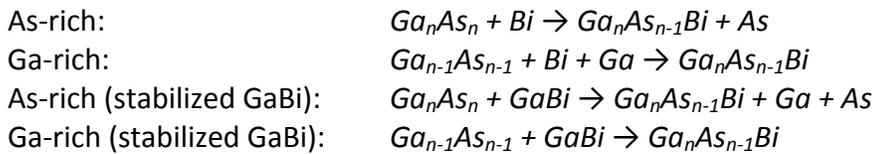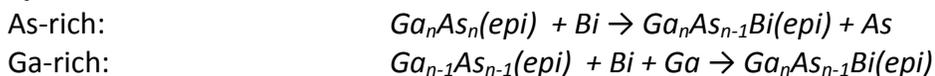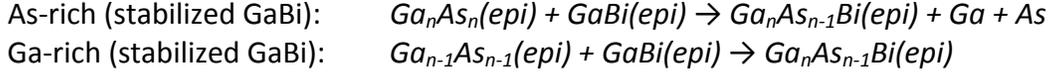
The relaxed bulk reference states for Ga, As, Bi, GaAs, and GaBi were used for the formation of relaxed bulk $GaAs_{1-x}Bi_x$. It was assumed that Ga, As, and Bi do not maintain coherency, so the bulk reference states were used for the formation energy of epitaxial $GaAs_{1-x}Bi_x$. GaAs and GaBi are assumed to maintain coherency, so the reference states are strained epitaxially to the same lattice parameter as the epitaxially strained $GaAs_{1-x}Bi_x$.

Spin-orbit coupling (SOC) becomes significant for calculations involving large atoms, such as Bi, with more electrons that move at a high speeds[52]. Since including SOC greatly slows the calculations, the extent to which SOC was required was investigated. The difference between the energy of $GaAs_{1-x}Bi_x$ calculated using SOC for the full relaxation and the energy of $GaAs_{1-x}Bi_x$ calculated using SOC for only the static calculation differed by <1 meV/atom. Formation energies increased by as much as 90 meV when including SOC effects. Therefore, a full relaxation of the supercells was done without SOC, and then a static SOC calculation was performed for the Bi-containing compounds.

Bismuth is an isoelectronic impurity in GaAs, similar to N. At low concentration and low temperature, few-atom Bi clusters have been shown to create localized bound states in the band gap of GaAs[27]. However, while N, like many other isoelectronic impurities, is a pseudo-acceptor, Bi may be a pseudo-donor[27]. This could potentially lead to stabilized charged states of $GaAs_{1-x}Bi_x$. The formation energies of charged states of $GaAs_{1-x}Bi_x$, when $\Delta q = \pm 1$ were calculated using Eq. (2) and compared to the formation energy of neutral $GaAs_{1-x}Bi_x$. The potential alignment must be included[44] for defect calculations in supercells with a net charge. The value of the correction term was found by using the mean difference of the electrostatic potentials between the defected cell and pure GaAs averaged over ion cores. The Fermi energy is defined by the relation, $\mu_F = E_{VBM} + E_F$. The Fermi level E_F is therefore zero at the valence band maximum. With the addition of the potential alignment term ΔE_{PA}^{def}, the Fermi energy becomes $\mu_F = (\Delta E_{PA}^{def} + E_{VBM} + E_F)$[44]. From the calculations of charged supercells, Bi was found to not be a stable pseudo-donor or pseudo-acceptor. The calculated levels for the +1/0 and 0/-1 transitions are 180 meV below the valence band maximum and 680 meV above the calculated conduction band minimum, respectively. Therefore, Bi was not considered as a charged impurity, and the $\Delta q \mu_F$ term from Eq. (2) is zero.

Elasticity calculations can be used to derive the equilibrium solubility as a function of the strain state using both the composition, x and $\Delta E_{dilute}^{Bi,bulk}$. The results are summarized here; the full derivation is given in Appendix B.
For an epitaxial thin film, the formation energy per Bi with Bi metal as a reference state is

$$\Delta G_f(ref:Ga,Bi) = E_{epi}^f(ref:Ga,Bi) =$$
$$\Delta E_{dilute}^{Bi,bulk} + E(GaAs) - E(Ga) - E(Bi) + \frac{U(GaAs_{1-x}Bi_x,\varepsilon) - (1-x)U(GaAs,\varepsilon)}{x} \qquad (4)$$

where $\Delta E_{dilute}^{Bi,bulk}$ is the dilute Bi relaxation energy, determined from the supercell convergence, and $U(X,\varepsilon)$ is the strain energy of X as a function of ε_t^X, the strain of the lattice parameter in the x and y directions. This work will calculate the strain terms with the elastic coefficients of X up to 3rd-order terms.

