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CHAPTER 11

Theory of Hydrogen in GaN

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I. Introduction

GaN exhibits some unique properties among semiconductors such as a large direct bandgap ($E^{gap} = 3.5\,eV$), a high thermal conductivity, and very

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strong chemical bonds. Because of these properties, the materials system consisting of GaN and its alloys with AlN and InN has been considered ideal for fabricating optoelectronic devices in the blue/ultraviolet region of the optical spectrum (Maruska and Tietjen, 1969). Furthermore, the large melting temperature and the high thermal conductivity make it a good choice for high-temperature and/or high-power devices (see, e.g., Morkoc *et al.*, 1994). Despite significant research in the 1970s and 1980s, severe doping problems hampered the development of GaN technology.

First, as-grown GaN was commonly *n*-type with large carrier background concentrations of up to $10^{20}\,\mathrm{cm}^{-3}$. The high background concentrations commonly were attributed to the presence of N vacancies (see, e.g., Maruska and Tietjen, 1969; Ilegems and Montgomery, 1973). However, recent theoretical (Neugebauer and Van de Walle, 1994b; Van de Walle and Neugebauer, 1997) and experimental (Götz *et al.*, 1996b, 1997; Wetzel *et al.*, 1997) investigations provide strong evidence that unintentional doping with O and Si causes the high carrier concentrations. In fact, modern growth techniques now allow the growth of GaN epilayers with background concentrations of $<10^{16}\,\mathrm{cm}^{-3}$.

Second, *p*-type doping had been difficult to achieve. Efforts to incorporate acceptors in GaN did not produce *p*-type material. In 1989, Amano *et al.* (1989) achieved a major breakthrough when they observed that GaN grown by MOCVD (metal-organic chemical vapor deposition) can be activated by low-energy electron-beam irradiation (LEEBI). Nakamura *et al.* (1992a) later showed that the Mg activation also can be achieved by thermal annealing at 700°C under N_2 ambient. Nakamura *et al.* (1992a) further observed that the process was reversible, with *p*-type GaN reverting to semi-insulating when annealed in a NH_3 ambient, revealing the crucial role played by hydrogen.

Since many of the techniques commonly used to grow GaN, such as MOCVD and HVPE (hydride vapor-phase epitaxy), introduce large quantities of hydrogen-containing species into the growth chamber, the presence of large concentrations of hydrogen in the as-grown material should not come as a surprise. The involvement of hydrogen in the activation of acceptor-doped MOCVD-grown GaN is also confirmed by the achievement of *p*-type GaN by Mg doping in MBE (molecular-beam epitaxy) without any postgrowth treatment (Molnar *et al.*, 1993; Lin *et al.*, 1993); MBE growth, of course, does not introduce hydrogen into the material.

In this chapter we will summarize the properties hydrogen exhibits in GaN and discuss how hydrogen affects doping in GaN. In particular, it will be shown that H in GaN exhibits unique features not observed in the more "traditional" semiconductors such as Si or GaAs. Examples are a very large negative-U effect ($U \approx 2.4\,\mathrm{eV}$), the instability of the bond-centered (BC) site

for positively charged H, high energies for H_2 molecules, and an unusual geometry for the Mg-H complex. All these features are shown to be a consequence of distinctive properties of GaN, namely, the strongly ionic nature and the large bond strength of the Ga-N bond. The formation and dissociation of the Mg-H complex and the consequences for activating of *p*-type GaN will be discussed. Finally, it will be explained why hydrogen is *beneficial* for acceptor incorporation in GaN based on the principle of codoping; the limitations of the codoping process are also identified.

II. Method

First-principles methods have had a major impact on description of the properties of hydrogen in semiconductors. The first applications focused on obtaining defect wave functions and levels in the bandgap. With the advent of the capability to calculate total energies, it becomes possible to identify the stable configurations of hydrogen in the semiconductor lattice and their formation energy, migration paths, and diffusion barriers (Van de Walle *et al.*, 1989). Furthermore, the interaction of H with defects and impurities and the formation of complexes have been studied (Van de Walle *et al.*, 1993). For a comprehensive overview of theoretical work on hydrogen in semiconductors, we refer the reader to the overview article by Estreicher (1995). More recently, formalisms have been developed to use these data to calculate defect and impurity concentrations and solubility limits (Laks *et al.*, 1991).

1. Defect Concentrations and Solubility

The key to describing solubility and doping issues is the calculation of the equilibrium concentration of defects and impurities:

$$c = N_{\text{sites}} g \exp(-E^{\text{f}}/k_{\text{B}}T) \tag{1}$$

where N_{sites} is the number of sites the defect or impurity can be incorporated on, k_{B} is the Boltzmann constant, T is temperature, and E^{f} is the formation energy. g is a degeneracy factor representing the number of possible configurations a defect can assume on a single site.

The formation energy depends on the various growth parameters. For example, the formation energy of interstitial H depends on the abundance of H atoms. The formation energy of a substitutional Mg acceptor on a Ga

site is determined by the relative abundance of Mg, Ga, and N atoms. In a thermodynamic context these abundances are described by the chemical potentials μ_{Ga}, μ_N, and μ_{Mg}. If the defect or impurity is charged, the formation energy depends further on the Fermi level (E_F), which acts as a reservoir for electrons. To be more specific, let us consider the creation of an Mg acceptor. Forming a substitutional Mg acceptor requires the removal of one Ga atom and the addition of one Mg atom. The formation energy is therefore

$$E^f(\text{GaN:Mg}^q_{Ga}) = E_{tot}(\text{GaN:Mg}^q_{Ga}) - \mu_{Mg} + \mu_{Ga} + qE_F \tag{2}$$

where $E_{tot}(\text{GaN:Mg}^q_{Ga})$ is the total energy derived from a calculation for substitutional Mg, and q is the charge state of the Mg acceptor. Similar expressions apply to the hydrogen impurity and to the various native defects.

In order to compare the stability for different structures, the *free energy* instead of the *total energy* has to be employed. The difference between both energies is the energy contribution $-TS$, which can be divided into vibrational and configurational entropy. For point defects, the configurational entropy is simply given by the number of sites at which the defect can be created; this contribution is already taken into account in Eq. (1). The vibrational entropies are, at the present stage, not explicitly included, which would be computationally very demanding. Such entropy contributions cancel to some extent (Qian *et al.*, 1992) and are small enough not to affect any qualitative conclusions. However, more powerful computers and improved methods will make accurate calculations of vibrational entropies more feasible to be carried out for various systems in the near future.

