

Interactions of hydrogen with native defects in GaN

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The atomic and electronic structure of hydrogen-vacancy complexes in GaN is investigated with pseudopotential-density-functional calculations. Calculated formation energies provide information about the likelihood of incorporation of these complexes in *n*-type and *p*-type material, and binding energies provide a measure for the dissociation energy. Vibrational frequencies yield a signature of the complex that should facilitate experimental identification. The behavior of hydrogenated nitrogen vacancies during annealing of acceptor-doped GaN is discussed, and a correlation with the frequently observed luminescence band around 420 nm is proposed. [S0163-1829(97)51640-7]

Native point defects are known to play an important role in GaN. Nitrogen vacancies were long suspected to be the source of *n*-type conductivity; recently, however, unintentional impurities have been shown to be the dominant donors.^{1,2} Nonetheless, nitrogen vacancies still act as compensating centers in *p*-type GaN. Gallium vacancies are deep acceptors and as such more likely to occur in *n*-type material.³ They have been associated with compensation of highly doped *n*-type GaN,⁴ and proposed to be the source of the commonly observed “yellow luminescence.”⁵ Other types of point defects (antisites or self-interstitials) have sometimes been invoked to explain experiments; first-principles calculations of formation energies³ have shown, however, that their formation energies are high and, therefore, they are unlikely to form in appreciable concentrations during GaN growth.

Hydrogen also strongly affects the properties of GaN. Growth techniques such as metal-organic chemical vapor deposition (MOCVD) or hydride vapor phase epitaxy introduce large concentrations of H into the growing material. In *p*-type material, H behaves as a donor and forms complexes with acceptors; post-growth annealing is required in order to activate the acceptors.^{6,7} It is to be expected that H interacts with other impurities and defects in the material. The present study addresses the interactions with native point defects. Since antisites and self-interstitials are very unlikely to form in GaN,³ we focus our investigations on H interacting with vacancies.

The interaction of H with vacancies is often described in terms of tying off of dangling bonds. We find that this picture does not apply in the case of the nitrogen vacancy (V_N), which is surrounded by Ga atoms at a distance of 1.95 Å from the center of the vacancy. A typical Ga-H bond distance (about 1.6 Å, Ref. 8) is too large for more than one H to fit inside the vacancy. We previously pointed out³ that the dangling bonds on the Ga neighbors of the nitrogen vacancy strongly hybridize. This observation is consistent with the notion that H will not bond to any of the Ga neighbors in particular; rather, the H atom sits at the center of the vacancy, in a rather shallow potential well. For the Ga vacancy (V_{Ga}), we find that one, two, three, or four H atoms can be accommodated in the vacancy, and levels are removed from the band gap as more hydrogens are attached. Distinct N-H

bonds are formed, with a bond length of about 1.02 Å and characteristic vibrational modes.

After a brief description of the computational approach we will discuss the atomic and electronic structure of these complexes in more detail. We will emphasize links to experimental observations, for instance, by providing calculated vibrational frequencies for the complexes. We also propose that the dissociation of a hydrogenated nitrogen vacancy is responsible for the observed shifts in photoluminescence lines during annealing of acceptor-doped GaN.

The calculations are based on density-functional theory in the local-density approximation, using *ab initio* pseudopotentials and a supercell geometry. Details about the computational approach can be found in Refs. 3, 9, and 10. Our calculations have been carried out for the zinc-blende structure; we previously found that formation energies of native defects were very similar in the zinc-blende and wurtzite structures.¹⁰ The interaction between H and the native defects is very localized in nature and is expected to be insensitive to the differences between wurtzite and zinc-blende structures. We used the so-called “nonlinear core correction” (nlcc), which was previously found to provide reliable results for H interactions with GaN.¹¹ We also carried out calculations explicitly including the Ga 3*d* electrons as valence electrons for various test cases. Inclusion of the 3*d* states produced results within 0.2 eV of those obtained with the nlcc. The only exception occurs in the formation energy of the hydrogenated gallium vacancy. Consistent with previous results for V_{Ga} we find that the formation energy of $V_{Ga}H_n$ is underestimated when using the nlcc.¹⁰ However, the binding energies of H to the vacancy are still accurate (to within 0.2 eV). We will therefore report results for the formation energies of $V_{Ga}H_n$ taking the contribution of the 3*d* states to the formation energy into account.