An additional term accounting for the GaBi strain energy is included when epitaxial GaBi is the Bi reference state and the formation energy per Bi becomes

$$\Delta G_f(ref:Ga,GaBi) = E_{epi}^f(ref:Ga,GaBi)$$

$$= \Delta E_{dilute}^{Bi,bulk} + E(GaAs) - E(Ga) - E(GaBi) + \frac{U(GaAs_{1-x}Bi_x,\varepsilon) - (1-x)U(GaAs,\varepsilon) - xU(GaBi,\varepsilon)}{x}$$

$$(5)$$

III. RESULTS

A. Bulk Calculations

The calculated GaAs lattice parameter was 0.5627 nm, in good agreement to the experimental value of 0.56534 nm[24, 53]. The GaBi lattice parameter was calculated to be 0.6271 nm, also in good agreement with the range of estimated lattice parameters for GaBi of 0.618-0.647 nm[2, 8-10, 13, 27]. The calculated band gap for GaAs was 0.393 eV, significantly lower than the experimental value of 1.519 eV at 0 K[51, 53]. Standard DFT calculations using GGA and LDA pseudopotentials are well known to underestimate the band gap of semiconductors by a significant amount[54, 55]. The formation energy of GaAs$_{1-x}$Bi$_x$ was found to be 572 meV/Bi for infinitely dilute Bi in GaAs under Ga-rich conditions with Bi metal as the Bi reference state. The chemical potential of Bi in the GaBi metal reference state is 141 meV greater than Bi in the Bi metal reference state. Thus, the formation energy of GaAs$_{1-x}$Bi$_x$ was found to be 432 meV/Bi for infinitely dilute Bi in GaAs under Ga-rich conditions using GaBi as the reference state. A comparison between the bulk formation energies of dilute Bi as calculated for different reference states considered is shown in Figure 2. With metallic Bi as the Bi reference, the formation energy varies from 1219 meV/Bi to 572 meV/Bi as the conditions are varied from As-rich to Ga-rich, while the formation energies with respect to the GaBi reference state are 141 meV lower. Janotti et al. found a formation energy of ~45 meV/anion for bulk GaAs$_{0.875}$Bi$_{0.125}$ using Ga-rich conditions and a GaBi reference state[26], about 20% different from the value of 431 meV/Bi, or 54.0 meV/anion, calculated from this work. The difference is likely since Janotti et al. included a correction factor for the band gap energy but did not include SOC in their calculations. A correction factor was not used in the present calculations since they do not involve band gap estimation.

B. Epitaxial Calculations

The epitaxial formation energies were calculated using Equations (4) and (6) and the volumes of the GaAs$_{1-x}$Bi$_x$ cell and the pure GaAs and GaBi cells obtained from the VASP calculations. The comparison between the epitaxial formation energies of Ga$_8$As$_7$Bi calculated using both VASP and elasticity calculations for Ga-rich conditions is shown in Figure 3. The

values calculated using these two methods for a 12.5% concentration of Bi are in good agreement.

There is a significant difference between the trends of the epitaxial formation energies using Bi metal as a reference state and those using GaBi as a reference state. For the Bi metal reference state, epitaxially straining GaAs$_{1-x}$Bi$_x$ to the GaAs substrate lattice parameter increases the formation energy from the bulk value, decreasing the Bi solubility. As the substrate lattice parameter is increased, straining the GaAs, the formation energy decreases, increasing the Bi solubility. With GaBi as the Bi reference state, constraining GaBi to the GaAs lattice parameter leads to a film under considerable compressive strain. This strain can be relieved through the incorporation of GaBi into the GaAs lattice, thereby expanding the lattice parameter. Therefore, the formation energy of GaAs$_{1-x}$Bi$_x$ using a GaBi reference state drops dramatically when going from bulk to epitaxial conditions. Furthermore, the formation energy of GaAs$_{1-x}$Bi$_x$ using GaBi as the reference state is lower than the formation energy using Bi metal for any given amount of tensile strain introduced into the substrate.

The formation energy of GaAs$_{1-x}$Bi$_x$ can be calculated as a function of both strain and Bi composition using an elastic energy model. This calculation was performed for a range of Bi compositions up to $x = 0.125$, close to the maximum Bi incorporation that has been achieved experimentally to date, with the results shown in Figure 4.

In Figure 4 it is shown that, increasing strain in the GaAs causes a significant decrease in the formation energy of GaAs$_{1-x}$Bi$_x$ across a range of dilute Bi compositions for the Bi metal reference state. A drop in formation energy of ~400 meV is observed. The change in formation energy between $x = 0$ and $x = 0.125$ Bi compositions at a given strain is only about 60 meV/Bi atom. When GaBi is the reference state, then, the change in the formation energy is dominated by the strain state of the substrate, since increasing the lattice parameter makes it easier for the Bi metal to be incorporated into the GaAs lattice.

The formation energy when employing the GaBi reference state, however, is relatively unaffected by the expanded or strained GaAs substrate lattice parameter. In this case, the drop in formation energy caused by increasing substrate lattice parameter is compensated by the decreasing compressive strain within the GaBi, making it a more stable reference state. Under these conditions, then, the changes in formation energy are primarily by the Bi composition and the strain in the substrate.

With the bulk formation energy in the dilute Bi limit determined from the supercell convergence, the Bi solubility in epitaxial GaAs can be determined using Equations (4) and (5). The temperature for these calculations is set at 400° C, a typical epitaxial growth temperature for GaAs$_{1-x}$Bi$_x$ [4, 7-10]. The solubility at 400° C is plotted in Figure 5 as a function of the strain state (expanded lattice parameter) of GaAs under Ga-rich conditions.

