

Sources of unintentional conductivity in InN

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Using first-principles methods, we investigate the effects of monatomic hydrogen in InN. We find that hydrogen can occupy interstitial and substitutional sites. Interstitial hydrogen is stable in the bond-center configuration and acts exclusively as a shallow donor, with a H–N stretching vibration at 3050 cm^{-1} . Hydrogen can also substitute for nitrogen in InN, bonding equally to the four In nearest neighbors in a multicenter-bond configuration. Substitutional hydrogen has low formation energy and, counterintuitively, is a double donor. Our results suggest that monatomic hydrogen is a plausible cause of the unintentional *n*-type conductivity that is often observed in as-grown InN.

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InN crystallizes in the wurtzite structure and has a direct band gap of $\sim 0.7\text{ eV}$.¹ It can be combined with GaN (also wurtzite, but with a much larger band gap of 3.4 eV) into InGaN alloys with direct band gaps spanning the spectrum from infrared to ultraviolet.^{2,3} These alloys have enormous potential in optoelectronic devices such as high-efficiency solar cells, light-emitting diodes (LEDs), and laser diodes. Although GaN and Ga-rich InGaN alloys are already in use in commercially available blue LEDs and lasers,⁴ many questions still exist about the basic electronic and optical properties of InN and In-rich InGaN alloys. InN could enable high-electron-mobility transistors that take advantage of the very favorable velocity/field characteristics in this material, leading to enhanced performance over GaN-based devices.⁵ InN also has promising applications for terahertz devices.⁶ High-quality epitaxial films of InN have recently been synthesized that allowed for the determination of band gap and electron effective mass.^{1,2,7} However, these epitaxial films of InN invariably exhibit *n*-type conductivity, the cause of which is widely debated.^{1,8} Among the proposed causes are nitrogen vacancies and unintentional impurities, such as oxygen or interstitial hydrogen.^{1,2,8–11}

Hydrogen is a common impurity in semiconductors, found in almost all growth and processing environments.¹² Hydrogen is primarily thought of as an interstitial impurity that passivates intrinsic defects and other impurities, thereby significantly improving the electronic properties. In most semiconductors, interstitial hydrogen is amphoteric: it is stable as a donor in *p* type and as an acceptor in *n*-type material, always counteracting the prevailing conductivity.¹² In contrast, interstitial hydrogen (H_i) in InN was predicted to be stable exclusively as a donor.^{9,12,13} H_i strongly bonds to nitrogen, causing a breaking (or at least weakening) of a N–In chemical bond. Interstitial hydrogen can be found in the bond-center or in the antibonding configurations, as shown in Figs. 1(a) and 1(b).

Despite the strength of the N–H bond, we find that interstitial hydrogen is a fast diffuser in InN, causing it to be mobile at relatively modest temperatures. Interstitial hydrogen that is incorporated during growth or processing will therefore still be mobile while the samples are cooled down.

This behavior compels us to reexamine the role of hydrogen and its interaction with point defects in InN.

Based on first-principles calculations, we perform a comprehensive investigation of the electronic and structural properties of monatomic hydrogen in InN. We find that hydrogen, in addition to occurring on interstitial sites, can also substitute for nitrogen, bonding equally to the four In nearest-neighbors in a “multicenter bond” configuration (H_N) [Fig. 1(c)]. Most unexpectedly, we find that H_N acts as a double donor. Substitutional hydrogen is surprisingly stable, and has a lower formation energy than the nitrogen vacancy (V_N) [Fig. 1(d)] for all allowed values of nitrogen chemical potentials.

Our first-principles calculations are based on density functional theory (DFT) within the local density approximation (LDA).¹⁴ The calculations are performed using projector augmented wave potentials as implemented in the VASP code.^{15,16} We use 96 atoms supercells, an energy cutoff of 400 eV in the plane-wave basis set expansion, and a $2 \times 2 \times 2$ set of special *k* points for the integrations over the Brillouin zone. We treat the In *4d* electrons explicitly as valence states, and include on-site Coulomb correlation for these semicore states in the LDA+*U* approach.^{17,18} The LDA underestimates the binding energy of these semicore *d* states and consequently overestimates their hybridization with the N *p* states. This amplifies the effects of the *p*–*d* coupling and leads to an underestimation of the band gap of InN (beyond

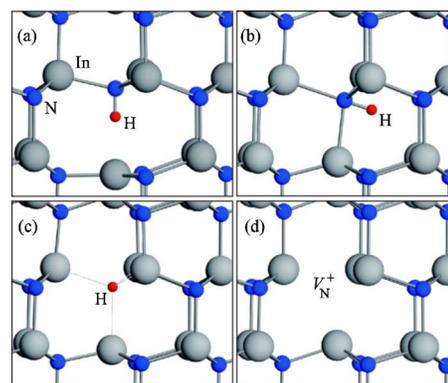


FIG. 1. (Color online) Local structure of interstitial hydrogen in (a) the bond-center configuration and (b) the antibonding configuration. (c) Substitutional hydrogen on a nitrogen site. (d) Nitrogen vacancy in the positive charge state.

