Hydrogen in GaN: Novel Aspects of a Common Impurity

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We have studied electronic structure, energetics, and migration of hydrogen and hydrogen complexes in GaN, based on first-principles total-energy calculations. Our calculations reveal a number of features very different from those exhibited by hydrogen in more traditional semiconductors such as Si or GaAs: a very large negative-U effect ($U \approx 2.4$ eV), the instability of the bond-center site, high energies for hydrogen molecules, and an unusual geometry for the Mg-H complex. All of 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. We propose a simple model for the negative-U behavior, which should be valid for H in *any* semiconductor.

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Hydrogen is a common impurity in many semiconductors. Despite its simplicity (only one proton and one electron), the hydrogen impurity exhibits a very complex behavior. The ability of H to terminate dangling bonds, to passivate or compensate both shallow and deep defects, and to induce extended defects has had a large impact on technology [1]. While these features are well understood in the more traditional semiconductors such as Si and GaAs, little is known about H in a class of semiconductors that has recently received a lot of attention, namely, the group III nitrides (AlN, GaN, InN). Due to specific properties such as a large band gap, strong interatomic bonds, and a high thermal conductivity, these semiconductors have attracted a lot of attention as candidates for optoelectronic devices and for high-power, high-temperature applications. The group III nitrides are already successfully being used for manufacturing bright, highly efficient blue and green light-emitting diodes [2].

As-grown GaN is commonly n-type conductive, and p-type conductivity has been more difficult to obtain. It was first shown by Amano *et al.* that p-type conductivity can be achieved by activating Mg-doped GaN using low-energy electron irradiation (LEEBI) [3]. Subsequently, Nakamura *et al.* demonstrated that the activation of the Mg acceptors can also be achieved by thermal annealing [4]. Based on these observations it has been suggested that H plays a crucial role in passivating the Mg acceptors [4,5].

Despite the active role played by hydrogen, the understanding of its fundamental properties in GaN and in the group III nitrides in general is still in its infancy. We therefore performed a comprehensive and detailed study of the migration, energetics, and electronic structure of hydrogen and hydrogen complexes in GaN, employing first-principles total-energy calculations based on density-functional theory and *ab initio* pseudopotentials. 32-atom supercells were used, and atomic relaxation is fully taken into account. The calculations were performed for cubic GaN which has a higher symmetry then the wurtzite structure. As shown in Ref. [6] the wurtzite and the cubic phase show nearly equivalent formation energies and electronic structure for defects. We expect therefore that the results are valid for H in both zinc blende and wurtzite GaN. Details of the method and convergence checks are discussed elsewhere [7–10].

We first calculated the total energy surface for *monatomic interstitial hydrogen* in GaN, giving immediate insight into stable sites, migration paths, and diffusion barriers. The total energy surface $E_{\text{tot}}(\mathbf{R}_{\text{imp}})$ is calculated by fixing the H atom at different positions $\mathbf{R}_{\text{imp}}$ and allowing all other atoms to relax [11]. The calculations were performed for all three charge states of hydrogen (H^+, H^0, H^-); the resulting total energy surfaces for H^+ and H^- are shown in Figs. 1(a) and 1(b). The most striking feature is the qualitatively very different behavior for the positive and negative charge states.

Positively charged hydrogen (H^+) favors positions on a sphere with a radius of ≈ 1 Å centered on a N atom, i.e., H^+ prefers positions with N as a nearest neighbor [see Fig. 1(a)]. The calculated H-N bond length for all these positions is 1.02–1.04 Å, close to the experimental bond length in NH_3 ($d_{\text{N-H}} = 1.04$ Å) [12]. Among these positions, the nitrogen antibonding site (AB_{N}) is energetically most stable. All other sites, where a H-N bond cannot be formed, are found to be energetically unfavorable.

The preference for the N antibonding site is in striking contrast with the behavior of H^+ in Si or GaAs, where the bond-center (BC) position was found to be energetically most stable [11,13]. This difference can be understood by noting the different character of the chemical bond in GaN compared to GaAs. In Si and GaAs 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 a monotonic increase in the charge density from the Ga towards the much more electronegative N, resulting in a nearly spherically symmetric charge density around the N atom. H^+, which is simply a proton, prefers a position where it obtains maximum screening, i.e., it prefers sites with a high charge density. This explains why

