

Interactions between nitrogen, hydrogen, and gallium vacancies in $\text{GaAs}_{1-x}\text{N}_x$ alloys

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The effects of H on the interaction between Ga vacancies V_{Ga} and N in $\text{GaAs}_{1-x}\text{N}_x$ dilute alloys are studied through first-principles total-energy calculations. We find that N binds to Ga vacancies and that in the presence of H this binding is enhanced. The formation energy of V_{Ga} bonded to N and H (resulting in a N-H- V_{Ga} complex) can be more than 2 eV lower than that of the isolated Ga vacancy V_{Ga} in GaAs. Our finding that the concentration of V_{Ga} increases with N and even more in the presence of H allows us to interpret several recent experiments.

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The differences in size and electronegativity between N and the other column-V elements have resulted in dilute III-V-N alloys with unique properties: just a few atomic percent of N in GaAs causes a huge band gap reduction.¹ InGaAsN alloys can be lattice matched to GaAs by controlling the $[\text{N}]/[\text{In}]$ ratio. These InGaAsN alloys are currently being investigated for applications ranging from lasers to solar cells. However, defects have been observed to strongly affect the alloy properties. As-grown material is typically of poor optical quality, and annealing is required in order to improve the luminescence. Despite an intense effort to improve the structural quality and electronic properties of $\text{GaAs}_{1-x}\text{N}_x$ and InGaAsN, these dilute-nitride alloys still exhibit low carrier mobility and short minority-carrier lifetime, as evidenced by low photoluminescence (PL) intensity and lifetime.^{2,3} The nature and origin of the defects responsible for these phenomena are still being debated.

Some recent experimental studies have implied the effect of N on the presence of gallium vacancies in InGaAsN. Li *et al.* described positron annihilation measurements of gallium vacancies in InGaAsN grown by gas-source molecular-beam epitaxy (MBE).⁴ Toivonen *et al.*, also using positron annihilation spectroscopy, reported an increase in defect complexes containing Ga vacancies up to 10^{18} cm^{-3} when the N concentration is increased (up to 5%).⁵ They found that the concentration of gallium vacancies, $[V_{\text{Ga}}]$, decreases and the PL lifetime and intensity improve upon annealing at 700°C. Moreover, InGaAsN grown without the intentional addition of dopants is frequently observed to have a significant ($\sim 10^{17} \text{ cm}^{-3}$) acceptor concentration.^{6,7} Although these acceptors have sometimes been ascribed to unintentional carbon doping, the acceptor concentration often exceeds the observed carbon concentration, implying that intrinsic defects may be acting as acceptors.⁷ These experiments provide strong motivation for developing a microscopic understanding of defect physics in the dilute nitride alloys.

In addition, hydrogen could also affect the formation of Ga vacancies in InGaAsN. Indeed, growth of $\text{GaAs}_{1-x}\text{N}_x$ alloys usually involves hydrogen,¹ as in the case of metal

organic chemical vapor deposition (MOCVD)³ or gas-source MBE.^{8,9} The important effect of hydrogen on the band gap and on doping of $\text{GaAs}_{1-x}\text{N}_x$ has been previously noted: it was shown that N can drastically change the behavior of H in dilute $\text{GaAs}_{1-x}\text{N}_x$ and InGaAsN alloys, stabilizing the H_2^{\pm} complexes when associated with N,¹⁰ or making H predominantly a donor.¹¹ Moreover, H can reverse the effect of nitrogen on the GaAs band gap.^{11,12} Here we focus on hydrogen's interactions with native defects, and show that the presence of hydrogen renders the formation of V_{Ga} even more likely.