Also, the pressure dependence of the energy is generally small compared with the absolute value. The *formation enthalpy* thus can be replaced by the *total energy*.

2. Energetics, Atomic Geometries, and Electronic Structure

In most of the theoretical studies, the total energy has been calculated employing density-functional theory, a plane-wave basis set, and a supercell geometry (Neugebauer and Van de Walle, 1995a; Bosin *et al.*, 1996; Okamota *et al.*, 1996). Only one study has been performed using a different approach: Estreicher and Maric (1996) performed Hartree-Fock–based cluster calculations. We will provide here only a brief overview of these techniques. A thorough discussion has been given by Estreicher (1994, 1995).

a. Density-Functional Theory Calculations

Density-functional theory (DFT) calculations based on pseudopotentials, a plane-wave basis set, and a supercell geometry are now regarded as standard for performing first-principles studies of defects in semiconductors. DFT in the local density approximation (LDA) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) allows a description of the many-body electronic ground state in terms of single-particle equations and an effective potential. The effective potential consists of the ionic potential due to the atomic cores, the Hartree potential describing the electrostatic electron-electron interaction, and the exchange-correlation potential that takes into account the many-body effects. This approach has proven to describe with high accuracy quantities such as formation energies, atomic geometries, charge densities, etc. One shortcoming of this method is its failure to produce accurate excited-states properties—the bandgap is commonly underestimated. In cases where the bandgap enters the calculations, a careful analysis of the results still allows extraction of reliable data. Such situations will be discussed where appropriate (see Neugebauer and Van de Walle, 1994a, 1995b).

b. Hartree-Fock–Based Cluster Calculations

Hartree-Fock–based models commonly employ quantum-chemistry approaches that have been applied successfully to atoms and molecules. The main problems with the technique are the neglect of correlation effects (resulting in too high bandgaps) and the computational demands; *ab initio* Hartree-Fock methods can only be applied to systems with small numbers of atoms. The problem is that these methods require the evaluation of a large number of multicenter integrals. Simpler semiempirical methods have been developed that either neglect or approximate some of these integrals. The accuracy and reliability of these semiempirical methods are hard to assess.

III. Monatomic Hydrogen in GaN

Several groups have calculated energetics, atomic geometries, and electronic structure for isolated hydrogen in a variety of different interstitial positions in GaN. Neugebauer and Van de Walle (1995a, 1995b) and Bosin *et al.* (1996) employed pseudopotential-density-functional theory calcula-

tions, and their conclusions are very similar. Some quantitative differences will be discussed where appropriate. Estreicher and Maric (1996) reported preliminary Hartree-Fock–based calculations on 44 atom clusters of zinc-blende GaN.

The calculation of the total energy surface for monatomic hydrogen in semiconductors is a powerful approach to get a very direct insight into basic properties such as stable geometries, formation energies, and migration behavior. For hydrogen in *zinc-blende* GaN, such calculations have been reported by Neugebauer and Van de Walle (1995a). Bosin *et al.* (1996) studied hydrogen in *wurtzite* GaN but restricted their calculations to sites with C_{3v} symmetry. Since the zinc-blende and wurtzite structures only differ beyond third nearest neighbors, the differences with respect to atomic and electronic structure of the hydrogen impurity are expected to be small.

1. Atomic Geometries and Stable Positions

a. *Hydrogen in the Positive Charge State*

Hydrogen in the positive charge state favors positions on a sphere with a radius of ~ 1 Å centered on an N atom; that is, H^+ prefers only positions with N as a nearest neighbor. The calculated H-N bond length for all these positions is $1.02 \cdots 1.04$ Å, close to the experimental bond length in NH_3 ($d_{N\text{-}H} = 1.04$ Å). Among these positions, the nitrogen antibonding site (AB_N) is energetically most stable (see Fig. 1b). All other sites, where a H-N bond cannot be formed, are found to be energetically less favorable.

The preference for the N antibonding site is in striking contrast with the behavior of H^+ in Si or GaAs, where the bond-centered (BC) position (see Fig. 1c) was found to be energetically most stable (Van de Walle *et al.*, 1989; Pavesi and Gianozzi, 1992). This difference can be understood by noting the very different character of the chemical bond in GaN and, for example, GaAs. In GaAs or Si there is a pronounced maximum of the charge density at the bond center due to the strong covalent character of these materials. For the more ionic GaN, however, there is no local maximum at the bond center but an almost spherical distribution of the charge density around the strongly electronegative nitrogen atom. H^+, which is simply a proton, prefers a position where it obtains maximum screening; that is, it prefers sites with a high charge density. This explains why H^+ prefers the BC position in covalent semiconductors such as Si and GaAs, whereas in an ionic compound such as GaN, *all* positions around the N atom are low in energy. At the BC site an extra energy cost needs to be paid due to the strain energy involved in relaxing the Ga and N atoms outward. The Ga-N bond

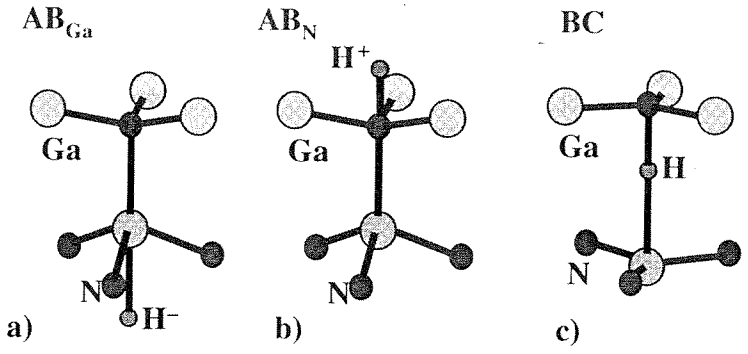

FIG. 1. Ball and stick model of configurations of interstitial hydrogen in GaN: (a) the Ga antibonding site (AB_{Ga}); (b) the N antibonding site (AB_N); (c) the bond-centered position (BC).

has to be stretched by more than 40% of the bond length. Since GaN has very strong interatomic bonds, this process is energetically very costly, rendering the BC site unfavorable.

