Nitrogen Solubility and Induced Defect Complexes in Epitaxial GaAs:N

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Thermodynamic calculation suggests that the formation of bulk GaN pins N chemical potential $\mu_N \leq \mu_N^{max}$, resulting in low equilibrium N solubility [N] in bulk GaAs:N. In epitaxial growth, however, a fully relaxed GaN phase cannot form prior to the spontaneous formation of a N-rich layer on the surface. First-principles total-energy calculations show that in the epitaxial regime one can increase μ_N^{max} considerably from equilibrium μ_N^{max} without triggering the spontaneous formation of such a N-rich layer. This enhances [N] by 8 orders of magnitude to about 4% at $T = 650\,^\circ\mathrm{C}$ in agreement with experiments. The dominant defects at high N concentration are qualitatively different from those at low [N].

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Doping and alloying semiconductors by large size-mismatched atoms are of fundamental interest [1]. Not only are the physical properties of such alloys expected to be qualitatively different from conventional alloys, their growth often poses serious challenges because the alloys are often thermodynamically unstable [2]. $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ dilute alloy is an example. With a few percent of N, its band gap can be significantly smaller than GaAs [3]. As such, $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ is a potential candidate for infrared lasers and as an absorber for high-efficiency tandem solar cells. It is also a natural buffer layer for the epitaxial growth of cubic-phase GaN on GaAs, thus integrating two important optoelectronic materials. However, the doping mechanism of GaAs:N is largely unknown. The thermodynamic solubility of N in bulk GaAs is exceedingly low ($[\mathrm{N}] < 10^{14}\ \mathrm{cm}^{-3}$ at $T = 650\,^\circ\mathrm{C}$) [2–4] due to the formation of a fully relaxed, secondary GaN phase; and, yet, single-phase epitaxial films grown at $T = 400\text{–}650\,^\circ\mathrm{C}$ with [N] as high as ~10% have been reported [5–10]. To explain the approximately 8 orders of magnitude difference in GaAs:N, surface-reconstruction-induced subsurface strain has been implicated [4]. This model requires atomic diffusion from the surface to the second subsurface layer to "deliver" N to the desired sites, but requires no further diffusion in order to "freeze-in" the nitrogen. However, the calculated [N] by this model is 4 orders of magnitude too small. Another puzzle about GaAs:N with high [N] is the considerable degradation of the minority carrier lifetimes [11,12], not seen in ordinary binaries.

In this paper, we suggest that the formation of the secondary GaN phase can be suppressed during epitaxial growth due to surface effects. Indeed, a key factor in fabricating high [N] homogeneous GaAs:N films is to eliminate the formation of GaN precipitates [12]. As such, there exists a new region of the atomic chemical potentials $(\mu_{\mathrm{Ga}}, \mu_{\mathrm{As}}, \mu_{\mathrm{N}})$, available for epitaxial growth but not for equilibrium bulk growth. The chemical potentials are the energies of individual atoms in the reservoirs (such as in the gas sources) that affect impurity substitutional energy [13]. As a result, the calculated maximum solubility [N] at $T = 650\,^\circ\mathrm{C}$ is about 4%, instead of $<10^{14}\ \mathrm{cm}^{-3}$ for equilibrium growth. Because defect formation energies are also functions of the chemical potentials, defect physics at high N concentration is qualitatively different from defect physics at low [N]. For example, the dominant charge-neutral defect is no longer the As antisite in GaAs but the N-N split interstitial. While the As antisite has a doubly occupied (and relatively benign) midgap state, the N-N split interstitial has a singly occupied midgap state. Thus, the split interstitial is a deep trap for both electron and hole. This suggest a microscopic mechanism for the so-far mysterious degradation of the minority carrier lifetimes in epitaxial GaAs:N.