The bulk equilibrium solubility of Bi in GaAs is about $x = 5.2 \times 10^{-5}$ in GaAs$_{1-x}$Bi$_x$. The solubility in epitaxial dilute GaAs$_{1-x}$Bi$_x$ on unstrained GaAs as a substrate is also about $x = 5.2 \times 10^{-5}$, but it increases exponentially as the GaAs lattice parameter is expanded. When there is a 5% strain/expansion in the GaAs lattice parameter, the solubility of Bi increases by two orders of magnitude to about $x = 7.3 \times 10^{-3}$. In practice, a larger substrate lattice parameter can be achieved through the use of a substrate such as InP or the use of graded or metamorphic buffer layers[56]. Note that we consider strains of up to 0.1 (10%) in the GaAs

lattice parameter to be sure to include even the largest strains that might be realized in the future. While 10% is beyond what is practical, strain values up to a few percent (typically compressive) have been achieved for epitaxially grown semiconductor systems[57].

The VASP calculations predict that $x = 5.2 \times 10^{-5}$ for epitaxial growth of GaAs$_{1-x}$Bi$_x$ on an unstrained GaAs surface. The largest Bi solubility experimentally reported has been $x = 0.11$ for GaAs$_{1-x}$Bi$_x$ layers grown on bulk GaAs substrate[20-22]. This result implies that the Bi is kinetically trapped in a non-equilibrium supersaturated state over three orders of magnitude above the calculated equilibrium Bi solubility.

The solubility in GaAs$_{1-x}$Bi$_x$ using GaBi as a reference state, however, increases from a bulk solubility of $x = 5.9 \times 10^{-4}$ to $x = 8.3 \times 10^{-2}$ under epitaxial conditions on an unstrained or bulk GaAs substrate. Forcing the system to stay in the zincblende lattice, without the formation of Bi metal, could therefore dramatically enhance Bi solubility.

IV. CONCLUSIONS

The thermodynamics of incorporating bismuth into the GaAs lattice structure was examined using DFT analysis. The most favorable V/III ratio growth conditions for incorporations of Bi are Ga-rich conditions, where the chemical potential of Ga in GaAs is equal to the energy of Ga metal, in agreement with experimental conditions used to grow GaAs$_{1-x}$Bi$_x$ [1, 3, 4, 6-10, 12, 14-16, 20-22, 58]. Incorporation of Bi in bulk GaAs$_{1-x}$Bi$_x$ growth is also more favorable when the reference state for Bi is Bi existing within GaBi rather than Bi metal. The epitaxial formation energy of GaAs$_{1-x}$Bi$_x$ is significantly lower than the bulk formation energy when strained GaBi is the Bi reference state. This indicates that the incorporation of Bi in GaAs could be increased if GaBi could be stabilized within the strained zincblende structure, which may be experimentally achieved through kinetic inhibitions and alloying[26, 45]. The epitaxial formation energy of GaAs$_{1-x}$Bi$_x$ using Bi metal as a reference state on an unstrained bulk GaAs lattice parameter is higher than the bulk formation energy in which the GaAs$_{1-x}$Bi$_x$ relaxes to its own unstrained lattice parameter. However, epitaxial GaAs$_{1-x}$Bi$_x$, using the Bi metal reference state, becomes increasingly stabilized when constrained to a larger lattice parameter as represented by tensile-strained GaAs in this study.

The use of a GaBi under the conditions of epitaxial growth stabilizes GaAs$_{1-x}$Bi$_x$ significantly, even on a bulk or unstrained GaAs substrate. The difference between the Bi metal and GaBi reference state indicates that the strained GaBi reference state has a more stabilizing effect on alloy formation than growth on a lattice parameter larger than bulk GaAs.

The equilibrium solubility of epitaxial GaAs$_{1-x}$Bi$_x$ using a Bi metal reference state at 400° C was calculated to be $x = 5.2 \times 10^{-5}$ when constrained to the bulk GaAs lattice parameter. The Bi solubility increases to $x = 7.3 \times 10^{-3}$ when epitaxially constrained to an in-plane lattice parameter 5% larger than the bulk GaAs. These calculations imply that the $x = 0.11$ achieved in previous MBE growth studies for films grown on a GaAs substrate results from kinetically inhibition or solute trapping. The equilibrium solubility of epitaxial GaAs$_{1-x}$Bi$_x$ on an unstrained or bulk GaAs substrate using the GaBi reference state at 400° C is $x = 8.3 \times 10^{-2}$, an increase of over two orders of magnitude over the bulk solubility within an unstrained GaAs$_{1-x}$Bi$_x$ material of $x = 5.9 \times 10^{-4}$.

V. ACKNOWLEDGMENTS

APPENDIX A: HYBRID CALCULATIONS

Hybrid functionals provide higher accuracy by including a fraction of exact nonlocal exchange in the exchange-correlation potential[50]. Hybrid functionals were initially considered for use in this work because they have been shown to produce more accurate structural parameters than semilocal calculations when applied to semiconductors and insulators[50, 51]. However, the thermodynamic values found using hybrid functionals produced a lower formation energy of GaAs$_{1-x}$Bi$_x$ when the Bi metal is used as a reference state, rather than the GaBi reference state[7, 13, 25].