The energetics of a complex can be described by the *formation energy*, the *binding energy*, and the *removal energy*. The formation energy is defined as follows, for the example of a $(V_{Ga}H_n)^q$ complex, where *n* is the number of H atoms and *q* is the charge state of the complex:

$$E_{\text{form}}[(V_{Ga}H_n)^q] = E_{\text{tot}}[(V_{Ga}H_n)^q] - E_{\text{tot}}(\text{GaN, bulk}) + \mu_{Ga} - n\mu_H + qE_F, \quad (1)$$

where $E_{\text{tot}}(V_{\text{Ga}}\text{H}_n)^q$ is the total energy derived from a supercell calculation for the hydrogenated vacancy, and $E_{\text{tot}}(\text{GaN, bulk})$ is the total energy for a supercell containing only bulk GaN. μ_{Ga} and μ_{H} are the chemical potentials of Ga and H, respectively, i.e., the energies of the reservoirs with which Ga and H atoms are exchanged. We will fix the value of μ_{Ga} to correspond to Ga-rich conditions; the results for other conditions could easily be obtained by lowering the value of μ_{Ga} . μ_{H} is fixed to correspond to the energy of H in an H_2 molecule.¹² Finally, q is the charge state of the complex, and E_F is the Fermi level. In the following, we assume that specific charge states have been chosen, as will become clear below.

The *binding energy* reflects how much energy is gained, per H atom, by placing n H atoms in the vacancy:

$$nE_{\text{bind}}(V_{\text{Ga}}\text{H}_n) = -E_{\text{form}}(V_{\text{Ga}}\text{H}_n) + E_{\text{form}}(V_{\text{Ga}}) + nE_{\text{form}}(\text{H}_{\text{int}}). \quad (2)$$

The sign has been chosen such that a positive value indicates a bound configuration. $E_{\text{form}}(\text{H}_{\text{int}})$ represents the formation energy of a hydrogen atom in an interstitial configuration, i.e., the state H assumes after it is released from the hydrogenated vacancy.

The *removal energy*, finally, reflects how much energy is needed to remove one H atom from a complex initially containing n H atoms, leaving $(n-1)$ H atoms behind:

$$E_r(n \rightarrow n-1) = -E_{\text{form}}(V_{\text{Ga}}\text{H}_n) + E_{\text{form}}(V_{\text{Ga}}\text{H}_{n-1}) + E_{\text{form}}(\text{H}_{\text{int}}). \quad (3)$$

Note that we have refrained from calling this quantity a *dissociation energy*; the latter would refer to the activation barrier that needs to be surmounted in order for the complex to break up. The removal energy does not include a barrier, but reflects the energy difference between initial and final states.

Hydrogenated nitrogen vacancies. The nitrogen vacancy is a single donor in GaN.³ Its electronic structure arises from interactions between dangling bonds on the neighboring Ga atoms, leading to one s -like A_1 state and three p -like T_2 states. The small lattice constant of GaN leads to a Ga-Ga distance of only 3.18 Å, quite close to the bond length in bulk Ga.³ The interactions between the Ga atoms surrounding the vacancy are therefore very strong, causing a splitting of A_1 and T_2 states that is larger than the band gap: the A_1 state lies near the top of the valence band (VB), the T_2 states above the bottom of the conduction band (CB). Out of the three electrons contributed by the surrounding Ga atoms, two are placed in the A_1 state, and one would be placed in a T_2 state above the CB; this latter electron would of course be transferred to the bottom of the CB. V_{N} thus acts as a donor.

As discussed in the introduction, putting more than one H atom in the nitrogen vacancy results in large repulsion and high energy. A single H prefers to be located near the center of the vacancy. Hydrogen placed in a totally symmetric position interacts with the A_1 state, lowering its energy, and introducing an additional electron in the CB. In the neutral charge state the $V_{\text{N}}\text{H}$ complex therefore has two electrons in the state above the CB. Allowing the atomic coordinates to relax causes the H to move slightly off center, by less than 0.1 Å; the adiabatic potential energy surface for motion of H

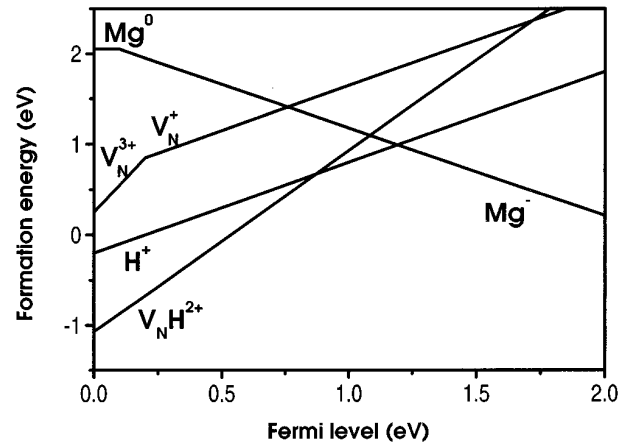


FIG. 1. Formation energy as a function of Fermi energy for the hydrogenated nitrogen vacancy in GaN. For completeness, the formation energies of the unhydrogenated vacancy (V_{N}), of interstitial H^+ , and of the Mg acceptor, are also included (Ref. 12).