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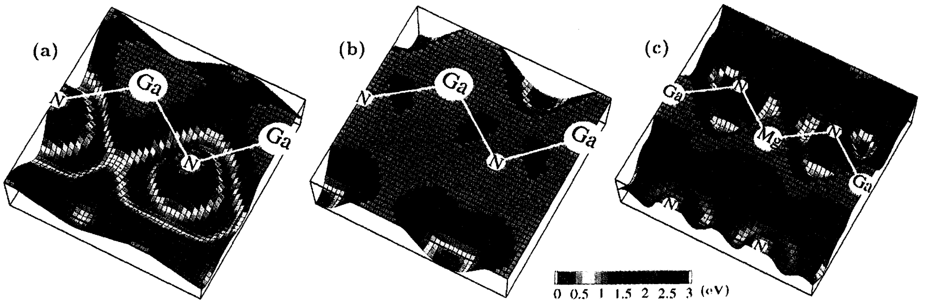

FIG. 1 (color). Total energy surface for (a) H^+, (b) H^-, and (c) H around a Mg_{Ga} acceptor in GaN. The zero of the energy is chosen arbitrarily at the global minimum of each total energy surface.

H^+ prefers the bond center in Si and GaAs, whereas in GaN *all* positions around the N atom are low in energy. At the BC position an extra energy cost needs to be paid due to the strain energy involved in relaxing the Ga and N atoms outwards. The strong bonding in GaN makes this a costly process, rendering the BC site unfavorable.

Figure 1(a) also shows that the migration barrier for H^+ is 0.7 eV, which is slightly larger than for H^+ in silicon but still sufficiently small to ensure high mobility even at temperatures slightly above room temperature.

For *neutral hydrogen* we find much smaller energy differences between different sites, indicating a rather flat total energy surface. The energetically most stable site for H^0 is the Ga antibonding site (AB_{Ga}). It is interesting to note that the Ga-H 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}).

For *negatively charged hydrogen* we also find the Ga antibonding site (or T_d^{Ga}) to be energetically most stable [see Fig. 1(b)]. At this position the distance to the neighboring Ga atoms is maximized, and the charge density of the bulk crystal has a global minimum. As can be seen in Fig. 1(b), H^- is strongly confined at the T_d^{Ga} site, giving rise to a very large migration barrier of ≈3.4 eV. H^- therefore has a very limited mobility in GaN.

Based on the above analysis, we obtain the energetically most stable position of H in GaN for each charge state q. We can then calculate the formation energy as a function of the Fermi level. The formation energy E_H^f of an interstitial H atom in GaN is defined as

$$E_H^f(q) = E_H^{\mathrm{tot}}(q) - E_{\mathrm{bulk}}^{\mathrm{tot}} - \mu_H - qE_F. \qquad (1)$$

Here $E_H^{\mathrm{tot}}(q)$ is the total energy of H^q in GaN, $E_{\mathrm{bulk}}^{\mathrm{tot}}$ is the total energy of the corresponding bulk supercell, and μ_H is the chemical potential for hydrogen. For the following discussions we assume that μ_H is fixed at the energy of a free H atom, as a reference. E_F is the Fermi level which is set to zero at the top of the valence band.

Results for formation energies 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. From Fig. 2 we further conclude that the solubility of H is considerably higher under p-type conditions than under n-type conditions.

Our theoretical predictions are confirmed by the very recent experimental observations of Götz and Johnson [14] on plasma hydrogenation of MOCVD-grown GaN: H is readily incorporated in p-type GaN, consistent with a high diffusivity of H^+, whereas no detectable levels of H were found in n-type GaN, consistent with a low diffusivity, as well as lower solubility, of H^-.

The fact that H^0 is never stable is characteristic of a "negative-U" system. From the $+/0$ and $0/-$ transition levels we find $U = E^{0/-} - E^{+/0} \approx -2.4$ eV. A negative-U behavior was also found for H in Si [11] and GaAs [13]; however, the value found here for GaN is unusually large, and, to our knowledge, larger than any measured or predicted value for any defect or impurity in any semiconductor.

Let us discuss the origin of the large negative-U behavior in more detail. Figure 3 shows the variation of the hydrogen formation energy along a line between the