Hybrid calculations were performed using the generalized gradient approximation (GGA) pseudopotentials[59] and the hybrid functionals of Heyd, Scuseria and Ernzerhof (HSE)[60, 61]. A 6 x 3 x 6 Γ-centered k-point mesh was used for GaAs$_{1-x}$Bi$_x$, GaAs and GaBi, which were 16-atom zincblende cells. The same unit cells were used for Ga, As and Bi metal, but a 6 x 6 x 6 k-point mesh was used for Ga, a 5 x 5 x 5 Γ-centered k-point mesh was used for As, and a 4 x 4 x 4 Γ-centered k-point mesh was used for Bi.

For this work, the amount of nonlocal Fock exchange required was found by determining the amount yielding the best estimate of the GaAs band gap energy. The nonlocal Fock exchange fraction used was 0.399, which gives a band gap energy for GaAs of 1.521 eV, close to the experimental value of 1.519 eV at 0 K[51, 53]. Spin-orbit coupling was included for compounds containing Bi.

The calculated GaAs lattice parameter was 0.5743 nm, which was further from the experimental value of 0.56534 nm[24, 53] than the GaAs lattice parameter calculated using LDA calculations alone (0.5627 nm). The GaBi lattice parameter was calculated to be 0.6434 nm, in good agreement with the range of estimated lattice parameters reported for GaBi of 0.618-0.647 nm[2, 8-10, 27]. The calculated band gap for GaAs was 1.521 eV, which provided a closer estimate to the experimental GaAs band gap than LDA calculations (0.393 eV).

The calculations of charged supercells using HSE functionals also found that Bi will not be a stable pseudo-donor or pseudo-acceptor. The transition levels for the +1 and -1 charged states of GaAs$_{0.875}$Bi$_{0.125}$ occur at E_F = -0.11 eV and 2.34 eV, 110 meV below the valence band maximum and 823 meV above the calculated conduction band minimum, respectively. This result is in agreement with the original LDA calculations, which also predict no stable charged states of GaAs$_{1-x}$Bi$_x$.

The chemical potential of Bi in GaBi is calculated to be 214 meV lower than in Bi metal. Therefore, formation energies calculated with respect to a GaBi reference state are 214 meV higher than using Bi metal as the reference state. These results are contrary to the values calculated using LDA, where the formation energy of GaAs$_{1-x}$Bi$_x$ for all Ga chemical potentials was 137 meV higher when Bi metal was the reference state as opposed to GaBi. Since GaBi is an experimentally unstable compound[7, 13, 25], the chemical potential of Bi in GaBi is expected to be higher than pure Bi metal, which is not the case for the results obtained using HSE functionals.

Since HSE functionals are mainly used for semiconductors and insulators, they may not accurately predict the energies for metals[62]. Further HSE calculations were conducted using GaBi, Ga and Bi at mixing parameters approaching zero to see if there were an error in using

such a high nonlocal Fock exchange fraction. Values for the formation energy of GaBi were obtained at α = 0.25, 0.10, 0.01 and 0. The formation energy versus mixing parameter is shown below in Figure A1, with points for the GaBi formation energy using GGA, LDA, GGA+SOC, LDA+SOC, HSE using both LDA and GGA, and HSE+SOC for both LDA and GGA at α values which gave the best prediction for the GaAs band gap energy for the LDA and GGA (α = 0.399 for GGA and α = 0.306 for LDA). For this work, LDA without hybrid functionals was used since it predicted a positive GaBi formation energy.

APPENDIX B: ELASTICITY CALCULATIONS

In this appendix, equations are derived for calculating the formation energy and solubility of Bi in an epitaxial layer of GaAs as a function of the substrate lattice parameter and growth conditions (chemical potentials).

The formation reaction for epitaxial $GaAs_{1-x}Bi_x$ is

$$(GaAs)_{bulk} + xBi \rightarrow (GaAs_{1-x}Bi_x)_{bulk} + xAs , \qquad (B1)$$
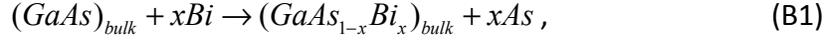
The formation energy per Bi is

$$xE_{epi}^f = E_{bulk}\left(GaAs_{1-x}Bi_x\right) + U\left(GaAs_{1-x}Bi_x, \varepsilon\right) + x\mu_{As} - E_{bulk}\left(GaAs\right) - U\left(GaAs, \varepsilon\right) - x\mu_{Bi}$$
$$(B2)$$

where μ_X is the chemical potential of material X, $E_{bulk}(X)$ is the energy of relaxed X, and $U(X,\varepsilon)$ is the strain energy of X at strain ε.

The chemical potential terms are also strain dependent. Assuming Bi-rich conditions, the chemical potential terms are defined as

$$\mu_{Ga} + \mu_{As} = E_{bulk}(GaAs) + U(GaAs, \varepsilon) , \qquad (B3)$$

$$\mu_{Bi}^{metal} = E_{bulk}(Bi) , \qquad (B4)$$

$$\mu_{Ga} + \mu_{Bi}^{GaBi} = E_{bulk}(GaBi) + U(GaBi, \varepsilon) . \qquad (B5)$$

The experimental conditions set the limiting values of μ_{Ga} and μ_{As}. Under Ga-rich conditions, $\mu_{Ga} = E(Ga)$, while under As-rich conditions, $\mu_{As} = E(As)$.