The calculations were carried out using the first-principles pseudopotentials method and local-density approximation. The Ga 3D electrons were treated as core with the nonlinear core correction. At a 40 Ry plane wave cutoff, the calculated formation enthalpies of GaAs and GaN are $\Delta H(\mathrm{GaAs}) = -0.62$ eV vs experimental value of -0.74 eV, and $\Delta H(\mathrm{GaN}) = -1.32$ eV vs experimental value of -1.1 eV. In most of the calculations, however, we used a 25 Ry cutoff to maximize cell sizes. The smaller cutoff results in a slightly larger magnitude of $\Delta H(\mathrm{GaN}) = -1.57$ eV, but has no effect on GaAs. For defect calculations, we used a 64-atom supercell and k points equivalent to the zinc blende ten special k points. For surface calculations, we used a 58-atom plus three vacuum-layer (2×4) surface cell and two k points. We found a 0.25 eV underestimation of the bulk N substitutional energy $\Delta E_{\mathrm{sub}}(\mathrm{N_{As}})$ in comparison with converged, all-electron linearized augmented plane wave calculation [3]. We expect to see similar errors for defect complexes involving one $\mathrm{N_{As}}$. The relative errors in ΔE_{sub} at different sites are, however, less than 0.1 eV.

Equilibrium N solubility.—The absolute formation energy of a charge-neutral defect is defined [13] as

$$\Delta H_f = E_{\mathrm{tot}}(\mathrm{defect}) - E_{\mathrm{tot}}(\mathrm{host}) + n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} + n_{\mathrm{As}}\mu_{\mathrm{As}} + n_{\mathrm{N}}\mu_{\mathrm{N}}, \quad (1)$$

where $E_{\mathrm{tot}}(\mathrm{host})$ is the total energy of the supercell containing 32 GaAs, $E_{\mathrm{tot}}(\mathrm{defect})$ is the total energy for the same supercell but with a defect, and $n = (n_{\mathrm{Ga}}, n_{\mathrm{As}}, n_{\mathrm{N}})$ is the number of particles being removed (upon the defect formation) from the host to a reservoir of chemical potentials $\mu = (\mu_{\mathrm{Ga}}, \mu_{\mathrm{As}}, \mu_{\mathrm{N}})$. If we set the energies of bulk Ga, bulk As, and N_2 gas as the reference zeros, then the chemical potentials satisfy

$$\mu_{\mathrm{Ga}} \le 0, \qquad \mu_{\mathrm{As}} \le 0, \qquad \text{and} \quad \mu_{\mathrm{N}} \le 0. \tag{2}$$

This happens because, if $\mu > 0$, an elemental solid (or gas) will spontaneously form that hinders any further increase of μ. For GaAs to be thermodynamically stable, it also requires that $\mu_{\mathrm{Ga}} + \mu_{\mathrm{As}} = \mu_{\mathrm{GaAs}} = \Delta H(\mathrm{GaAs}) = -0.62$ eV. Thus, defect formation energies in GaAs:N are functions of only two independent variables, $(\mu_{\mathrm{As}}, \mu_{\mathrm{N}})$, satisfying (see Fig. 1)

$$-0.62\ \mathrm{eV} \le \mu_{\mathrm{As}} \le 0 \quad \text{and} \quad \mu_{\mathrm{N}} \le 0. \tag{3}$$

Physically, less negative μ_{As} (or μ_{N}) corresponds to more As (or N)-rich growth conditions, and vice versa. Spontaneous formation of the secondary bulk GaN phase puts a further restriction on the chemical potentials, namely,

$$\mu_{\mathrm{Ga}} + \mu_{\mathrm{N}} \le \mu_{\mathrm{GaN}}. \tag{4}$$

Because $\mu_{\mathrm{GaN}} = \Delta H(\mathrm{GaN}) = -1.57$ eV, the upper limit for μ_{N} is not $\mu_{\mathrm{N}}^{\max} = 0$ in Eq. (3), but $\mu_{\mathrm{N}}^{\max} = -1.57 + 0.62 = -0.95$ eV at $\mu_{\mathrm{Ga}} = -0.62$ eV ($\mu_{\mathrm{As}} = 0$). This defines the "original region" in Fig. 1. Nitrogen substitution is a special case of Eq. (1):