In this paper, we examine the important roles of N and H in the formation of gallium vacancies V_{Ga} . We employ first-principles local-density approximation (LDA) calculations to study the interaction between V_{Ga} and N in the presence of H in dilute $\text{GaAs}_{1-x}\text{N}_x$. We find that (i) the binding energy of V_{Ga}^{-3} and N is 0.43 eV, although N is an isovalent impurity; (ii) hydrogen strongly binds to V_{Ga} in GaAs, with binding energies as high as 1.27 eV; (iii) in the presence of N, the binding energy between H and $N-V_{\text{Ga}}$ increases to 2.15 eV; (iv) in the presence of hydrogen, the binding energy between N and H- V_{Ga} increases to 1.31 eV. Our results show that V_{Ga} binds strongly with both N and H. This binding lowers the formation energy of the V_{Ga} in the alloy and raises $[V_{\text{Ga}}]$ well beyond the levels expected in GaAs. We note that the presence of In in an InGaAsN alloy would not directly affect our results about interactions between N or H and V_{Ga} ; therefore, our conclusions also apply to InGaAsN alloys.

The calculations are based on density-functional theory within the local-density approximation¹³ as implemented in the VASP code.¹⁴ The Ga 3d electrons were treated as valence electrons through the use of the ultrasoft pseudopotentials,¹⁵ and supercells containing 64 host atoms were used, where all atomic positions are relaxed according to the calculated Hellmann-Feynman forces. We used a 300 eV kinetic-energy cutoff and have tested the convergence by increasing the cutoff. The uncertainty in the absolute formation energies is estimated to be ± 0.2 eV, mostly due to the LDA error.¹⁶ However, the errors for the binding energies of defect complexes are expected to be much smaller.

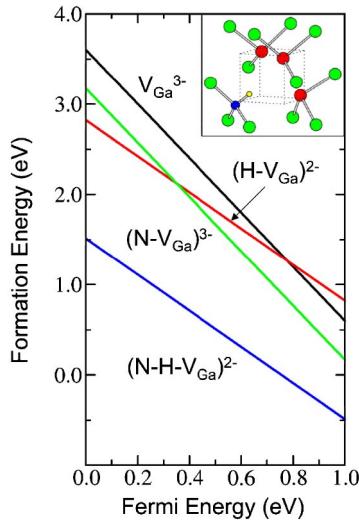


FIG. 1. Formation energy vs. Fermi energy for V_{Ga}^{3-} and $(\text{H}-V_{\text{Ga}})^{2-}$ in GaAs, and for the same defects bonded to N, $(\text{N}-V_{\text{Ga}})^{3-}$ and $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$, in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys under Ga-rich and H-rich conditions. The inset shows the local atomic configuration for the $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$ complex.

The formation energy of a defect α with charge state q is defined as

$$E_f(\alpha^q) = \Delta E_{\text{tot}}(\alpha^q) + n_{\text{Ga}}\mu_{\text{Ga}} + n_{\text{H}}\mu_{\text{H}} + q\varepsilon_F. \quad (1)$$

Here, $\Delta E_{\text{tot}}(\alpha^q) = E_{\text{tot}}(\alpha^q) - E_{\text{tot}}(\text{host}) + n_{\text{Ga}}\mu_{\text{Ga}}^{\text{solid}} + n_{\text{H}}\mu_{\text{H}}^{\text{H}_2} + q\varepsilon_{\text{VBM}}$. $E_{\text{tot}}(\alpha^q)$ is the total energy of the defect, and $E_{\text{tot}}(\text{host})$ is the total energy of the host (GaAs or $\text{GaAs}_{1-x}\text{N}_x$, which is represented by a 64-atom GaAs supercell where one of the As is substituted by a N atom). n_{Ga} and n_{H} are the number of Ga and H atoms removed from the host to form the defect. For example, for $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$ in $\text{GaAs}_{1-x}\text{N}_x$, $q = -2$, $n_{\text{Ga}} = 1$ and $n_{\text{H}} = -1$. μ_{H} is the chemical potential of hydrogen referenced to H_2 molecule in vacuum at $T=0$, and μ_{Ga} is the Ga chemical potential referenced to bulk Ga crystal, which obeys the equilibrium condition $\mu_{\text{Ga}} + \mu_{\text{As}} = \Delta H_f(\text{GaAs})$, where $\Delta H_f(\text{GaAs}) = -0.67$ eV is the calculated enthalpy of formation of GaAs. We report our results for Ga-rich conditions, i.e., $\mu_{\text{Ga}} = 0$, and H-rich conditions, i.e., $\mu_{\text{H}} = 0$. Results for other achievable chemical potentials can be easily derived from Eq. (1).¹⁷ Finally, ε_F is the Fermi energy with respect to the valence-band maximum (VBM).