Assuming that the Bi concentration is sufficiently dilute that the Bi-Bi interactions are negligible, the bulk $GaAs_{1-x}Bi_x$ energy can be determined from the dilute Bi relaxation energy calculated from the limiting case of increasingly larger supercells:

$$E_{bulk}(GaAs_{1-x}Bi_x) = x\Delta E_{dilute}^{Bi,bulk} + E_{bulk}(GaAs) \qquad (B6)$$

$$\Delta E_{dilute}^{Bi,bulk} = \lim_{N \to \infty}[E_{bulk}(Ga_N As_{N-1}Bi) - E_{bulk}(Ga_N As_N)] \qquad (B7)$$

Using up to 3rd-order terms, the strain energy of material X is

$$U(X,\varepsilon) = V_{bulk}^X \left[\frac{1}{2!} \sum_{i,j=1,6} C_{ij}^X \varepsilon_i^X \varepsilon_j^X + \frac{1}{3!} \sum_{i,j,k=1,6} C_{ijk}^X \varepsilon_i^X \varepsilon_j^X \varepsilon_k^X \right], \qquad (B8)$$

where V_{bulk}^X is the volume of the unstrained reference state, C_{ij}^X are the second-order coefficients, C_{ijk}^X are the third-order coefficients, and ε^X is the strain[63]. The elastic coefficients

for pure GaAs and GaBi were determined by fitting the *ab initio* calculations of distortions of GaAs and GaBi (not including an epitaxial strain) using the method of Wang and Li[63]. It was confirmed that the third-order terms are needed and that the resulting coefficients accurately reproduce the *ab initio* calculated energy of epitaxially strained GaAs and GaBi for a very large strain region, as shown in Figure B-1. The elastic coefficients of GaAs$_{1-x}$Bi$_x$ can be approximately as a function of composition using the form

$$C_{ijk}^{GaAs_{1-x}Bi_x} = (1-x)C_{ijk}^{GaAs} + xC_{ijk}^{GaBi} - x(1-x)b_{ijk} \tag{B9}$$

where b_{ijk} is a bowing parameter, here determined by fitting to *ab initio* calculations with a Bi composition of $x = 0.125$ along with GaAs and GaBi. For epitaxial strain, the transverse strains in the plane of the film are fixed by the substrate lattice parameter ($\varepsilon_1 = \varepsilon_2 = \varepsilon_t$), the shear strains are zero ($\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$), and the stress perpendicular to the plane is relaxed ($\sigma_3 = 0$). Then ε_3 is determined from the elastic constants and transverse strain ε_t using the condition that $\sigma_3 = 0$ [63]:

$$\sigma_3 = 0 = \frac{\partial U}{\partial \varepsilon_t} = \frac{\partial V_{bulk}^X \left[\frac{1}{2!} \sum_{i,j=1,6} C_{ij}^X \varepsilon_i^X \varepsilon_j^X + \frac{1}{3!} \sum_{i,j,k=1,6} C_{ijk}^X \varepsilon_i^X \varepsilon_j^X \varepsilon_k^X \right]}{\partial \varepsilon_t}. \tag{B10}$$

The value of the transverse strain, ε_t, felt by each material at a given substrate lattice constant, a^s, is:

$$\varepsilon_t^{GaAs} = \frac{a^{GaAs} - a^s}{a^s}, \tag{B11}$$

$$\varepsilon_t^{GaBi} = \frac{a^{GaBi} - a^s}{a^s}, \tag{B12}$$

$$\varepsilon_t^{GaAs_{1-x}Bi_x} = \frac{a^{GaAs_{1-x}Bi_x} - a^s}{a^s}, \tag{B13}$$

The reference volume and lattice parameter of GaAs$_{1-x}$Bi$_x$ as a function of x are approximated as

$$V_{GaAs_{1-x}Bi_x}^{bulk} = (1-x)V_{GaAs}^{bulk} + xV_{GaBi}^{bulk} \tag{B14}$$

$$a_{GaAs_{1-x}Bi_x} = \sqrt[3]{V_{GaAs_{1-x}Bi_x}^{bulk}} \tag{B15}$$

Note that the linear interpolation use in Eq. (B14) is very accurate when compared to our *ab initio* calculations. Using all of the above equations, the epitaxial formation energy E_{epi}^f

can be calculated as a function of Bi composition and substrate lattice parameter. For Ga-rich conditions, the formation energy with a Bi metal reference state is

$$
\begin{aligned}
\Delta G_f(ref:Ga,Bi) &= E_{epi}^f(ref:Ga,Bi) = \\
\Delta E_{dilute}^{Bi,bulk} &+ E(GaAs) - E(Ga) - E(Bi) + \frac{U(GaAs_{1-x}Bi_x,\varepsilon) - (1-x)U(GaAs,\varepsilon)}{x}
\end{aligned}
\tag{B16}
$$

The formation energy for Ga-rich conditions with a GaBi reference state is

$$
\begin{aligned}
\Delta G_f(ref:Ga,GaBi) &= E_{epi}^f(ref:Ga,GaBi) \\
&= \Delta E_{dilute}^{Bi,bulk} + E(GaAs) - E(Ga) - E(GaBi) + \frac{U(GaAs_{1-x}Bi_x,\varepsilon) - (1-x)U(GaAs,\varepsilon) - xU(GaBi,\varepsilon)}{x}
\end{aligned}
\tag{B17}
$$

These equations correspond to Equations (4) and (5), respectively, in the main body of the paper.