Despite the high cost, the BC site is still only 0.1 eV higher in energy than the AB_N site, where virtually no relaxation is necessary. Estreicher and Maric (1996), in their Hartree-Fock–based calculations, actually found H^+ to prefer the BC site.

b. Hydrogen in the Neutral Charge State

For neutral hydrogen (H^0), much smaller energy differences (<1 eV) between different sites are found (except for regions within 1 Å of the nuclei, where a strong repulsion is found), indicating a rather flat total energy surface (Neugebauer and Van de Walle, 1995a). A similar behavior also has been found for H^0 in silicon (Van de Walle *et al.*, 1989). Neugebauer and Van de Walle (1995a) find the Ga antibonding site (AB_{Ga}) to be energetically preferred (see Fig. 1a). The H-Ga bond length for this site is only 0.1 Å smaller than the Ga-N bond length, causing the Ga antibonding site to nearly coincide with the position of the tetrahedral interstitial site (T_d^{Ga}). Bosin *et al.* (1996) find the BC site to have the lowest energy. The difference can be traced back to the difference in the bandgap. Because of the small value of the gap in the calculations by Bosin *et al.*, the lowest state to be occupied (for H^0 or H^-) was probably not a H-induced impurity level but a conduction-band state. Estreicher and Maric (1996) reported that the T_d^{Ga} and BC sites are almost degenerate in energy.

c. *Hydrogen in the Negative Charge State*

All calculations find that negatively charged hydrogen (H^-) prefers the Ga antibonding site (very close to the T_d^{Ga} site, as discussed earlier). At this site the distance to the neighboring Ga atoms is maximized, and the charge density of the bulk crystal has a local minimum. The Ga-H bond length is 1.76 Å (Neugebauer and Van de Walle, 1995b).

2. MIGRATION PATH AND DIFFUSION BARRIERS

Based on the total energy surfaces, the migrational path and diffusion barriers of H in GaN can be obtained immediately. In the *positive* charge state, intermittent diffusion occurs; the diffusion path is characterized by a basin of attraction around the N atoms with barriers smaller than 0.1 eV in which the H atom is localized until an intermittent jump to a nearby basin of attraction occurs. The diffusion barrier to jump from one basin to the next is 0.7 eV. This barrier is slightly larger than for H^+ in Si (Van de Walle *et al.*, 1989) but still sufficiently small to ensure high mobility even at temperatures only slightly above room temperature. Indeed, experiments on hydrogen diffusion by Götz *et al.* (1995) have confirmed this prediction.

For *negatively* charged H, a very different migration behavior has been found. H^- is strongly confined to the T_d^{Ga} site, giving rise to a very large migration barrier of ~ 3.4 eV. H^- is therefore virtually immobile in GaN.

3. FORMATION ENERGIES AND NEGATIVE-*U* EFFECT

Results for the formation energies of hydrogen in the positive, neutral, and negative charge state are shown in Fig. 2. For Fermi energies below ~ 2.1 eV, H^+ is the energetically most stable species. For Fermi levels higher in the gap, H^- is more stable. Since hydrogen has the lowest formation energies under extreme *n*- or *p*-type conditions, where it behaves as an acceptor or donor, respectively, it can be potentially a very efficient compensating center. We will come back to this point in Section VII.

The fact that hydrogen has a significantly lower formation energy under *p*-type conditions than under *n*-type conditions implies that the solubility of hydrogen is considerably higher in *p*-type than in *n*-type GaN. These theoretical predictions have been confirmed by the recent experimental observations of Götz *et al.* (1995) on plasma hydrogenation of MOCVD-grown GaN. H is readily incorporated in *p*-type GaN, consistent with a high diffusivity and solubility of H^+, whereas no detectable levels of H were

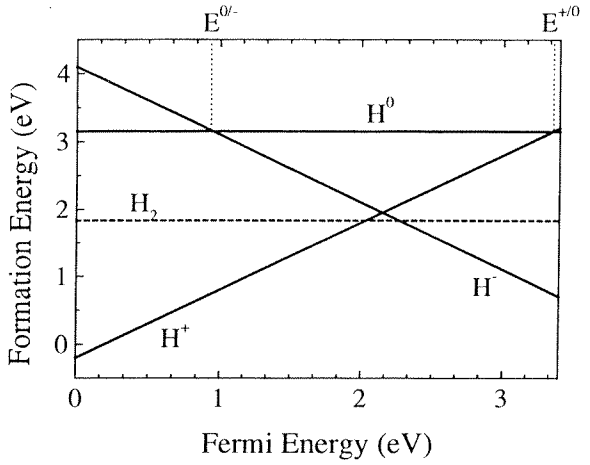

FIG. 2. Formation energy as a function of the Fermi level for H^+, H^0, and H^- (solid lines). Further included are the formation energies for a hydrogen molecule (dashed line) and for a magnesium-hydrogen complex (long-dashed line). $E_F = 0$ corresponds to the top of the valence band. The formation energy is referenced to the energy of a free H_2 molecule. (From Neugebauer and Van de Walle, 1995a.)

found in *n*-type GaN, consistent with a low diffusivity, as well as a lower solubility, of H^-.

The formation energies shown in Fig. 2 indicate that neutral hydrogen is never stable in GaN. This behavior is characteristic of a negative-U system. The value of U is given by the difference between acceptor $(0/-)$ and donor $(+/0)$ levels: $U = E^{0/-} - E^{+/0} \approx -2.4\,\text{eV}$. A negative-$U$ behavior also was found for H in Si ($U = 0.4\,\text{eV}$) (Van de Walle *et al.*, 1989; Johnson *et al.*, 1994). The value of $-2.4\,\text{eV}$, however, is unusually large and, to our knowledge, larger than any measured or predicted value for H in any other semiconductor.