around the center of the vacancy is quite flat. In the 2+ charge state, only VB states are occupied; here the H occupies the symmetric on-center position. The potential energy surface for displacements of H is quite shallow; the corresponding vibrational frequency is less than 600 cm^{-1} . This frequency is obviously much smaller than frequencies associated with Ga-H bonds, consistent with the notion that no specific Ga-H bonds are being formed.

The calculated binding energy of the $(V_{\text{N}}\text{H})^{2+}$ complex, expressed with respect to interstitial H in the positive charge state, is 1.56 eV; this same value is also the removal energy. The calculated formation energy of the complex is shown in Fig. 1. The charge state of the hydrogenated vacancy is 2+ for all Fermi level positions; introduction of the hydrogen removes the defect level near the VB that is characteristic of the $+3+$ transition³ of V_{N} (see Fig. 1). $V_{\text{N}}\text{H}$ has a 0/+ level near the CB: within the accuracy of our calculations we cannot determine whether it is actually a resonance or slightly below the CB minimum.

We note that for extreme p -type conditions the formation energy of $(V_{\text{N}}\text{H})^{2+}$ becomes quite low. During high-temperature growth, however, charge neutrality pins the Fermi level near the intersection of the formation energies for Mg acceptors and H^+ interstitials.¹² The formation energy of $(V_{\text{N}}\text{H})^{2+}$ is then comparable to that of V_{N} and some concentration of hydrogenated vacancies will be formed. Note that incorporation during growth is the only way for $V_{\text{N}}\text{H}$ complexes to be formed; formation *after* growth, by diffusion of a hydrogen atom towards V_{N} , is highly unlikely, since both H and V_{N} are donors and occur in the positive charge state in p -type GaN; they therefore repel one another.

Hydrogenated gallium vacancies. Typical N-H bond lengths are around 1.01 Å, allowing for several H atoms to be incorporated in V_{Ga} . The isolated Ga vacancy is a triple acceptor; in the 3- charge state a triply degenerate defect level about 1 eV above the VB is fully occupied (see Fig. 2). Introducing one H atom in the vacancy splits the defect level. H also contributes an electron, so that only two extra electrons are now required to fully occupy the defect levels; $V_{\text{Ga}}\text{H}$ is therefore a double acceptor. In $V_{\text{Ga}}\text{H}_2$, two electrons are contributed, leading to a single acceptor. A symmetry

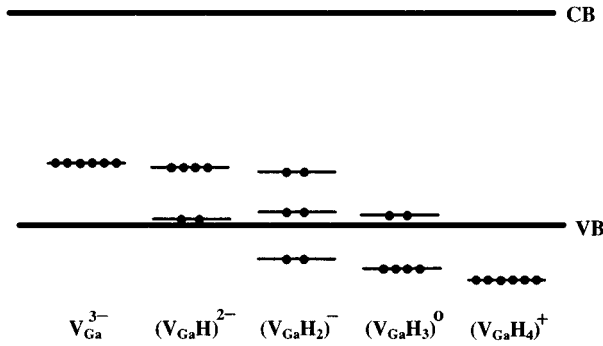


FIG. 2. Schematic diagram depicting Kohn-Sham eigenvalues for hydrogenated Ga vacancies in GaN. The occupation of the levels is shown for charge states corresponding to full occupation.

lowering occurs due to H-H repulsion, causing the H atoms to be no longer oriented strictly along (111) directions. The bond direction of the N-H bonds deviates from (111) by about 9° , and the complex has C_{2v} symmetry. A similar distortion (bond direction deviating by about 12°) appears in $V_{Ga}H_3$. Finally, in $V_{Ga}H_4$ all defect levels are removed from the gap. The fourth H atom contributes an electron that would need to go in a state near the CB, turning this defect into a single donor; when only the levels near the VB are filled, the charge state is +1. These changes in electronic structure upon hydrogenation are very similar to those calculated by Ewels *et al.*¹³ for the case of hydrogenated indium vacancies in InP.