I. FINDING THE EQUILIBRIUM SOLUBILITY OF Bi IN GaAs

When the solubility is sufficiently dilute, the equilibrium Bi composition (site fraction) can then be solved for using the implicit equation

$$
C_{Bi}^{eq} = N_s \exp\left(-\frac{\Delta G_f}{k_B T}\right), \qquad\qquad \text{or} \tag{B18}
$$

$$
x_{Bi}^{eq} = \frac{C_{Bi}^{eq}}{N_s} = \exp\left(-\frac{\Delta G_f}{k_B T}\right), \tag{B19}
$$

where N_s is the number of available sites for Bi per unit volume, ΔG_f is the Gibbs free energy of formation for GaAs$_{1-x}$Bi$_x$, k_B is Boltzmann's constant, and T is temperature.

The equilibrium solubility for Bi in GaAs for Ga-rich conditions for a Bi metal reference state then becomes

$$
x_{Bi}^{eq} = \exp\left(-\frac{1}{k_B T}\left[\Delta E_{dilute}^{Bi,bulk} + E(GaAs) - E(Ga) - E(Bi) + \frac{U(GaAs_{1-x}Bi_x,\varepsilon) - (1-x)U(GaAs,\varepsilon)}{x}\right]\right)
\tag{B20}
$$

and the equilibrium solubility for Bi in GaAs for Ga-rich conditions and a GaBi reference state becomes

$$x_{Bi}^{eq} = \exp\left(-\frac{1}{k_B T}\left[\begin{array}{c} \Delta E_{dilute}^{Bi,bulk} + E(GaAs) - E(Ga) - E(GaBi) \\ +\dfrac{U(GaAs_{1-x}Bi_x, \varepsilon) - (1-x)U(GaAs, \varepsilon) - xU(GaBi, \varepsilon)}{x} \end{array}\right]\right). \tag{B21}$$

Equations (B20) and (B21) are used to find the equilibrium solubility of GaAs$_{1-x}$Bi$_x$ under Ga-rich conditions for all reference states.