The unusually large negative-U behavior can be understood by analyzing the total energy surface in more detail (Neugebauer and Van de Walle, 1995a). Figure 3 shows the variation in the hydrogen formation energy along a line between the AB_N site (preferred by H^+) and the AB_{Ga} site (preferred by H^0 and H^-). The results in Fig. 3 reveal some remarkable features: (1) for a *fixed* hydrogen position x, the transition levels $(0/-$ and $+/0)$ are nearly equal (within 0.1 eV), and (2) the total energy surface for neutral hydrogen is flat compared with both positively and negatively charged hydrogen. These observations apply not only to those positions depicted in Fig. 3 but also to *all* positions. The only exceptions are sites near the atomic cores, where the energy of H in any charge state is very high due

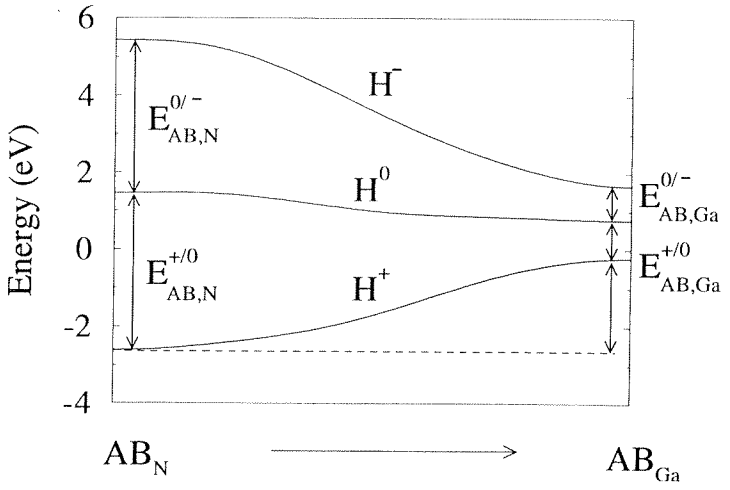

FIG. 3. Variation of the hydrogen formation energy for all three charge states along the shortest path between the AB_N and AB_{Ga} sites. The Fermi level is set to the top of the valence band. (From Neugebauer and Van de Walle, 1995a.)

to atomic repulsion. We note that these features are not specific to GaN but also apply to GaAs or Si (Van de Walle *et al.*, 1989).

Both these features, as well as the large negative-U character, can be explained by analyzing the nature of the interaction between hydrogen and the semiconductor (Neugebauer and Van de Walle, 1995a). Neutral H consists of a proton and an electron. The *proton* prefers regions of high charge density, whereas the *electron* tends more toward regions where the charge density is low. This already explains the location of H^+ (a proton) in Si, GaAs, and GaN, as discussed earlier, and it explains why H^- (in which electrons dominate) prefers T_d or AB sites. Moving *neutral* hydrogen into regions with higher charge density causes the proton to gain about the same amount of energy as the electron loses. To first order, the total energy of H^0 is then independent of the charge density, which explains the flat total energy surface. Deviations occur because the electronic orbital (contrary to the proton) has a finite size and thus experiences variations in the charge density over a certain spatial extent. Nevertheless, this simple model works remarkably well, even for the BC site where the electron is known to reside in an antibonding combination of host-atom orbitals. For the preceding discussion, no assumptions about the specific nature of the semiconductor were made. Therefore, these features should be a general property of hydrogen in *any* semiconductor.

Based on the preceding discussion, a model can be constructed with the following assumptions: (1) the transition levels $E_x^{+/0}$ and $E_x^{0/-}$ are exactly

equal for all positions x, and (2) the total energy surface for H^0 is completely flat. It then follows immediately that the total energy surface of the positive charge state is the exact mirror image of the negative charge state. Consequently, minima in the total energy surface for H^+ correspond to maxima in the charge density of H^- and vice versa (see Fig. 3). This immediately predicts that $U = E^{0/-} - E^{+/0}$, calculated for the most stable positions of each charge state, will be negative. As discussed earlier, for H^+, minima and maxima correspond to maxima and minima in the charge density. Consequently, in covalent systems (Si) or weakly ionic systems (GaAs), possible sites for H have a modest variation in charge density—hence the absolute value of U will be modest, although U will be negative. However, much larger variations in the charge density exist in ionic crystals—therefore, for this class of materials the largest negative-U values are expected.

IV. Hydrogen Molecules in GaN

Relatively little is known concerning hydrogen molecules in GaN. To our knowledge, there have been no experimental reports about the existence of H_2 molecules in GaN or its alloys. Hydrogen molecules have been studied theoretically using a standard first-principles method by Neugebauer and Van de Walle (1995a). The atomic geometry and formation energy for several symmetric as well as asymmetric configurations were considered. The value for the energetically most stable configuration has been included in Fig. 2. The H_2^* geometry, as proposed by Chang and Chadi (1990), also was investigated by Neugebauer and Van de Walle (1995b). Here one hydrogen atom is located at the BC site and the other at either the N or Ga antibonding site. It was found that H_2^* is even less favorable than the H_2 molecule geometry. As can be seen in Fig. 2, H_2 is unstable with respect to dissociation into monatomic hydrogen. The formation energy of ~ 1.8 eV is much higher than that of H_2 molecules in vacuum. Both features, the low stability of the hydrogen molecule and its unfavorably high formation energy, are distinct properties of GaN and again very different from the case of Si or GaAs.

V. Hydrogen-Acceptor Complexes in GaN

Hydrogen is well known to form complexes with shallow impurities in semiconductors. Here we focus on acceptor-hydrogen complexes since, as discussed in Section III.1.c, hydrogen has a low solubility in n-type GaN.

On formation of the acceptor-hydrogen complex, the acceptor level disappears into the valence band—the acceptor is passivated and electrically inactive. Hydrogen-acceptor complexes have been observed in a variety of semiconductors, and properties such as local vibrational modes, binding and activation energy, bonding geometry, etc. have been studied extensively (see, e.g., Pankove and Johnson, 1991).

1. THE Mg-H COMPLEX

The technologically most commonly used acceptor is magnesium, and consequently, most investigations focused on hydrogen interaction with Mg. The structure, energetics, and vibrational frequencies of the Mg-H complex have been studied by several groups for zinc-blende GaN (Neugebauer and Van de Walle, 1995a) and wurtzite GaN (Bosin *et al.*, 1996; Okamoto *et al.*, 1996).

Neugebauer and Van de Walle (1995a) and Bosin *et al.* (1996) find that the hydrogen atom does not form a bond with the Mg_{Ga} acceptor (as one could naively expect for a Mg-H complex) but prefers the AB site of one of the N neighbors (see Fig. 4). In cubic GaN, all four N neighbors are equivalent (Fig. 4a). Bosin *et al.* (1996) found that in wurtzite GaN a H-Mg complex with the H attached to the N neighbor along the *c* axis (Fig. 4b) is less stable than for a H atom on one of the three equivalent neighbors (the so-called *a*-axis orientation; see Fig. 4c). Okamoto *et al.* (1996) find the BC site to be slightly more favorable than the AB site, but only by 0.1 eV. This small quantitative difference may be due to their use of a smaller wurtzite supercell (16 atoms, as opposed to 32 atoms used by the other groups).