$$\Delta E_{\mathrm{sub}} = \Delta E_{\mathrm{tot}} - \mu_{\mathrm{N}} + \mu_{\mathrm{As}}, \tag{5}$$

where $\Delta E_{\mathrm{tot}} = E_{\mathrm{tot}}(\mathrm{N_{As}}) - E_{\mathrm{tot}}(\mathrm{GaAs})$. The higher the $\mu_{\mathrm{N}}^{\max}$ (and the lower the $\mu_{\mathrm{As}}^{\min}$), the lower the minimum $\Delta E_{\mathrm{sub}}^{\min}$. The calculated $\Delta E_{\mathrm{sub}}^{\min}$ is 1.64 eV, which accounts for the low [N] in equilibrium grown GaAs:N.

Surface enhanced solubility.—In epitaxial growth, a relaxed GaN phase can form if both of the following conditions are satisfied: (i) the spontaneous formation of an N-rich surface layer enabling nitrogen accumulation and clustering. (ii) The nitrogen cluster sizes (or layer thickness) exceed the critical size for dislocation formation. Condition (i) proceeds condition (ii) and sets the physical limit on μ_{N} in epitaxial GaAs:N [cf. Eq. (4)],

$$\mu_{\mathrm{Ga}} + \mu_{\mathrm{N}} \le \mu_{\mathrm{N\,rich}}^{\mathrm{surf}}, \tag{6}$$

where $\mu_{\mathrm{N\,rich}}^{\mathrm{surf}} = \Delta H^{\mathrm{surf}}(\mathrm{N\ rich})$ is the heat of formation of the N-rich layer on the surface. Neglecting the energy of N clustering (ΔE_{clus}), $\mu_{\mathrm{N\,rich}}^{\mathrm{surf}}$ is independent of N concentration. The spontaneous formation of the N-rich layer is equivalent to having the single nitrogen substitutional energy $\Delta E_{\mathrm{sub}}^{\mathrm{surf}}$ [cf. Eq. (5)] equal zero. Thus, to find the N solubility in epitaxial GaAs:N films, we first solve

$$\Delta E_{\mathrm{sub}}^{\mathrm{surf}}(\mu_{\mathrm{As}}^{\min}, \mu_{\mathrm{N}}^{\max}) = 0 \tag{7}$$

to find $(\mu_{\mathrm{As}}^{\min}, \mu_{\mathrm{N}}^{\max})$. Second, we plug $(\mu_{\mathrm{As}}^{\min}, \mu_{\mathrm{N}}^{\max})$ into Eq. (5) to determine $\Delta E_{\mathrm{sub}}^{\min}$. Finally, [N] is calculated using the Boltzmann statistics.

Nitrogen incorporates into GaAs via an N-As exchange mechanism at the topmost surface layer [14–17]. The GaAs (001) surface is As terminated with a (2 × 4) reconstruction (see the inset of Fig. 2) [18]. The $n = 1$ (and $n = 3$) layer contains six (and eight) surface As atoms per 2 × 4 cell. Figure 2 shows ΔE_{sub} for the surface (labeled as 1 and 3D, respectively) and bulk sites along the N- and As-rich boundaries in Fig. 1. We see that (i) $\Delta E_{\mathrm{sub}}(\mathrm{3D})$ and $\Delta E_{\mathrm{sub}}(\mathrm{bulk})$ are only moderately higher than $\Delta E_{\mathrm{sub}}(1)$, 0.30, and 0.24 eV, respectively. Thus, ΔE_{sub} is relatively insensitive to whether the N is in the surface layer or inside the bulk, as well as where it is in the surface. (ii) Using the lower $\Delta E_{\mathrm{sub}}(\mathrm{surface}) = \Delta E_{\mathrm{sub}}(1)$, we determined that $(\mu_{\mathrm{As}}^{\min}, \mu_{\mathrm{N}}^{\max}) = (-0.44\ \mathrm{eV}, 0.0)$, at which $\Delta E_{\mathrm{sub}}^{\min}(\mathrm{bulk})$ is significantly reduced from the original 1.64 to 0.24 eV.