Figures
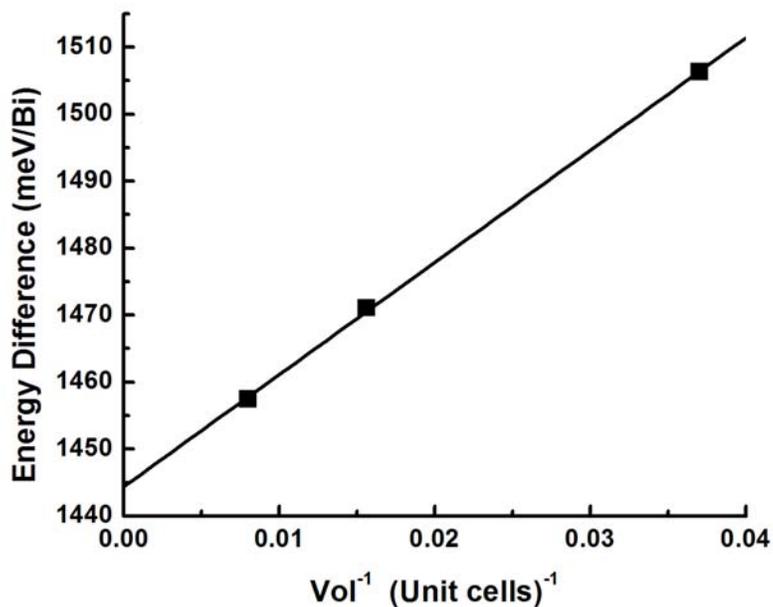
FIG 1. Supercell convergence of the difference in energy between pure Ga_NAs_N and $Ga_NAs_{N-1}Bi$ with respect to the inverse volume of the cell, $1/L^3$.
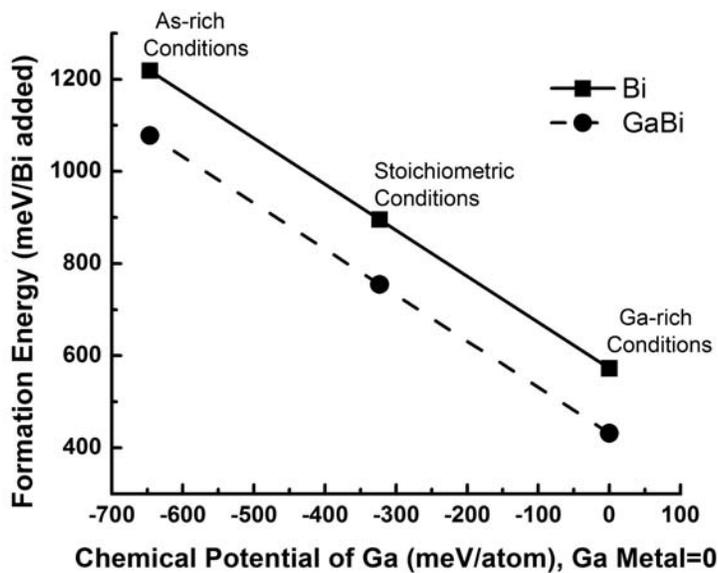
FIG 2. Plot of the bulk formation energy of Bi in GaAs using Bi metal and GaBi as the sources for Bi, calculated across a range of chemical potentials of Ga.
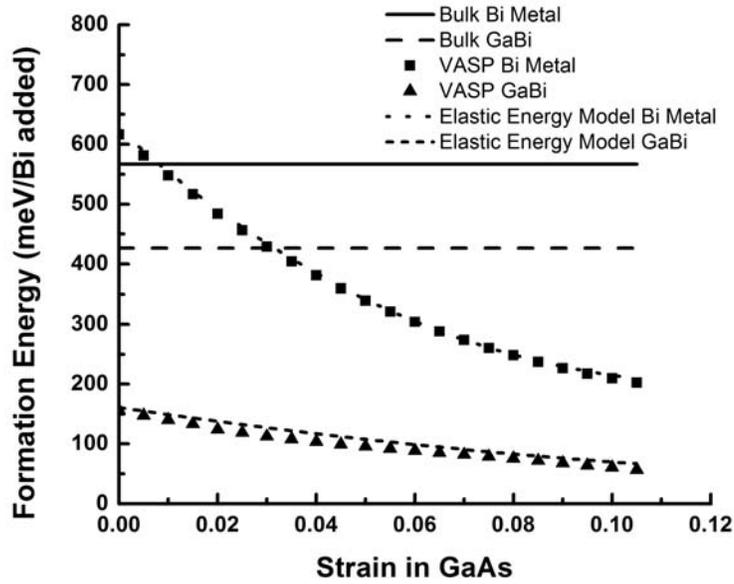
FIG 3. Epitaxial formation energies for Ga_8As_7Bi versus strain in GaAs lattice parameter using different Bi reference states under Ga-rich conditions, calculated using VASP and linear elasticity calculations.
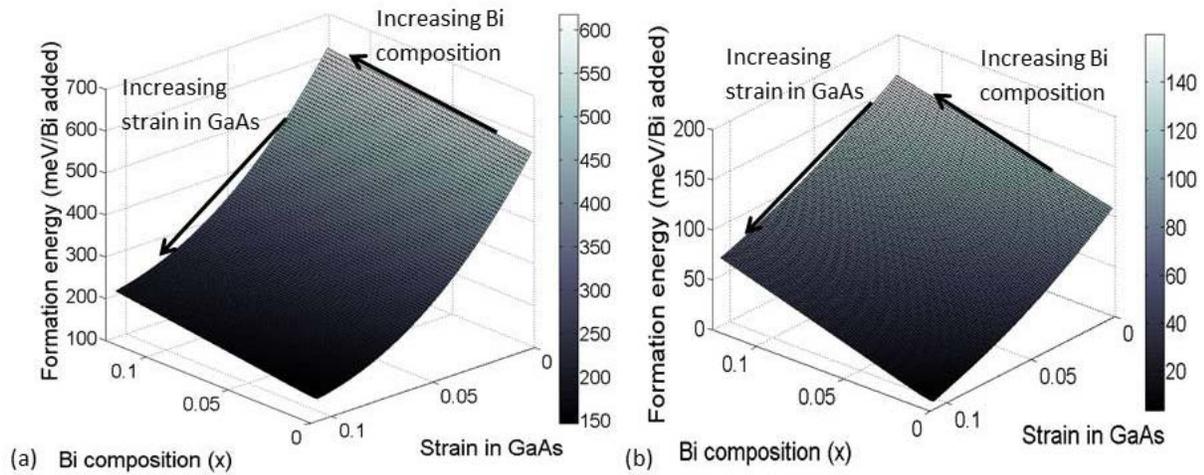
FIG 4. Epitaxial formation energy for $GaAs_{1-x}Bi_x$ vs. Bi composition and strain in the substrate under Ga-rich conditions for (a) the Bi metal as the Bi source and (b) GaBi as the Bi source.