First, we discuss the effect of nitrogen on the formation energy of V_{Ga} in dilute $\text{GaAs}_{1-x}\text{N}_x$. We find that the isolated V_{Ga} in GaAs is an acceptor that is predominantly stable in the 3- charge state (V_{Ga}^{3-}). The transition levels to other charge states (-2, -1, and 0) occur at less than 0.2 eV above the VBM.¹⁸ The formation energy E_f of V_{Ga}^{3-} is 3.60 eV for $\varepsilon_F = 0$. Now we examine what happens when V_{Ga} is associated with N in $\text{GaAs}_{1-x}\text{N}_x$, i.e., the vacancy is surrounded by three As and one N atoms. The complex $\text{N}-V_{\text{Ga}}$ is still an acceptor predominantly in the 3- charge state [$(\text{N}-V_{\text{Ga}})^{3-}$],¹⁹ but in the presence of N, the formation energy of V_{Ga} is 0.43 eV, lower than for the isolated V_{Ga}^{3-} . This

lowering provides clear evidence of an attractive interaction between nitrogen and V_{Ga} . The formation energies of these defects are illustrated in Fig. 1.

Figure 1 also shows the effect of hydrogen on the formation energy of a Ga vacancy. We studied two cases: isolated V_{Ga} in GaAs, and V_{Ga} bonded with a N atom in $\text{GaAs}_{1-x}\text{N}_x$. For the isolated V_{Ga} , H bonds to one of the As neighbors, saturating its dangling bond, and forms a $V_{\text{Ga}}-\text{H}$ complex occurring predominantly in the 2- charge state [$(\text{H}-V_{\text{Ga}})^{2-}$]. The formation energy of $(\text{H}-V_{\text{Ga}})^{2-}$ is 0.78 eV lower than the isolated V_{Ga}^{3-} . In the case of $(\text{N}-V_{\text{Ga}})^{3-}$ in $\text{GaAs}_{1-x}\text{N}_x$, H forms a strong chemical bond with N and the formation energy of $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$ is 1.66 eV lower than that of $(\text{N}-V_{\text{Ga}})^{3-}$. In this case, the energy lowering by 1.66 eV compared to 0.78 eV in the absence of nitrogen reflects mostly the stronger chemical bond between N and H compared to As-H. Since lower formation energies translate into higher concentrations, our results clearly show that in the presence of N, $[V_{\text{Ga}}]$ will increase, and that the presence of H will strongly enhance the effect of nitrogen on $[V_{\text{Ga}}]$ in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys.

In order to provide a systematic description of the reduction of the V_{Ga} formation energy in the presence of N and H in GaAs, we calculated the binding energy E_b for a series of reactions involving N, H, and V_{Ga} in GaAs, described below. Note that these binding energies are independent of the position of the Fermi level and atomic chemical potentials, since charge and number of atoms are conserved in each of these following reactions.

(1) $(\text{N}-V_{\text{Ga}})^{3-} + E_b \rightleftharpoons V_{\text{Ga}}^{3-} + \text{N}$. The binding energy for this reaction is $E_b = 0.43$ eV, which, by our definition, is exactly the lowering of formation energy of V_{Ga}^{3-} in $\text{GaAs}_{1-x}\text{N}_x$ relative to that in GaAs (Fig. 1). The reason for this energy lowering is due to the level repulsion between the occupied $t_{2v}(V_{\text{Ga}})$ and the empty $t_{2c}(N_{\text{As}})$ states that pushes the $t_{2v}(V_{\text{Ga}})$ states down in energy. This level repulsion is most efficient when the V_{Ga} state is fully occupied, i.e., in the 3- charged state, but less efficient when V_{Ga} is neutral.^{19,20} The binding between N and V_{Ga}^{3-} leads us to expect an increase in $[V_{\text{Ga}}]$ with the nitrogen concentration.