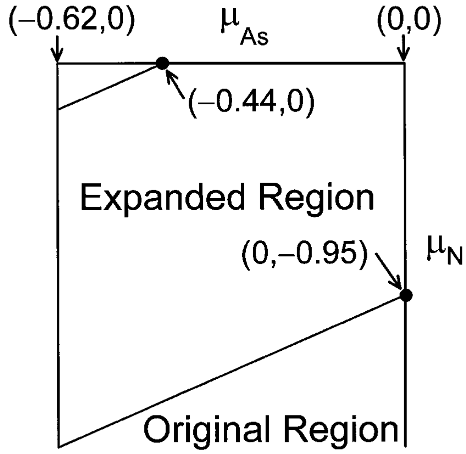

FIG. 1. The physically accessible region of the chemical potentials, $(\mu_{\mathrm{As}}, \mu_{\mathrm{N}})$, is shown. The "original region" is defined by Eqs. (2) and (4), while the "expanded + original" region is defined by Eqs. (2) and (6).

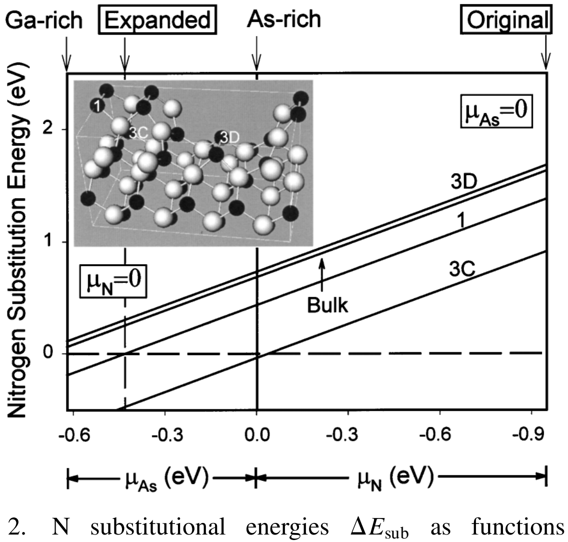

FIG. 2. N substitutional energies ΔE_{sub} as functions of $(\mu_{\mathrm{As}}, \mu_{\mathrm{N}})$. The inset is the GaAs(2 × 4) surface, indicating the various substitution sites. The anion is denoted by a dark circle, while Ga is denoted by a light circle.

This gives rise to [N] ~ 4% at 650 °C. The corresponding accessible ($\mu_{\mathrm{As}}, \mu_{\mathrm{N}}$) is the (expanded + original) region in Fig. 1.

The physics of surface-enhanced N solubility resides in the difference between $\mu_{\mathrm{N\,rich}}^{\mathrm{surf}}$ for the N-rich layer on GaAs surface and μ_{GaN} for bulk GaN. A higher ($\mu_{\mathrm{N\,rich}}^{\mathrm{surf}} - \mu_{\mathrm{GaN}}$) leads to higher N solubility.

The above discussions ignore condition (ii). Consequently, N concentration increases with temperature T. In practice, surface N atoms form clusters and then lower their energies by forming dislocations and relaxed GaN. The probability of clustering enhances significantly when N concentration increases. When such a process dominates, N concentration can decrease with T. This is because, as the temperature increases, it is easier for the N to overcome kinetic barriers to form clusters and, hence, dislocations. This might explain the recent observations [6,10,11] that [N] in high concentration samples is nearly unchanged or decreases slightly as T increases in the range between 400 and 650 °C.