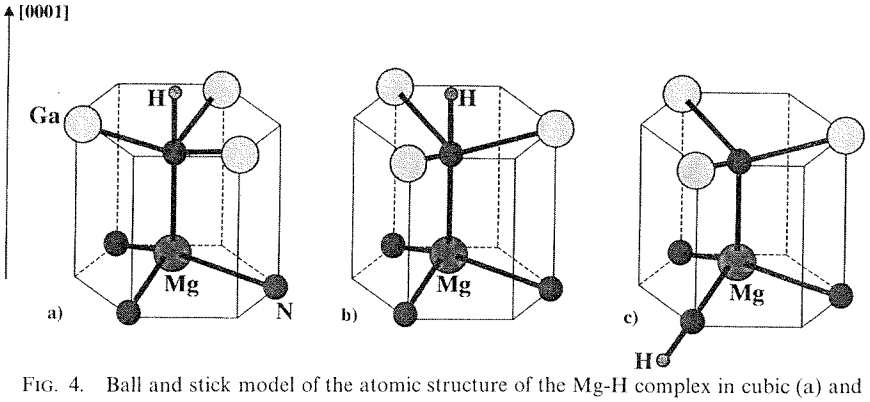

FIG. 4. Ball and stick model of the atomic structure of the Mg-H complex in cubic (a) and wurtzite (b, c) GaN with H on the N antibonding site. In wurtzite GaN two inequivalent configurations exist with the complex parallel to the *z* axis (b) and parallel to the *a* axis (c).

It is interesting to note that the atomic geometry (AB_N site) found for the Mg-H complex in GaN is very different from the well-established structure for acceptor-H complexes in other semiconductors where a BC configuration is preferred. The physical mechanism behind the unusual geometry of the Mg-H complex can be understood by analyzing the character of the acceptor level. First, it should be noted that the H atom donates its electron to the Mg acceptor level. The resulting H^+ prefers positions where (1) the charge density is high and (2) it is close to the donated electron (minimization of the electrostatic energy). Both conditions are closely related to the character of the Mg acceptor level. As can be seen in Fig. 5, this level is not characterized by Mg orbitals but by *p*-like orbitals located on the N atoms surrounding the Mg acceptor. The locations with the highest charge density are the BC position and the AB_N site. At the BC site, however, an additional relaxation energy has to be paid, explaining why H favors the AB_N site.

The calculated H stretch mode is $3360\,cm^{-1}$ for cubic GaN (Neugebauer and Van de Walle, 1995a) and $2939\,cm^{-1}$ for wurtzite GaN (Bosin *et al.*, 1996). Both frequencies are close to the stretch mode of H in NH_3 ($\sim 3444\,cm^{-1}$), indicating that the Mg-H complex is mainly characterized by a H-N bond.

Experimentally, local vibrational modes (LVMs) in Mg-doped GaN had been observed for the first time by Brandt *et al.* (1994). Room-temperature frequencies of 2168 and $2219\,cm^{-1}$ were tentatively assigned to inequivalent configurations of hypothetical Mg-H complexes or to H-Ga bonds in the wurtzite lattice. Neither isotopic substitution nor correlations with activation/deactivation of the *p*-type conductivity were available in the study. Looking specifically in the region predicted by theory, Götz *et al.* (1996a) found a vibrational mode at $3125\,cm^{-1}$. There are strong experimental indications that the mode is a stretch mode from the Mg-H complex; activation of the Mg-dopants reduces the intensity of the local vibrational modes, and deuteration of the activated material shifts the mode to $2321\,cm^{-1}$.

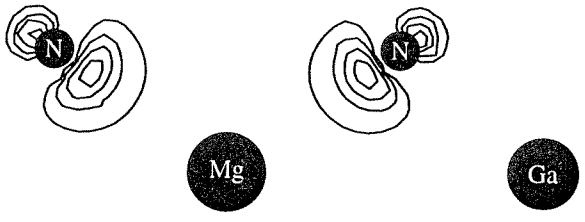

FIG. 5. Contour plot of the Mg acceptor level in GaN. The contour spacing is 0.005 $bohr^{-3}$. (From Neugebauer and Van de Walle, 1995a.)

The value calculated by Neugebauer and Van de Walle (1995a) of 3360 cm^{-1} is somewhat larger than the experimental value of 3125 cm^{-1}. It should be kept in mind that the calculated value does not include anharmonic effects, which are sizable in the case of N-H vibrations; in NH_3 the anharmonicity lowers the frequency by 170 cm^{-1} (Johnson *et al.*, 1993).

The total energy surface for a H atom around a Mg_{Ga} acceptor in GaN has been calculated by Neugebauer and Van de Walle (1995a). From the total energy surface the dissociation barrier of the Mg-H complex can be estimated. Considering only a jump from the N antibonding site to a neighboring N atom, a value of 1.5 eV is found.

2. OTHER H-ACCEPTOR COMPLEXES

H complexes with other acceptors (Be_{Ga}, C_N, Ca_{Ga}, and Zn_{Ga}) have been studied by Bosin *et al.* (1996). However, the authors pointed out that their results were preliminary due to the limited size of the supercell (16 atoms) and an incomplete investigation of all possible sites. For each complex, two possible geometries have been calculated—the BC site and the N antibonding site, where the complex is parallel to the *c*-axis. Complexes oriented along the *a* axis have not been considered. For all complexes, the formation energy is exothermic. Thus at low temperatures we generally expect the formation of H-acceptor complexes and an efficient passivation of the acceptors. All complexes exhibit a competition between the BC and AB_N site; for Be and Zn, hydrogen prefers the BC site; for Ca and C, it prefers the AB_N site. One should keep in mind, however, that the *a*-axis orientation of the complex, which was the energetically most stable configuration for the Mg-H complex, had not been considered. Further experimental and theoretical studies are necessary to clarify the precise geometry of these complexes.

VI. Complexes of H with Native Defects

Besides interacting with impurities, hydrogen also can interact with native defects. By forming a complex, hydrogen modifies the character of the defect; defects can be passivated, but as found by Van de Walle (1997), defects also can be converted from acceptors to donors. Further, attaching hydrogen to defects can reduce their formation energy (resulting in higher concentrations) and affect their migration behavior.