(2) $(\text{H}-V_{\text{Ga}})^{2-} + E_b \rightleftharpoons V_{\text{Ga}}^{3-} + \text{H}^+$. Here, in the absence of N, H^+ at the bond center site next to an As atom is attracted to the V_{Ga}^{3-} to form a stable complex $(\text{H}-V_{\text{Ga}})^{2-}$ with $E_b = 1.27$ eV. The binding between H and V_{Ga} also indicates that $[V_{\text{Ga}}]$ in GaAs will increase with H concentration. Note that we have assumed H to be in the (+) charge state. However, when ε_F is close to the conduction-band minimum, isolated H^- and V_{Ga}^{3-} could be more stable.

(3) $(\text{N}-\text{H}-V_{\text{Ga}})^{2-} + E_b \rightleftharpoons V_{\text{Ga}}^{3-} + (\text{N}-\text{H})^+$. This reaction is intended to illustrate that in the presence of the (N-H) pair in GaAs, the formation energy of V_{Ga}^{3-} is lowered by $E_b = 1.48$ eV, forming the stable $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$ complex. The increase of the binding energy [1.05 eV compared to reaction (1) or 0.21 eV compared to reaction (2)] suggests that the presence of H enhances the coupling between N and V_{Ga} and lowers the formation energy of V_{Ga} -related complexes.

Alternatively, the formation of the $(\text{N}-\text{H}-V_{\text{Ga}})^{2-}$ complex

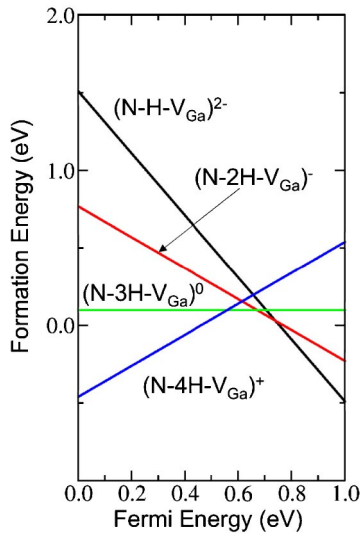


FIG. 2. Formation energy vs Fermi energy for $(\text{N-H-V}_{\text{Ga}})^{2-}$, $(\text{N-2H-V}_{\text{Ga}})^-$, $(\text{N-3H-V}_{\text{Ga}})^0$, and $(\text{N-4H-V}_{\text{Ga}})^+$ complexes in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys. Ga-rich conditions and equilibrium with H_2 at $T=0$ are assumed.

in equation (3) can be considered as a product of the reaction $(\text{N-H-V}_{\text{Ga}})^{2-} + E_b \rightleftharpoons (\text{N-V}_{\text{Ga}})^{3-} + \text{H}^+$. The presence of H^+ significantly lowers the formation energy of the $(\text{N-V}_{\text{Ga}})^{3-}$ defect complex, with $E_b = 2.15$ eV. The formation of the $(\text{N-H-V}_{\text{Ga}})^{2-}$ complex in equation (3) can also be considered as a product of the reaction $(\text{N-H-V}_{\text{Ga}})^{2-} + E_b \rightleftharpoons (\text{H-V}_{\text{Ga}})^{2-} + \text{N}$. This reaction shows that in the presence of N, the formation energy of $(\text{H-V}_{\text{Ga}})^{2-}$ is lowered by $E_b = 1.31$ eV in $\text{GaAs}_{1-x}\text{N}_x$. These large binding energies [compared to reactions (1) and (2) above] are mainly due to the formation of the strong N-H chemical bond in the $(\text{N-H-V}_{\text{Ga}})^{2-}$ complex.

