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Influence of crystal structure on the lattice sites and formation energies of hydrogen in wurtzite and zinc-blende GaN

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Charge-state calculations based on density-functional theory are used to study the formation energy of hydrogen in wurtzite and zinc-blende GaN as a function of Fermi level. Comparison of these results reveals notable differences including a 0.56 eV lower formation energy for H_2 in wurtzite, and different configurations for H_2 and H^- in the two crystal structures. Furthermore, H^+ is found to be equally stable at bond-centered and antibonding sites in wurtzite, whereas it is unstable at a bond-centered site in zinc blende. N-H^+ stretch-mode vibration frequencies, clustering of H^+ in *p*-type material, and diffusion barriers for H^- are investigated in wurtzite GaN. A diffusion barrier of 1.6 eV is found for H^- in wurtzite GaN, significantly lower than a previous estimate, and a tendency for H^+ clustering in *p*-type material is found. [S0163-1829(99)50432-3]

Hydrogen is a common impurity in GaN films grown via metal-organic vapor-phase deposition (MOCVD) where it is introduced either from the source compounds or from H_2 when used as a carrier gas.[1] Hydrogen may also be introduced after growth for purposes of device isolation,[2] as a by-product of device processing,[1] or simply to study its annealing behavior.[2–4] Understanding the annealing behavior of hydrogen in GaN is particularly important because either low-energy electron-beam irradiation[5] or a postgrowth anneal step[6] is needed to dissociate Mg-H complexes, and activate *p*-type doping in MOCVD-grown material. Moreover, hydrogen is retained in GaN up to a temperature of approximately 900 °C, and is therefore expected to play a significant role in nearly all processing stages for GaN-based devices.[7]

Because of its importance to emerging nitride-based technologies, hydrogen in GaN has been the focus of a number of recent experimental and theoretical studies. (See Chaps. 6 and 11 in Ref. 1 for reviews.) Many questions remain unanswered, however, regarding topics such as the annealing behavior of hydrogen and its interaction with point and extended defects. A starting point for addressing these topics can be provided by theoretical studies of hydrogen in defect-free GaN. Neugebauer and Van de Walle (NVdW) performed such a study for zinc-blende GaN.[8,9] They found several interesting features including a large negative-*U* effect and a preference for the nitrogen antibonding site by H^+ instead of the bond-centered site favored in other semiconductors. Based on their previous studies of native point defects in GaN,[10] they also suggested that hydrogen should display similar behavior in the more technologically relevant wurtzite structure. There are notable differences in the two crystal structures, however, that could affect interstitial hydrogen (see also Chap. 6 in Ref. 1). The lower symmetry of wurtzite, for instance, results in there being two different Ga-N bond lengths and bond angles that could affect the relative stabilities of antibonding and bond-centered sties. An even more noticeable difference is revealed by examining the two crystal structures on a length scale larger than their bond lengths (Fig. 1). The wurtzite structure has threefold symmetric (trigonal) channels oriented along the [0001] direction and extending through the length of the crystal. In zinc blende, the analogous (trigonal) channels are oriented along ⟨111⟩ directions, but are blocked at intervals of 7.8 Å by a pair of gallium and nitrogen atoms.

In order to study the behavior of hydrogen in wurtzite GaN and to investigate the structural differences outlined above, we performed charge-state calculations for hydrogen in wurtzite and zinc-blende GaN. These calculations employed the Vienna *Ab Initio* Simulation Package[11] (VASP) utilizing ultrasoft pseudopotentials[12] within the framework of the Kohn-Sham formulation of density-functional theory.[13] The gallium and nitrogen atoms were modeled using pseudopotentials developed by Grossner, Furthmüller, and Bechstedt,[14] treating the Ga 3*d* electrons as valence, and the hydrogen atoms were modeled using the 200-eV set of pseudopotentials from the VASP database. The energy cutoffs used for the wave and augmentation functions were 241 and 400 eV, respectively. The calculations were performed using periodically repeated 72-atom wurtzite and 64-atom zinc-blende supercells. Test calculations using a 32-atom zinc-blende supercell were also performed to check the convergence of the 64-atom-cell results. No differences were found. Brillouin-zone sampling was accomplished using Monkhorst-Pack[15] parameters {222} yielding eight *k* points in the full Brillouin zone.