Native point defects are known to play an important role in GaN.

Previous first-principles studies showed that the dominant native defects in GaN are vacancies. Other types of point defects (antisites or self-interstitials) are high in energy and therefore are unlikely to form in appreciable concentrations during GaN growth (Neugebauer and Van de Walle, 1994b; Boguslawski *et al.*, 1995). We can therefore focus on the interaction of hydrogen with vacancies.

1. HYDROGEN INTERACTING WITH NITROGEN VACANCIES

The interaction of H with vacancies is often described in terms of the tying off of dangling bonds. This picture does not apply in the case of the nitrogen vacancy, 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 is too large for more than one hydrogen to fit inside the vacancy. It was previously pointed out (Neugebauer and Van de Walle, 1994b) 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.

These observations are confirmed by explicit first-principles calculations. The V_NH complex behaves as a double donor. In the 2+ charge state of the complex the hydrogen atom occupies a totally symmetric position, and the potential energy surface for displacements of the hydrogen atom is quite shallow; the corresponding vibrational frequency is less than 600 cm^{-1}. This frequency is obiously much smaller than frequencies associated with Ga-H bonds, consistent with the notion that no specific Ga-H bonds are being formed.

A binding energy of 1.56 eV was calculated for the V_NH complex, expressed with respect to interstitial H in the positive charge state. The formation energy of the complex (Van de Walle, 1997) is such that some concentration of V_NH complexes will be formed during high-temperature growth of *p*-type GaN. Note that formation of V_NH complexes *after* growth, by diffusion of a hydrogen atom toward 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 repel one another.

It has been proposed (Van de Walle, 1997) that the V_NH complex is responsible for the disappearance and appearance of photoluminescence (PL) lines during postgrowth annealing of Mg-doped layers grown by MOCVD, as described by Götz *et al.* (1996c) and Nakamura *et al.* (1992b). A PL line at 3.25 eV is present in as-grown material. Annealing at temperatures above 500°C causes this line to "redshift." It was suggested that this

shift actually corresponds to a decrease in intensity of the line at 3.25 eV (associated with the hydrogenated nitrogen vacancy), accompanied by an increase in intensity of a new line related to the isolated nitrogen vacancy. When the material is annealed, the hydrogenated vacancy complexes dissociate; the calculated removal energy of 1.56 eV is consistent with complex dissociation around 500°C. The resulting nitrogen vacancies have a level near the valence band, which may be responsible for the line around 2.9 eV.

2. HYDROGEN INTERACTING WITH GALLIUM VACANCIES

For the Ga vacancy it was found (Van de Walle, 1997) that one, two, three, or four hydrogen atoms can be accommodated in the vacancy, and levels are removed from the bandgap as more hydrogens are attached. Distinct N-H bonds are formed, with a bond length of about 1.02 Å and characteristic vibrational modes.

The isolated Ga vacancy is a triple acceptor; in the 3− charge state a triply degenerate defect level about 1 eV above the valence band is fully occupied. Introducing a H contributes an electron so that only two extra electrons are now required to fully occupy the defect levels; $V_{Ga}H$ is therefore a double acceptor. Similarly, the lowest-energy state of $V_{Ga}H_2$ is singly negatively charged, $V_{Ga}H_3$ is neutral, and $V_{Ga}H_4$ is actually positively charged (i.e., it behaves as a donor). All defect levels are removed from the gap in the latter configuration. The calculated formation energies (Van de Walle, 1997) indicate that these complexes may form during growth, depending on the likelihood of multiple hydrogen atoms being available at the time of incorporation. Capture of H at existing vacancies is unlikely; gallium vacancies are most likely to form in *n*-type GaN; hydrogen prefers the negative charge state here (Sec. III.1.a) 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 (see Fig. 2).

The calculated frequency (in the harmonic approximation) 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.

Hydrogenated gallium vacancies may play a role in GaN materials and devices similar to that played by isolated gallium vacancies, that is, compensation of donors (Yi and Wessels, 1996) and as a source of the yellow luminescence (YL) (Neugebauer and Van de Walle, 1996c). The $V_{Ga}H$ and $V_{Ga}H_2$ complexes have levels in the bandgap only slightly lower (by 0.1–0.2 eV) than the isolated gallium vacancy; they therefore also may 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.

VII. Role of Hydrogen in Doping GaN

Having analyzed the properties of interstitial monatomic hydrogen and its interaction with acceptors, we will now focus on how the presence of hydrogen affects doping in GaN. As pointed out in the introduction, there is strong experimental evidence that H plays an active role during the growth and activation of *p*-type GaN, as shown in the work of Nakamura *et al.* (1992a).

Based on these observations Van Vechten *et al.* (1992) suggested that hydrogen enables *p*-type doping by suppressing compensation by native defects. These authors went on to propose the incorporation (and subsequent removal) of hydrogen as a general method for improving *p*-type as well as *n*-type doping of wide-bandgap semiconductors. The Van Vechten *et al.* model highlighted the important role of hydrogen but left various issues unexplained, such as the lack of hydrogen incorporation in *n*-type GaN and the success of *p*-type doping (without postgrowth treatments) in MBE (molecular-beam epitaxy).

In order to identify the role of hydrogen in achieving *p*-type GaN, we first analyze the case where hydrogen is absent, corresponding, for example, to MBE growth. We will then consider hydrogen-rich conditions that are characteristic for many of the high-temperature growth techniques such as MOCVD and HVPE.