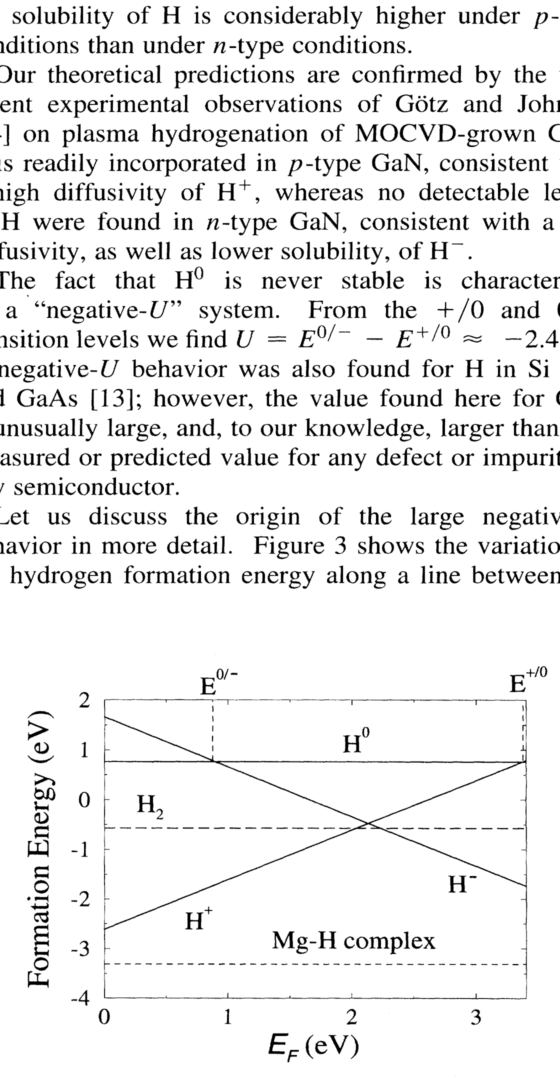

FIG. 2. Formation energy as a function of the Fermi level for H^+, H^0, and H^- (solid lines), for a hydrogen molecule (dashed line), and for a magnesium-hydrogen complex (long-dashed line). The formation energy is referenced to the energy of a free H atom.

AB_N site (preferred by H^+) and the AB_{Ga} site (preferred by H^0 and H^-). Figure 3 displays some remarkable features: (i) for a *fixed* hydrogen position x, the transition levels $E_x^{+/0}$ and $E_x^{0/-}$ are nearly equal (within 0.1 eV), and (ii) the total energy surface for neutral hydrogen is flat compared to charged hydrogen. These observations actually apply to *all* positions of hydrogen (not just those depicted in Fig. 3), with the exception of sites near the atomic cores, where the energy of H in any charge state is very high. The features described in Fig. 3 also apply to the case of H in Si [15] and GaAs [13].

We explain both of these features, as well as the negative-U character, by analyzing the nature of the interaction between H and the semiconductor. The *proton* prefers regions of high charge density, whereas *electrons* tend more to regions where the charge density is low. This already explains the location of H^+ (a proton) in Si, GaAs, and GaN, as discussed above, and it explains why H^- (in which electrons dominate) prefers T_d or AB sites. Moving *neutral* H 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, explaining the flat total energy surface. Deviations occur due to the fact that, contrary to the proton, the electronic orbital has a finite size and thus experiences variations in the charge density over a certain spatial extent. Nonetheless, the approximation 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 above discussion no assumptions about the specific nature of the semiconductor were made. We expect, therefore, that these features are a general property of hydrogen in *any* semiconductor.

We now go one step further and construct a model with the following assumptions: (i) the transition levels $E_x^{+/0}$ and $E_x^{0/-}$ are exactly equal, for all positions x, and (ii) the total energy surface for H^0 (outside of the core regions) is completely flat. It then follows immediately that the total energy surface of the negative charge state is the exact mirror image of the positive charge state, i.e., minima in the total energy surface for H^+ correspond to maxima in H^- and vice versa. The U value is then given simply by the difference between the minima and the maxima in the H^+ total energy surface (see Fig. 3). As discussed above, for H^+, minima and maxima in the total energy correspond to minima and maxima in the charge density. Consequently, in covalent systems (Si) or weakly ionic systems (GaAs), possible sites for hydrogen have a modest variation in charge density—hence the absolute value of U will be modest, though U will tend to be negative. Much larger variations in the charge density exist in ionic crystals—we expect, therefore, for this class of materials the largest negative-U values.

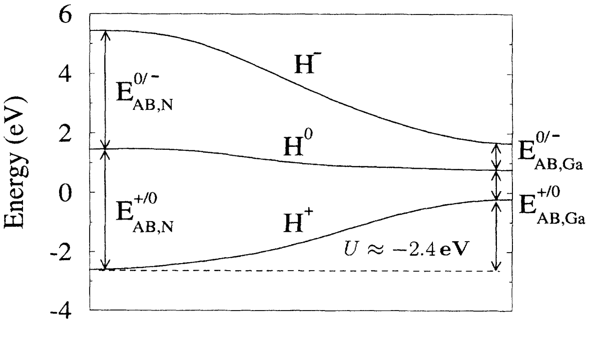

FIG. 3. Variation of the hydrogen formation energy for all three charge states along the shortest path between the AB_N and AB_{Ga} sites. The Fermi level is set to the top of the valence band.