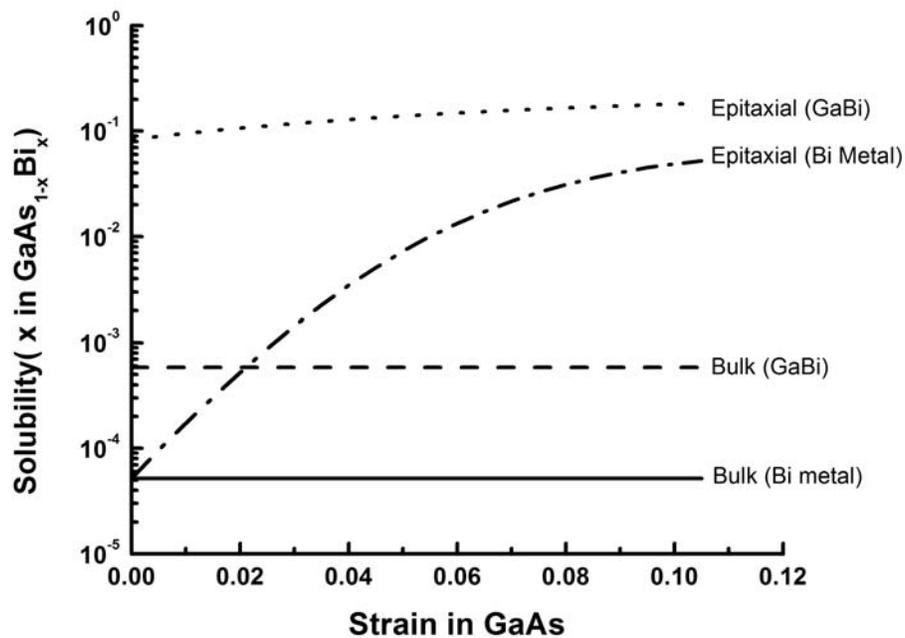
FIG 5. Solubility of Bi in GaAs versus the strain in the GaAs lattice parameter at 400° C under Ga-rich conditions using both Bi metal and GaBi as the reference state for Bi.
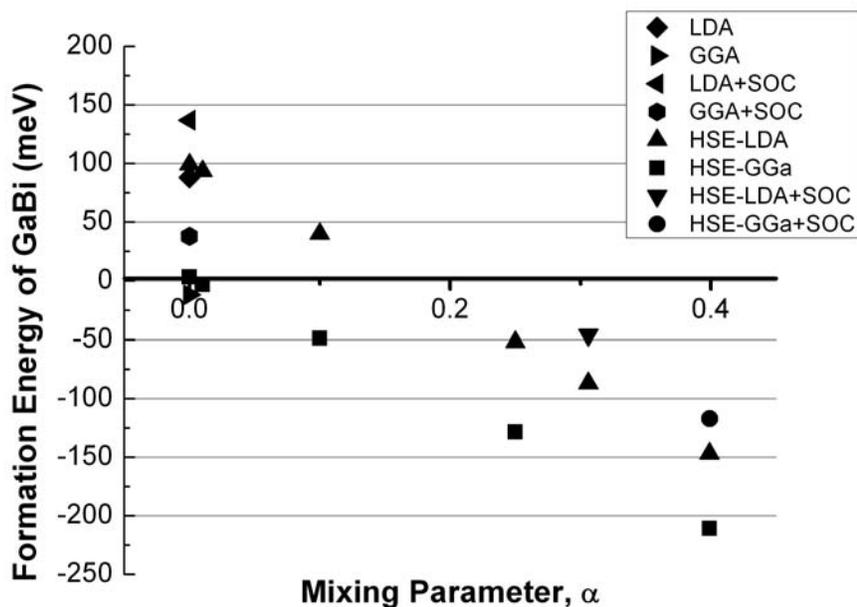
FIG A1. Plot of GaBi formation energy versus the mixing parameter for HSE functionals, with additional points for GGA, LDA, GGA+SOC, LDA+SOC, and HSE+SOC (α = 0.399 and α = 0.306) calculations for reference.
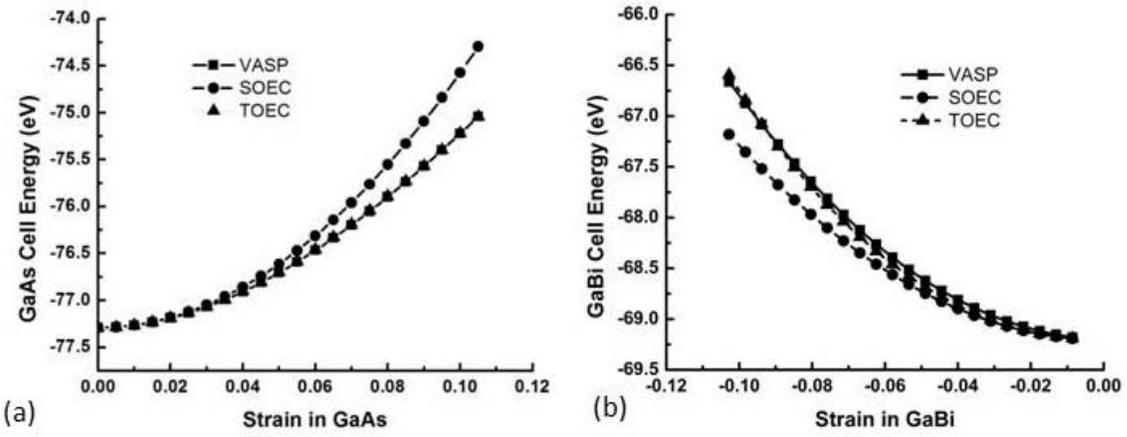
FIG B1. The cell energy vs. epitaxial strain in the cell calculated using VASP energies and second-order (SOEC) and third-order (TOEC) elastic coefficients for (a) GaAs and (b) GaBi.

Footnotes

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