1. DOPING IN THE ABSENCE OF HYDROGEN

Before discussing the role of hydrogen in *p*-type doping, let us briefly focus on the H-free case; that is, only the acceptor (we will here consider Mg) and native defects are present. Figure 6 shows the corresponding formation energies calculated by Neugebauer and Van de Walle (1996a) as a function of the Fermi energy. The dominant native defect under *p*-type conditions is the nitrogen vacancy; all other defects are higher in energy. The slope of the formation energies characterizes the charge state; a positive slope (as found for the nitrogen vacancy) indicates a positive charge state, corresponding to a donor. For Mg, the kink in the formation energy describes a change in the charge state from neutral to negative as characteristic for an acceptor. The position of the kink at $E_F \approx 0.2\,\text{eV}$ gives the

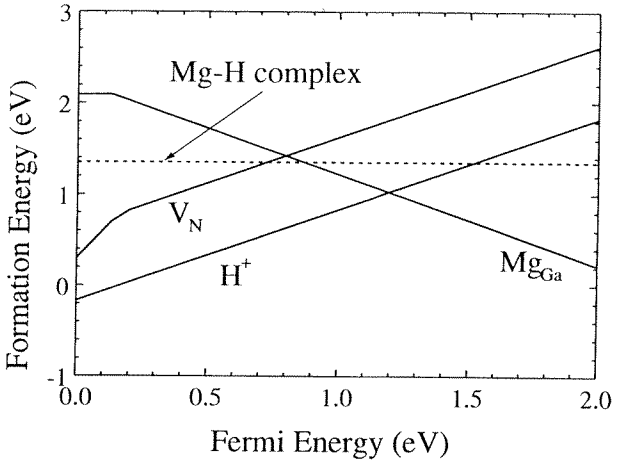

FIG. 6. Formation energy versus Fermi level for the Mg_{Ga} acceptor, the native defects, and interstitial hydrogen. Ga-rich conditions are assumed. (From Neugebauer and Van de Walle, 1996a. Copyright 1996 American Institute of Physics.)

position of the calculated acceptor level, which is close to the experimental value of 0.16 eV (Akasaki *et al.*, 1991).

Using the calculated formation energies, and taking into account that the Fermi energy is fixed by the condition of charge neutrality, the equilibrium concentration (Eq. 1) for each defect can be calculated as a function of temperature. The results are shown in Fig. 7. As expected, the Mg concentration increases with increasing temperature. However, with increasing temperature, the nitrogen vacancy concentration also increases; at temperatures exceeding 1000 K, the Mg acceptors become increasingly compensated by nitrogen vacancies. Native defect compensation is therefore potentially an important concern for high-temperature growth techniques. Lower-temperature growth techniques such as MBE should suffer less from this problem. This conclusion is consistent with the fact that only in MBE-grown GaN *p*-type conductivity can be achieved without any postgrowth processing (Molnar *et al.*, 1993; Lin *et al.*, 1993). It should be kept in mind that the low growth temperatures employed in MBE might not be sufficient to bring the system into full thermodynamic equilibrium. In particular, a low diffusivity at these temperatures could efficiently suppress the formation of Mg_3N_2, thus shifting the solubility to higher Mg concentrations. Also, the Mg sticking coefficient is higher at lower temperatures. This might explain the high Mg concentrations ($\sim 10^{20}\,cm^{-3}$) observed experimentally even at temperatures characteristic for MBE (between 1000 and 1100 K).

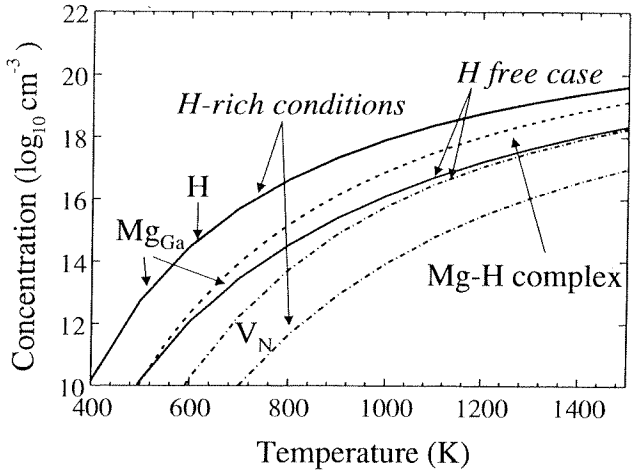

FIG. 7. Equilibrium concentrations of the Mg_{Ga} acceptors (solid line), nitrogen vacancies (dot-dashed line), and the Mg-H complexes (dashed line) as a function of the growth temperature. Two cases are assumed: H-free and H-rich conditions. Note that in the H-rich case the concentration of interstitial hydrogen is virtually identical with the Mg concentration. (From Neugebauer and Van de Walle, 1996a.)

2. DOPING IN THE PRESENCE OF HYDROGEN

We will now consider H-rich conditions that are characteristic for many of the high-temperature growth techniques such as MOCVD and HVPE. Figure 6 shows that under these conditions H becomes the dominant donor; the formation energy of H is always lower than the dominant native defect, the nitrogen vacancy. The calculated equilibrium concentrations are displayed in Fig. 7. The Mg and H concentration are for all temperatures virtually identical, indicating that H completely compensates the Mg acceptors. Further, compared with the H-free case, the concentration of Mg acceptors is increased and the defect concentration is decreased. Both effects contribute to increase doping levels.

What is the mechanism by which H changes the acceptor and defect concentration? In a plot such as Fig. 6, the Fermi-level position during growth can be roughly estimated to be near the crossing point between the acceptor and the dominant donor species. At this point their formation energies (and hence their concentrations) are equal, ensuring charge neutrality (ignoring the contributions from free carriers, which is small if E_{Fermi} is far from the band edges). By going from H-free conditions (only Mg and nitrogen vacancies present) to H-rich conditions, the crossing point shifts to

higher Fermi energies (from ~ 0.8 to ~ 1.2 eV). An increase in the Fermi energy decreases the formation energy of acceptors and increases the formation energy of donors, thus resulting in a lowered donor defect concentration and an increased acceptor concentration. We note that this mechanism works only if H is able to significantly shift the Fermi energy, which is the case if (1) H is the dominant donor (i.e., its formation energy must be lower than that of all native defects) and (2) its formation energy must be comparable with that of the dopant impurity (a crossing point must exist in the bandgap).

It is interesting to note that condition (2) is not valid for *n*-type doping with, for example, Si. The reason is that under *n*-type conditions hydrogen has a higher formation energy than under *p*-type conditions; the Si donor has for *all* Fermi energies a lower formation energy than the H^- acceptor (Neugebauer and Van de Walle, 1996a).

3. Activation Mechanism of the Dopants

We have thus established that growing under H-rich conditions enhances acceptor concentrations and suppresses defects. Figure 7 shows, however, that the Mg acceptors are almost completely compensated by the H impurities. In order to activate the Mg acceptors, postgrowth treatments are necessary to eliminate the compensation by hydrogen.