The formation energies of the $V_{Ga}-H_n$ complexes are shown in Fig. 3. The charge states depicted in Figs. 2 and 3 are obviously not the only ones that can occur—however, they are the ones that give rise to the lowest formation energy for each complex. Figure 3 shows that the hydrogenated vacancies have lower formation energies than the isolated gallium vacancy. Whether these complexes actually form during growth, however, depends on the likelihood of multiple H atoms being available at the time of incorporation. The $V_{Ga}H_4$ complex, in particular, is unlikely to occur, in

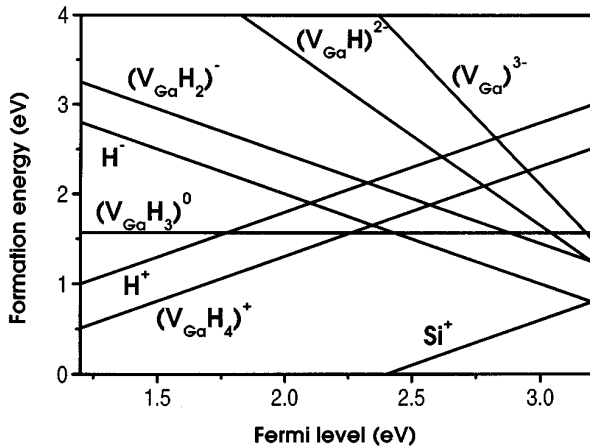


FIG. 3. Formation energy as a function of Fermi energy for hydrogenated gallium vacancies in GaN. For completeness, the formation energies of the unhydrogenated vacancy (V_{Ga}^{3-}), of interstitial H^+ and H^- , and of the Si donor are also included (Ref. 12).

TABLE I. Calculated binding energies [Eq. (2)] and removal energies [Eq. (3)] for hydrogenated gallium vacancies in GaN, expressed with respect to interstitial H^+ .

$V_{Ga}H_n$	E_{bind} (eV)	$E_r(n \rightarrow n-1)$ (eV)
$V_{Ga}H$	3.25	3.25
$V_{Ga}H_2$	3.13	3.00
$V_{Ga}H_3$	2.98	2.68
$V_{Ga}H_4$	2.75	2.06

spite of its low formation energy. From this kinetic point of view, complexes with one or two H atoms ($V_{Ga}H$, $V_{Ga}H_2$) are the most likely to be formed. Capture of H at existing vacancies is also unlikely: gallium vacancies are most likely to form in n -type GaN; hydrogen prefers the negative charge state here (H^-),^{7,12} and is repelled by the negatively charged vacancies. H^+ would be attracted by the gallium vacancies, but is not stable for Fermi level positions above 2.1 eV.⁷

Binding energies and removal energies for hydrogenated gallium vacancies are listed in Table I. These values are expressed with respect to interstitial H in the *positive* charge state [see Eqs. (2) and (3)]. This is a natural choice given the nature of the interaction between H and the vacancy, where each H *donates* an electron. Values with respect to H^- would depend on the position of the Fermi level; the binding energy values could be derived from Fig. 3. Table I shows that binding energies and removal energies decrease as more H atoms are introduced; this reflects repulsion between H atoms in the vacancy. The values in Table I indicate that this H-H repulsion energy is on the order of 0.2 eV.

We have calculated vibrational frequencies for stretch modes of the hydrogenated vacancies in the harmonic approximation. Anharmonic terms may lower the frequency considerably (by as much as 170 cm^{-1}) in the case of N-H vibrations. The calculated frequency for a hydrogen stretch mode in the $V_{Ga}H$ complex is 3100 cm^{-1} , somewhat lower than the value for an NH_3 molecule. For the $V_{Ga}H_4$ complex, the calculated frequency is 3470 cm^{-1} . The higher value reflects repulsion between H atoms.

Finally, we discuss the *role of hydrogenated vacancies in the properties of GaN materials and device structures*. First we focus on V_{Ga} . Gallium vacancies may compensate donors,⁴ and have been proposed as the source of the yellow luminescence (YL).⁵ Both of these roles could also be played by the $V_{Ga}H$ or $V_{Ga}H_2$ complexes (as discussed above, vacancies with larger numbers of hydrogens are unlikely to form). Figure 2 shows that these complexes have levels in the band gap only slightly lower (by 0.1–0.2 eV) than V_{Ga} . The $V_{Ga}H$ and $V_{Ga}H_2$ could, therefore, also contribute to the YL, through transitions between shallow donors and a deep acceptor level. The slight shift in the positions of the levels between various complexes could contribute to the width of the luminescence line. The large value of the binding energy (see Table I) makes dissociation of $V_{Ga}H_n$ complexes unlikely.