Structures containing hydrogen were relaxed until the forces on each atom were less than 50 meV/Å. Formation energies were then obtained using the expression[16]

$$E^f(q,E_F)=E_{\mathrm{tot}}(q)-n_{\mathrm{GaN}}\mu_{\mathrm{GaN}}-n_{\mathrm{H}}\mu_{\mathrm{H}}+qE_V+qE_P\,. \tag{1}$$

Here, E^f is the formation energy, E_{tot} is the energy of the supercell containing hydrogen, $n_{\mathrm{GaN}}\mu_{\mathrm{GaN}}$ is the energy of the supercell without hydrogen, n_{H} is the number of hydrogen atoms and μ_{H} is the hydrogen chemical potential, q is the charge state of the cell, and E_V is the energy of the valence-band maximum in bulk GaN including a supercell-dependent shift.[16] E_F is the Fermi level defined to be zero at the bulk valence-band maximum and to have a maximum value equal to the measured energy gap (3.25 eV for zinc blende and 3.48 eV for wurtzite). For μ_{H}, we used −0.90 eV, which is

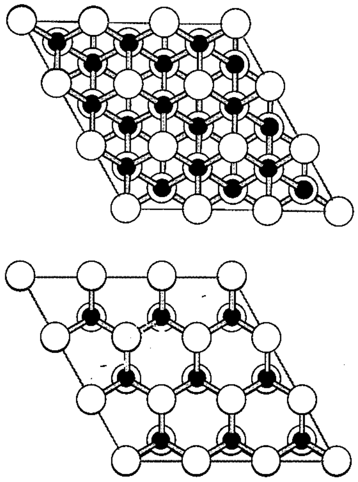

FIG. 1. (a) View of the zinc-blende structure along the [111] direction. (b) View of the wurtzite structure along the [0001] direction (c axis). Gallium atoms are shown as larger empty circles and nitrogen atoms as smaller filled circles.

the calculated spin-polarized energy of a hydrogen atom. Formation energies are thus given with respect to hydrogen atoms in the gas phase. To reference instead to H_2 gas, add 2.31 eV to the formation energies corresponding to the calculated binding energy of H_2 including the zero-point vibrational contribution. Many possible sites for interstitial hydrogen were investigated and formation energies for the three charge states, H^+, H^0, and H^-, were calculated at each site. We also studied cells containing two hydrogen atoms, in both associated (H_2) and unassociated ($2H^+$) configurations.

Due to the large difference in electronegativity between nitrogen and gallium, the bonding in GaN is partly ionic in nature. This ionicity is expected to have significant impact on the formation energies and stable lattice sites of the charged species, H^+ and H^-. NVdW,[8,9] for example, found that H^+ in zinc-blende GaN prefers to remain near the negatively charged nitrogen atoms whereas H^- sits as far as possible from nitrogen atoms. We find similar results for hydrogen in wurtzite GaN, but we also find noteworthy differences in the stable lattice sties between wurtzite and zinc blende. The most significant difference is in the lattice sites of H^+. In zinc blende, the nitrogen antibonding (AB_N) site is more stable than the bond-centered (BC) site by 0.26 eV. Due to its lower symmetry, there are two types of nitrogen-antibonding and bond-centered sites in the wurtzite structure. We refer to these as $AB_{N,\parallel}$ and $BC_\parallel$ when the N-H^+ direction is parallel the c axis, and $AB_{N,\perp}$ and $BC_\perp$ when the N-H^+ direction is roughly perpendicular to the c axis. The $AB_{N\perp}$ and $BC_\parallel$ sites have the same formation energy, the $BC_\perp$ site is 0.16 eV higher, and the $AB_{N,\parallel}$ site is an additional 0.03 eV higher. Our results therefore indicate that the $BC_\parallel$ site is stable in wurtzite, but unstable in zinc blende. We attribute the stability in wurtzite to an increased flexibility for relaxing bond angles between the nearby gallium and nitrogen atoms. In particular, placing H^+ in a bond-centered site causes the nearby gallium atom to relax into a planar configuration with its remaining three nearest-neighbor nitrogen atoms radically changing the Ga-N bond angles. As shown in a previous study of zinc-blende and wurtzite GaN elastic properties,[17] the wurtzite structure is more easily able to relax its bond angles than zinc blende. (See also Ref. 18 and Chap. 6 in Ref. 1.)