We also studied $\text{N-}n\text{-V}_{\text{Ga}}$ defects with multiple H atoms: $\text{N-}n\text{-H-V}_{\text{Ga}}$ with $n=2,3,4$. The formation energies are shown in Fig. 2. $(\text{N-H-V}_{\text{Ga}})^{2-}$ has a formation energy of 1.51 eV at $\varepsilon_F=0$ in $\text{GaAs}_{1-x}\text{N}_x$. A second hydrogen atom bonds to one of the As atoms that surrounds V_{Ga} and forms a $\text{N-2H-V}_{\text{Ga}}$ complex that can be stable in the $-$ and 0 charge states with formation energies of 0.77 and 0.70 eV, respectively [only the $-$ charge state is shown in Fig. 2]. The lowering of the formation energy of $(\text{N-2H-V}_{\text{Ga}})^-$ by 0.74 eV with respect to $(\text{N-H-V}_{\text{Ga}})^{2-}$ is mostly due to the formation of an As-H chemical bond at the V_{Ga} . Note that this value of 0.74 is smaller than the value of 1.66 eV for the addition of the first H^+ that forms the $(\text{N-H-V}_{\text{Ga}})^{2-}$ complex. This is because the first H is attached to N with a strong N-H chemical bond, whereas the second H is bonded to As with a weaker As-H bond. Furthermore, the second H also experiences H-H repulsion. When a third H atom is added, it bonds to a second As atom surrounding the V_{Ga} and forms the $(\text{N-3H-V}_{\text{Ga}})^0$ complex, which is stable only in the neutral charge state, $(\text{N-3H-V}_{\text{Ga}})^0$, with formation energy 0.10 eV. In this case the $t_2(\text{V}_{\text{Ga}})$ state in the band gap is fully occupied. Again, we find a lowering by 0.67 eV in the formation energy with respect to $(\text{N-2H-V}_{\text{Ga}})^-$. Finally, a fourth hydrogen atom can bond to the remaining As atom, resulting in

a complex that acts as a donor, $(\text{N-4H-V}_{\text{Ga}})^+$. The formation energy of -0.46 eV at $\varepsilon_F=0$ again reflects a lowering by 0.56 eV compared to $(\text{N-3H-V}_{\text{Ga}})^0$ due to formation of an additional As-H bond. We note that the lowering of the formation energy decreases as the number of added H atoms in the vacancy increases, presumably due to H-H repulsion in the complex.

These results indicate that the formation energies of $\text{N-}n\text{-H-V}_{\text{Ga}}$ complexes decrease as n increases up to $n=4$. However, we point out that for entropic reasons complexes with these larger numbers of H atoms are less likely to form when the H concentration is low and the temperature is high. In addition, we note that the formation energies shown in Fig. 2 assume equilibrium with H_2 molecules at $T=0$. Hydrogen incorporation takes place during growth at high temperature, which causes a strong decrease in μ_{H} .²¹ Lower values of μ_{H} lead to an increase of the formation energy, rendering defect complexes with multiple H less favorable.

Our results help in interpreting several recent experiments. The finding that $[\text{V}_{\text{Ga}}]$ increases in the presence of nitrogen agrees with the positron annihilation studies of Li *et al.* in InGaAsN grown by gas-source MBE,⁴ as well as those of Toivonen *et al.*⁵ in samples grown by MOCVD. Our results clearly show that in the presence of the N-H pair, the formation of V_{Ga} is enhanced, resulting in a $(\text{N-H-V}_{\text{Ga}})$ -type defect.