Nitrogen induced defects.—At the high N concentration, the defect physics changes from low [N] in two fundamental ways: (i) The dominant defects are no longer the same. (ii) The electronic properties of the leading defects are qualitatively different. To study minority carrier traps, we considered only charge-neutral defects. Several defects are shown in Fig. 3. (i) The N-N split interstitial. Here, an N_2 molecule replaces an As atom. Each N is threefold coordinated. The N-N is important because of the exceptionally strong N-N bond and the small size of the N atom. The calculated N-N bond length is 1.39 Å, compared to 1.10 Å for the N_2 molecule. (ii) The N-As split interstitial (as a variation to N-N). Here, the calculated N-As bond length is 1.85 Å. (iii) The $(\mathrm{As_{Ga}}\text{-}\mathrm{N_{As}})_{nn}$ pair, where *nn* stands for nearest neighbor. The $\mathrm{N_{As}}$ attracts the $\mathrm{As_{Ga}}$ because $\mathrm{N_{As}}$ is associated with compressive strain due to the small size of N, while $\mathrm{As_{Ga}}$ is associated with tensile strain due to two extra electrons in the nonbonding orbital. The ($\mathrm{As_{Ga}}$-$\mathrm{N_{As}}$) *nn* pair has a 0.5-eV binding energy. Thus, isolated $\mathrm{As_{Ga}}$ is rare at high [N]. The N-As separation in the *nn* pair is 2.86 Å, 47% larger than the sum of atomic radii. Hence, the *nn* pair, where both N and As are threefold coordinated, is qualitatively different from any other distant $\mathrm{As_{Ga}}$-$\mathrm{N_{As}}$ pairs. (iv) The $(\mathrm{V_{Ga}}\text{-}\mathrm{N_{As}})_{nn}$ pair. Despite being the nearest neighbor, the binding energy (<0.05 eV) is negligible.

Figure 4(a) shows the defect formation energy ΔH_f as a function of atomic chemical potentials. At the N solubility limit [($\mu_{\mathrm{As}}^{\mathrm{min}}, \mu_{\mathrm{N}}^{\mathrm{max}}$) = (−0.44 eV, 0)], the dominant

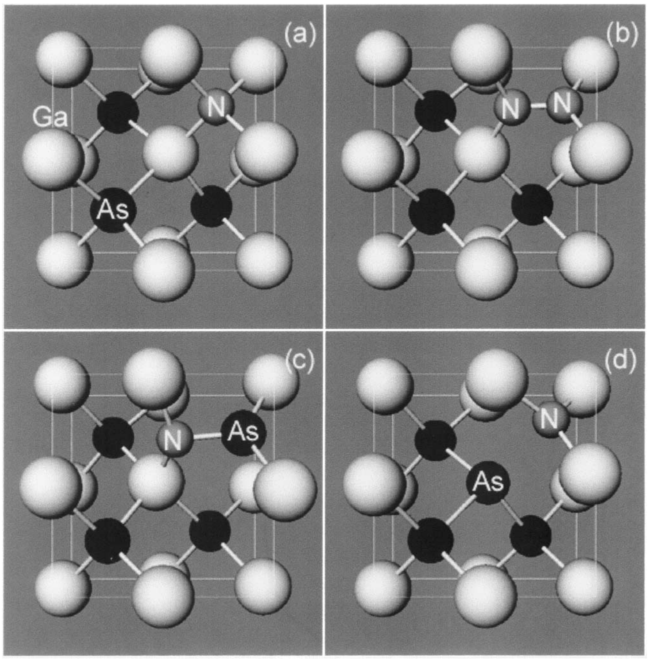

FIG. 3. Calculated atomic positions for (a) substitutional N, (b) N-N, (c) N-As split interstitials, and (d) $(\mathrm{As_{Ga}}\text{-}\mathrm{N_{As}})_{nn}$ complex. As is the dark circle, Ga is the light circle, and N is labeled.