We have also investigated *hydrogen molecules* in GaN, studying the formation energy and atomic geometry for several symmetric as well as asymmetric configurations of the molecules. The formation energies for all the investigated structures are nearly degenerate; the value for the energetically most stable configuration is included in Fig. 2. As can be seen, H_2 is unstable with respect to dissociation into monatomic hydrogen. The formation energy of ≈ -0.6 eV is also much higher than that of H_2 in vacuum (-2.4 eV) (no zero-point energies are included in the present values). Both features, the low stability of the hydrogen molecule and its unfavorably high formation energy, are distinct properties of GaN and very different from the case of Si or GaAs.

Finally, we have performed a detailed investigation of the *Mg-H complex*. There are strong experimental indications that this complex is responsible for the passivation of Mg acceptors in GaN [4], but an unambiguous determination of the passivation mechanism is still lacking. Here we provide support for the formation of a Mg-H complex, with specific predictions that can be experimentally tested. We focus on two aspects: (i) the atomic structure and (ii) the dissociation barrier of the Mg-H complex. We have calculated the complete three-dimensional total energy surface for a H atom around a Mg_{Ga} acceptor in GaN [Fig. 1(c)], revealing an unexpected atomic structure very different from the well-established acceptor-hydrogen complexes in other semiconductors. The hydrogen does not form a bond to the Mg atom (as one could naively expect for a Mg-H complex) but prefers the AB site of one of the N neighbors. Thus the Mg-H complex has a H-N bond as its main feature; indeed, the calculated H stretch mode is $\nu \approx 3360$ cm^{-1}, very close to the stretch mode of H in NH_3 ($\nu \approx 3444$ cm^{-1}) [12].

What is the physical mechanism behind this unusual geometry of the Mg-H complex? First, we note that the H atom donates its electron to the Mg acceptor level. The resulting H^+ prefers positions where (i) the charge density is high and (ii) 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. 4, 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.

From the total energy surface we can also estimate the dissociation barrier of the Mg-H complex. Considering only a jump from the N-antibonding site to a neighboring N atom, which is second-nearest neighbor to the Mg atom, we find a value of 1.5 eV. This jump is only the first step in the activation of the Mg acceptors; after dissociation, the Mg atom is still compensated by the H atom. In order to activate the Mg, the H has to be neutralized or it has to diffuse out of the p-type region. One possible mechanism in other semiconductors is the formation of H_2 molecules. However, as pointed out above, this mechanism can be excluded in GaN due to the high formation energy of H_2. Other possibilities are diffusion into the substrate material, to the surface, or to extended defects which occur in high concentrations in epitaxial GaN [16].

In conclusion, we have shown that hydrogen in GaN behaves very differently compared to the well established behavior in more traditional semiconductors. We predict a very large negative-U effect, for which we propose a simple model, which applies to other semiconductors as well. Finally, since the other group III-nitrogen compounds are chemically very similar to GaN, we expect similar behavior for H in AlN and InN.

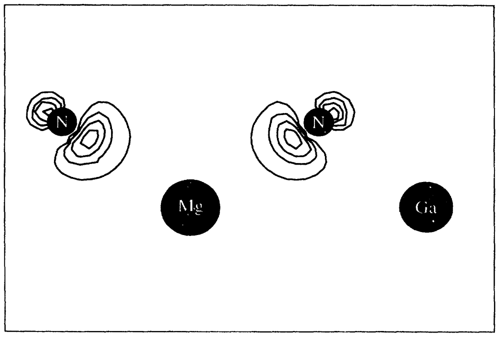

FIG. 4. Contour plot of the Mg acceptor level in GaN. The contour spacing is 0.005 bohr^{-3}.

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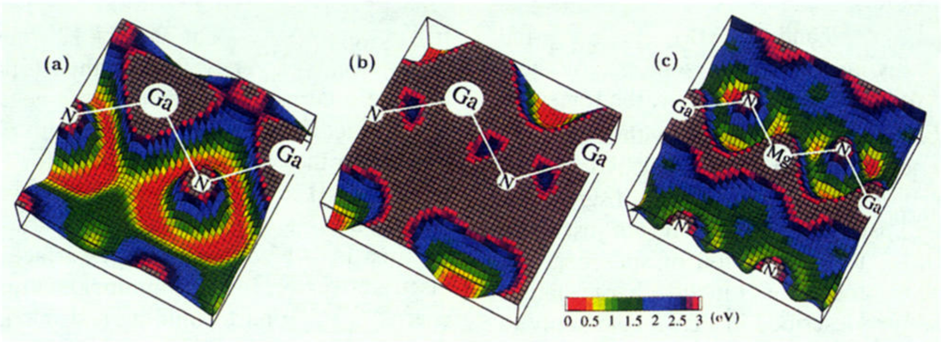

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