The most stable site for H^- is also different in wurtzite and zinc blende. In zinc blende, H^- is stable at the gallium antibonding (AB_{Ga}) site, although the tetrahedral gallium ($T_{d,Ga}$) site is only 0.08 eV higher in energy. In wurtzite, the stable site is at the center of the trigonal channel (see Fig. 1), 0.66 Å from a plane of gallium atoms, and roughly halfway between two planes of nitrogen atoms. The wurtzite analog to the zinc-blende $T_{d,Ga}$ site has a formation energy 1.76 eV higher than the trigonal site due to the presence of a nearby nitrogen atom. In general, the extended trigonal channel is an important structural feature distinguishing wurtzite from zinc blende.[19] As noted above, the trigonal channel in zinc blende is blocked at intervals of 7.8 Å by a pair of gallium and nitrogen atoms. This blockage might also be expected to affect the diffusion barrier of H^- in zinc-blende GaN. In wurtzite, a likely diffusion path for H^- is along the center of the trigonal channel. Based on calculations for this path, we estimate the diffusion barrier to be 1.6 eV. The analogous path in zinc blende is from a $T_{d,Ga}$ site to a tetrahedral nitrogen ($T_{d,N}$) site, and then to a different $T_{d,Ga}$ site. The energy barrier for this path is estimated to be 1.9 eV, about 20% higher than the wurtzite result. We note that both of these values are significantly lower than the 3.4 eV given by NVdW.[8,9] In particular, we do not see the sharp rise in energy shown in Fig. 1(b) of Ref. 9 near the midpoint of the path described above. The much smaller diffusion barriers found in this study imply that H^- will have noticeable mobility in GaN at growth and processing temperatures. A barrier of 3.4 eV, on the other hand, implies that H^- is practically immobile at these temperatures.

Due to its neutrality, NVdW found that the formation energy of H^0 in zinc-blende GaN was insensitive to position.[8,9] We find the same insensitivity for H^0 in zinc-blende and wurtzite GaN. However, the formation energy of neutral H_2 is very sensitive to position and the stable sites are also quite different in the two crystal structures. In wurtzite, the stable site is at the center of the trigonal channel with the H-H bond parallel to the c axis. One of the hydrogen atoms sits 0.45 Å from a plane of gallium atoms, the other sits 0.77 Å from a plane of nitrogen atoms, and the H-H bond length is 0.76 Å. In zinc blende, H_2 sits near a $T_{d\text{-}Ga}$ site in the trigonal channel with the H-H bond parallel to a $\langle 111 \rangle$ direction. One hydrogen atom sits 0.12 Å from a plane of gallium atoms, the other sits 1.09 Å from a plane of nitrogen atoms, and the H-H bond length is again 0.76 Å. In wurtzite, H_2 is located roughly equidistant between planes of gallium and nitrogen atoms. H_2 cannot sit at this same position in zinc blende because a nearby gallium atom is blocking the trigonal channel. As a result, the H_2 formation energy in wurtzite is 0.56 eV lower than in zinc blende. The increased stability in wurtzite is likely due to a polarization of the molecule, and the resulting attractive dipole interaction with the three nearby Ga-N pairs lining the trigonal channel. Polarization is not effective in zinc blende because the gallium atom blocking the trigonal channel has the same charge as the nearby hydrogen atom.

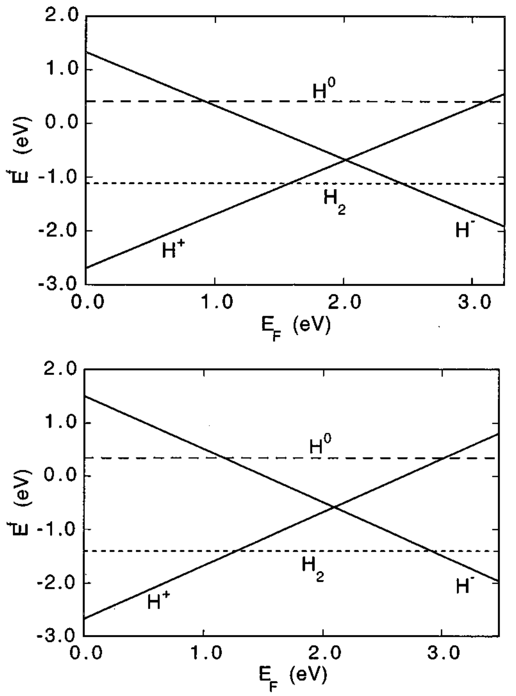

FIG. 2. Formation energies (per hydrogen atom) versus Fermi level in (a) zinc-blende, and (b) wurtzite GaN. *P*-type material corresponds to small values of the Fermi energy and *n*-type materials to large values.