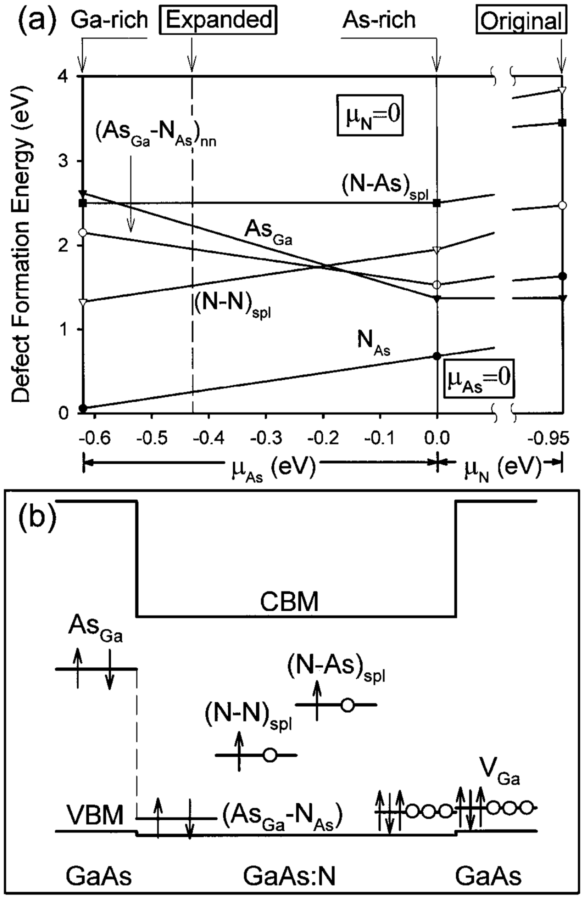

FIG. 4. (a) Defect formation energies. The ordinates and legends are the same as in Fig. 2. (b) Calculated single-particle defect energy levels with electron occupation indicated by arrows. The band diagrams are those of GaAs (ε_g = 1.57 eV) and GaAs:N (ε_g = 1.04 eV) calculated at the zinc blende ten special k points.

defect in GaAs:N is the $(\text{N-N})_{\text{spl}}$ split interstitial, not the As_{Ga} in GaAs. The calculated $\Delta H_f(\text{N-N})_{\text{spl}} = 1.52$ eV is considerably smaller than As_{Ga} (2.24 eV), $(\text{As}_{\text{Ga}}\text{-N}_{\text{As}})_{nn}$ (1.96 eV), and $(\text{N-As})_{\text{spl}}$ (2.49 eV). This gives an $(\text{N-N})_{\text{spl}}$ concentration at $T = 650\,^\circ\text{C}$ of $[\text{C}] = 1 \times 10^{14}\ \text{cm}^{-3}$. Figure 4(b) shows the calculated single-particle gap states, along with the band gaps of bulk GaAs and GaAs:N at $x = 3.125\%$ (i.e., one N in a 64-atom supercell). Inside GaAs, As_{Ga} forms a midgap double donor state, whereas V_{Ga} forms several shallow acceptor states. Inside GaAs:N, the As_{Ga} midgap state disappears with the formation of the $(\text{As}_{\text{Ga}}\text{-N}_{\text{As}})_{nn}$ pairs: The N_{As} state near the conduction band minimum (CBM) pushes down the As_{Ga} gap state to near the valence band maximum (VBM). On the other hand, the effect of N_{As} on V_{Ga} is negligible. Both $(\text{N-N})_{\text{spl}}$ and $(\text{N-As})_{\text{spl}}$ have a deep level (0.38 and 0.62 eV above the VBM or 0.66 and 0.42 eV below the CBM, respectively) with *single* electron occupancy. Assuming reasonable capture cross sections, we anticipate that the split interstitials will be important recombination centers for the minority carrier [19]. The unpaired electron also makes the split interstitials chemically active. They may act as nucleation centers, driving N into clusters [20].

In summary, we showed that one can significantly increase the N chemical potential in epitaxial GaAs:N from equilibrium bulk value without triggering the spontaneous formation of N-rich surface layers and subsequent GaN precipitation. This expanded chemical potential region accounts for experimentally observed high nitrogen solubilities in epitaxial GaAs:N films. At such high N concentrations, the physics of defects changes qualitatively. Nitrogen split interstitials (unimportant at low N concentration) dominate and are potentially detrimental to minority carrier lifetimes.

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