Turning now to the hydrogenated nitrogen vacancy, its character as a double donor makes it most favorable in p -type GaN, where it would act as a compensating center. We propose that this complex is responsible for the disappearance and appearance of photoluminescence (PL) lines

during post-growth annealing of Mg-doped layers grown by MOCVD, as described by Götz *et al.*¹⁴ and Nakamura *et al.*¹⁵ A PL line (labeled L1 in Ref. 14) at 3.25 eV is present in as-grown material. Annealing at temperatures above 500 °C causes this line to “redshift.” It was pointed out by Götz *et al.*¹⁴ that this shift occurs at temperatures where negligible activation of Mg acceptors occurs; the PL lines are, therefore, probably not directly associated with Mg or Mg-related complexes.

We suggest that the redshift actually corresponds to a decrease in intensity of the L1 line, accompanied by an increase in intensity of a new line, related to the nitrogen vacancy. The as-grown material may contain a certain concentration of hydrogenated nitrogen vacancies (which have a level near the conduction band that we propose to give rise to the L1 line). When the material is annealed, the hydrogenated vacancy complexes dissociate. Our calculated removal energy of 1.56 eV is consistent with complex dissociation around 500 °C. The resulting nitrogen vacancies have a level near the VB, which we propose to be responsible for

the line around 2.9 eV (~ 420 nm). The presence of compensating centers is certainly consistent with the experimental observations on Mg-doped GaN to date. We note that the $+3+$ transition of the nitrogen vacancy is distinguished by a very large lattice relaxation,³ which has a characteristic experimental signature; for instance, it may explain the observed persistent photoconductivity effects.^{16,17}

In summary, we have presented first-principles results for a variety of configurations of hydrogen-vacancy complexes in GaN. These complexes can incorporate up to four H atoms, occur in multiple charge states, and potentially act as compensating centers. Links to experiment have been pointed out, particularly with regard to vibrational frequencies and photoluminescence lines.

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- ¹C. Wetzel, T. Suski, J. W. Ager III, E. R. Weber, E. E. Haller, S. Fischer, B. K. Meyer, R. J. Molnar, and P. Perlin, *Phys. Rev. Lett.* **78**, 3923 (1997).
 - ²C. G. Van de Walle and J. Neugebauer, in *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, MRS Symposia Proceedings No. 449 (Materials Research Society, Pittsburgh, 1997), p. 861.
 - ³J. Neugebauer and C. G. Van de Walle, in *Festkörperprobleme/Advances in Solid State Physics*, edited by R. Helbig (Vieweg, Braunschweig/Wiesbaden, 1996), Vol. 35, p. 25.
 - ⁴G.-C. Yi and B. W. Wessels, *Appl. Phys. Lett.* **69**, 3028 (1996).
 - ⁵J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **69**, 503 (1996).
 - ⁶S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.* **31**, 1258 (1992).
 - ⁷J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.* **75**, 4452 (1995).
 - ⁸J. E. Northrup, R. Di Felice, and J. Neugebauer *Phys. Rev. B* **56**, 4325 (1997).
 - ⁹R. Stumpf and M. Scheffler, *Comput. Phys. Commun.* **79**, 447 (1994).
 - ¹⁰J. Neugebauer and C. G. Van de Walle, in *Diamond, SiC and Nitride Wide Bandgap Semiconductors*, edited by C. H. Carter, Jr., G. Gildenblat, S. Nakamura, and R. J. Nemanich, MRS Symposia Proceedings No. 339 (Materials Research Society, Pittsburgh, 1994), p. 687.
 - ¹¹J. Neugebauer and C. G. Van de Walle, in *Defect- and Impurity-Engineered Semiconductors and Devices*, edited by S. Ashok, J. Chevallier, I. Akasaki, N. M. Johnson, and B. L. Soporì, MRS Symposia Proceedings No. 378 (Materials Research Society, Pittsburgh, 1995), p. 503.
 - ¹²J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **68**, 1829 (1996).
 - ¹³C. P. Ewels, S. Öberg, R. Jones, B. Pajot, and P. R. Briddon, *Semicond. Sci. Technol.* **11**, 502 (1996).
 - ¹⁴W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, *Appl. Phys. Lett.* **68**, 667 (1996).
 - ¹⁵S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, *Jpn. J. Appl. Phys.* **31**, L139 (1992).
 - ¹⁶C. Johnson, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, *Appl. Phys. Lett.* **68**, 1808 (1996); J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, and H. Morkoc, *ibid.* **69**, 1474 (1996).
 - ¹⁷We recently learned about independent work by C. H. Park and D. J. Chadi that also proposes the nitrogen vacancy to be responsible for the persistent photoconductivity [*Phys. Rev. B* **55**, 12 995 (1997)].