In Fig. 2, we plot formation energies for the most stable sites in zinc blende and wurtzite as a function of Fermi level. The two plots are similar to each other and to the plot shown earlier by NVdW.[9] Both plots in Fig. 2, for example, display large negative-*U* values of -1.8 eV for wurtzite and -2.2 eV for zinc blende, similar to the -2.4 eV reported by NVdW. (The *U* value is the difference in crossing points of the H^0/H^- and H^+/H^0 formation energies.) Our H_2 formation energies are also roughly 0.7 eV lower than the value found by NVdW. The relatively low formation energy for H_2 may have important consequences for the behavior of hydrogen in GaN. Its value, given per atom in the plot, is lower than those of H^+ and H^- when the Fermi level lies near the middle of the gap. This will not be significant in material where the hydrogen concentration is small compared to those of other impurities, or native defects. However, in cases where the hydrogen concentration is large (such as in hydrogen-implanted material), hydrogen can become the dominant impurity, pinning the Fermi level near the middle of the gap and yielding a non-negligible concentration of H_2.[4] Another situation where the low formation energy may become significant is in the growth of magnesium doped *p*-type material. Hydrogen acts like a donor in *p*-type material and will therefore compensate magnesium, lowering its formation energy. This compensation, however, tends to shift the Fermi level toward the middle of the gap[20] where H_2 can begin to form, limiting the concentration of H^+.

For wurtzite GaN, we estimated vibration frequencies for the N-H^+ stretch modes. The values are 3240 cm^{-1} for the $AB_{N,\parallel}$ site, 3120 cm^{-1} for the $AB_{N,\perp}$ site, 3680 cm^{-1} for the $BC_\parallel$ site, and 3480 cm^{-1} for the $BC_\perp$ site. As expected, the frequencies are higher for the bond-centered sites due to the repulsive interaction between the hydrogen atom and the nearby gallium atom having a broken bond. In addition, we note that these values are similar to those observed in hydrogen implanted material by Weinstein *et al.*[21] In that case, it was suggested that the frequencies corresponded to hydrogen passivating defect sites. Finally, we point out that the zero-point vibrational energy of these modes is approximately 0.2 eV. This contribution was not included in the formation energies shown in Fig. 2.

In addition to the calculation for neutral H_2, we also considered two H^+ ions in wurtzite GaN to study the possibility of hydrogen clustering in *p*-type material. When separated by more than about 5 Å, the formation energy for the pair is roughly the sum of the formation energies for two isolated H^+ ions, indicating that screening is effective in this system. Surprisingly, we also found several configurations, having H^+ ions bonded to the same or nearby nitrogen atoms, with formation energies equal to or lower than the sum of formation energies for isolated ions. In addition to highlighting the effectiveness of screening in this system, these results suggest that either the strain fields surrounding two H^+ ions can complement each other, lowering the total formation energy for the complex, or new bonds are being formed.

Three structures were found having formation energies lower than for isolated H^+ ions. The first has H^+ ions at consecutive $BC_\parallel$ sites along the [0001] direction, and a new bond formed from gallium and nitrogen atoms relaxing in opposite directions due to the presence of the H^+ ions. The second structure consists of H^+ ions at $BC_\parallel$ and $BC_\perp$ sites related to the same nitrogen atom. That is, the H^+ ions were found to break two Ga-N bonds on the same nitrogen atom, a result that indicates strong reactivity for H^+ in GaN. The formation energies for these two configurations are 0.15 eV lower than for isolated H^+ ions in wurtzite GaN with the first structure likely benefiting from the formation of the new Ga-N bond and the second from complementary relaxations in the surrounding lattice. The third structure consists of H^+ ions in $BC_\parallel$ and $AB_{N,\parallel}$ sites in adjacent columns of atoms along the [0001] direction and lying roughly in the same plane perpendicular to the [0001] direction. The formation energy in this case is 0.31 eV below that for two isolated H^+ ions, with the low formation energy being due to relaxation in the surrounding gallium and nitrogen positions. While we have not considered all possible configurations with two H^+ ions nor complexes containing more than two ions, these results nevertheless suggest that hydrogen clustering may play a role in *p*-type material.

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