The H donors and Mg acceptors can form electrically neutral complexes with a binding energy of ~ 0.7 eV (see Sec. V.1). For the specific choice of chemical potentials made, this binding energy is low enough for the complexes to be dissociated at the growth temperature; however, the Mg and H will form pairs when the sample is cooled to room temperature, consistent with experimental observations (Götz *et al.*, 1995, 1996a).

The first step in the activation process is the dissociation of the Mg-H complex (see Fig. 8). The estimated dissociation barrier for the complex is 1.5 eV, calculated by considering a jump to a nearest-neighbor site; the total barrier may be slightly higher (Neugebauer and Van de Walle, 1995a). This barrier is low enough to be overcome at modest annealing temperatures (around 300°C). Experimental results show, however, that activation has to be carried out at much higher temperatures (>600°C). The reason is that dissociation alone is insufficient; in order to prevent the H from compensating the Mg acceptor, it has to be either removed from the *p*-type layer (to the surface or into the substrate) or neutralized (e.g., at an extended defect). Note that formation of H_2 molecules is not an option in GaN (see Sec. IV).

The calculated diffusion barrier for H^+ in GaN is low (~ 0.7 eV), indicating that H^+ is highly mobile and can easily migrate to the surface or

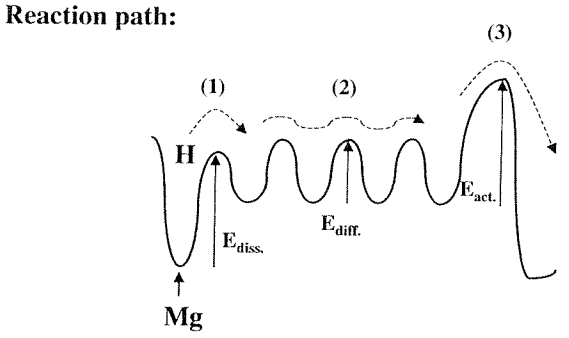

FIG. 8. Schematic picture of the reaction path and characteristic energy barriers for the activation of the Mg acceptors. At low temperatures, the H forms a neutral complex with the Mg atom. With increasing temperature, the Mg-H complex dissociates (1), and the positively charged H can easily migrate through the GaN crystal (2). Increasing the temperature further allows the H to overcome the activation barrier (3) and become electrically inactive.

extended defects. The high temperature necessary to activate the Mg acceptors therefore reflects an activation barrier for eliminating H as a compensating center by incorporating it at extended defects (which typically occur in high concentrations in GaN; Lester *et al.*, 1994) or by removal of H through desorption at surfaces.

VIII. General Criteria for Hydrogen to Enhance Doping

The mechanism by which hydrogen enhances doping works only under specific conditions. First of all, hydrogen must be the dominant compensating defect (i.e., its formation energy must be lower than that of all native defects and comparable with the formation energy of the dopant impurity). Second, it must be possible to remove hydrogen from the doped layer after growth; an anneal at high temperature will work only in a specific temperature window. On the one hand, the temperature must be *high* enough to enable all three processes necessary to eliminate H as compensating center: complex dissociation, migration, and overcoming of the activation barrier (see Fig. 8). We call the lowest temperature where this mechanism occurs T_1. On the other hand, the temperature must be *low* enough ($< T_2$) to keep the dopant impurity immobile and to prevent the formation of other compensating defects; in the case of Mg doping of GaN, an anneal at too high a temperature woud lead to Mg compensation by nitrogen vacancies,

as shown in Fig. 7. Thus a necessary condition for this mechanism to work is $T_1 < T_2$.

This condition is met in *p*-type GaN, judging by the success of thermal annealing procedures (Nakamura *et al.*, 1992a). We note that the preceding analysis is *general* and applies to dopants in any semiconductor. Whether the condition is realized, however, depends on the specific parameters of a system (migration barriers of impurities and defects, activation energies, etc.) and therefore must be addressed independently for each system. It is interesting to note that even for GaN (where the method works well for acceptor doping) it does not work for donor impurities. First of all, the formation energy of H is too high in *n*-type GaN for it to be incorporated in significant concentrations. And even if H *were* incorporated, the high diffusion barrier of H in *n*-type GaN ($\sim$3.4 eV) would render it immobile even at very high annealing temperatures, preventing the hydrogen from reaching the zones where it can be neutralized or removed.

Failure to meet these conditions is also the likely cause of the difficulties in obtaining *p*-type activity in MOCVD-grown nitrogen-doped ZnSe. Indeed, the N-H bond is very strong and would require high temperatures for dissociation; these temperatures exceed those at which the structural quality of the ZnSe crystal can be maintained.

IX. Conclusions and Outlook

First-principles total-energy calculations have had a major impact on exploring the properties of hydrogen and its interactions with dopant impurities and native defects in GaN. While many features are similar to the behavior of hydrogen in other semiconductors, a number of important differences occur. Computational studies revealed that H and acceptor-H complexes prefer unusual geometries and that hydrogen molecules are unstable. Furthermore, a huge negative-U effect is predicted for interstitial H. At this point, theory is leading experiment, and it would be extremely interesting to pursue these features experimentally.

Based on the computational studies, the mechanisms by which acceptors can be passivated and activated have been elucidated. Nevertheless, a number of aspects remain to be clarified. For instance, no conclusions have been reached regarding the mechanism by which hydrogen is removed from the *p*-type region, that is, whether it is brought to the surface (and thus disappears) or to extended defects (and stays in the sample). Also, the mechanism operative during the LEEBI treatment remains to be determined.

All theoretical investigations so far have focused on hydrogen in *bulk*

GaN. Experimentally, however, there is strong evidence that hydrogen at *surfaces* affects the growth rate and the crystalline quality (see, e.g., Ambacher *et al.*, 1997). Studies in this field could point the way toward improving growth, reducing defect densities, or enhancing dopant concentrations. We also note that investigations of the interaction between hydrogen and extended defects are still lacking.

Finally, it should be mentioned that all theoretical investigations and most of the experimental studies concerning hydrogen in the III-nitrides have focused on GaN. For device applications, however, ternary alloys such as AlGaN (as the cladding layer) and In GaN (as the active region) are crucial. Although qualitatively similar behavior of H in these alloys is expected, the quantitative results may turn out to be crucial. For instance, the larger bandgap and the stronger ionicity of AlGaN compared with GaN might severely affect the properties of interstitial H and its interaction with dopants. Studies of hydrogen at surfaces and in InGaN or AlGaN alloys are therefore called for.

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