In addition, Toivonen *et al.* found that the vacancy concentration decreases upon annealing at 700°C .⁵ We think this decrease in $[\text{V}_{\text{Ga}}]$ could be explained by the diffusion of V_{Ga} out of the sample. We note that in GaAs, the migration barrier of V_{Ga} is only 1.5 eV.²² In pure GaAs, the vacancies would therefore be mobile at temperatures well below 700°C . But in MOCVD-grown $\text{GaAs}_{1-x}\text{N}_x$, the vacancies can only move once their bond with N and H atoms is broken. The reaction that is most appropriate to describe this process is reaction (3) above, which has a binding energy of 1.48 eV. This binding energy needs to be added to the migration barrier for V_{Ga} in the absence of N and H, resulting in a total barrier of $1.48 + 1.5 \approx 3.0$ eV. Assuming reasonable values for the prefactor, a barrier of this magnitude would render Ga vacancies mobile above 650°C , in good agreement with Toivonen *et al.*⁵

We point out that these observations about mobility of V_{Ga} also nicely explain the observed interdiffusion on the group-III sublattice in quantum-well structures, as reported in Refs. 23 and 24. Interdiffusion of Ga and In is mediated by Ga vacancies, and as pointed out above, the interaction with N would render formation of V_{Ga} more likely than in pure GaAs, enhancing the concentration of vacancies and hence, the interdiffusion. Furthermore, Albrecht *et al.* also observed a PL band centered around 0.82 eV in the as-grown samples (about 0.1 eV below the band edge),²³ which was significantly reduced upon annealing. We speculate that this band may arise from N-V_{Ga} complexes, which have transition levels about 0.1 eV above the VBM.¹⁹

Finally, our calculations suggest that N-H-V_{Ga} may act as a shallow acceptor. Although the error bar on the calculated transition levels is too large to allow an unambiguous con-

clusion, N-H- V_{Ga} acting as a shallow acceptor could plausibly explain the reported background acceptor concentration in as-grown InGaAsN.^{6,7} Moreover, growth of InGaAsN by solid-source MBE has been shown to result in much lower acceptor concentrations,²⁵ consistent with the lower likelihood of V_{Ga} formation in this relatively H-free growth environment. Annealing at high temperature will cause both H and V_{Ga} to become mobile. If the hydrogen, which is bonded to an anion and behaves as a donor, is lost faster than V_{Ga} , then the acceptor concentration may increase, as was observed for InGaAsN annealed under nitrogen.⁶ However, when H is depleted more slowly than gallium vacancies, $[V_{\text{Ga}}]$ will decrease, and the observed conversion from p -type to n -type $\text{GaAs}_{1-x}\text{N}_x$ could be a result of the transformation from $(\text{N-H-}V_{\text{Ga}})^{2-}$ to $(\text{N-H})^+$.²⁶

In summary, we have studied the effects of H on the in-

teraction between the intrinsic defect V_{Ga} and N in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys. We have shown that presence of N in $\text{GaAs}_{1-x}\text{N}_x$ reduces the formation energy of V_{Ga}^{3-} by 0.43 eV, resulting in an increase of the V_{Ga} concentration. The effect of N is even stronger in the presence of hydrogen, resulting in a stable complex $(\text{N-H-}V_{\text{Ga}})^{2-}$ with a formation energy $E_f=1.51$ eV under Ga-rich and H-rich conditions in $\text{GaAs}_{1-x}\text{N}_x$, 2.09 eV lower than the isolated V_{Ga}^{3-} in GaAs for $\epsilon_F=0$. We therefore expect a moderate increase of $[V_{\text{Ga}}]$ in $\text{GaAs}_{1-x}\text{N}_x$ with respect to GaAs, and a further increase of $[V_{\text{Ga}}]$ under growth conditions, where H is present.

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¹⁸The $(3-/2-)$, $(2-/1-)$, and $(-/0)$ transition levels are 180, 150, and 130 meV above the valence-band maximum, respectively.

¹⁹In the case of N- V_{Ga} , the $(3-/2-)$ and $(2-/1-)$ transition energies are 110 and 30 meV above the valence-band maximum (VBM), respectively, while the $(-/0)$ is 10 meV below the VBM.

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