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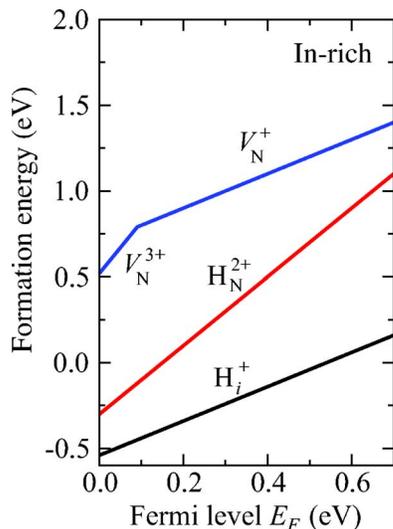


FIG. 2. (Color online) Formation energies of interstitial hydrogen (H_i^+), substitutional hydrogen (H_N^{2+}), and the nitrogen vacancy (V_N^+ and V_N^{3+}) as a function of Fermi level, under In-rich conditions. E_F is referenced to the valence-band maximum.

the well known DFT-LDA error). LDA+ U corrects this deficiency. LDA gives a band gap of -0.3 eV while LDA+ U gives a band gap of 0.1 eV for $U=1.9$ eV.¹⁹

Although LDA+ U does not reproduce the experimental value of the band gap, it partially corrects transition levels and formation energies. Thus, the calculations based on LDA and LDA+ U provide us with a systematic procedure to correct transition levels and formation energies. These are corrected according to the valence-versus conduction-band character of the defect/impurity states in the band gap. This procedure was applied with great success in the study of oxygen vacancies in ZnO.^{20,21}

The formation energy of interstitial hydrogen H_i in charge state q in InN is given by:²²

$$E^f(H_i^q) = E_{\text{tot}}(H_i^q) - E_{\text{tot}}(\text{InN}) - \mu_H + qE_F. \quad (1)$$

$E_{\text{tot}}(H_i^q)$ is the total energy of the InN supercell containing H_i in the charge state q , and $E_{\text{tot}}(\text{InN})$ is the total energy of the InN perfect crystal in the same supercell. The hydrogen chemical potential μ_H is taken as the energy per atom of an isolated H_2 molecule, i.e., $\mu_H = 1/2E_{\text{tot}}(H_2)$, and E_F is the Fermi level. For substitutional hydrogen the formation energy is given by

$$E^f(H_N^q) = E_{\text{tot}}(H_N^q) - E_{\text{tot}}(\text{InN}) + \mu_N - \mu_H + qE_F. \quad (2)$$

Since one nitrogen is replaced by a hydrogen atom, here the formation energy depends on the chemical potential μ_N , i.e., the energy of the nitrogen reservoir. μ_N can vary over a range given by the stability of InN: $1/2E_{\text{tot}}(N_2) + \Delta H_f(\text{InN}) \leq \mu_N \leq 1/2E_{\text{tot}}(N_2)$; the limits correspond to In-rich and N-rich InN, respectively. Because the enthalpy of formation $\Delta H_f(\text{InN})$ is only -0.4 eV [compared to the experimental value of -0.3 ± 0.1 eV at 298 K (Ref. 23)], the range over which the formation energies of H_N and V_N can vary is quite narrow.

The calculated formation energies are shown in Fig. 2 for indium-rich conditions, which are most favorable for formations of V_N and H_N . The results for V_N are consistent with previous calculations.²⁴ The vacancy is stable in the 3+ and + charge states, with the $\epsilon(3+/+)$ transition level at 0.1 eV

above the valence-band maximum (VBM). The formation energy in n -type material, e.g., with E_F at the conduction-band minimum (CBM), is 1.4 eV. This corresponds to an equilibrium concentration of V_N^+ of $2 \times 10^{13} \text{ cm}^{-3}$ at a typical growth temperature of ~ 500 °C.¹¹ The observed electron concentrations in as-grown InN are several orders of magnitude higher and therefore cannot be explained by the presence of nitrogen vacancies.

Turning to substitutional hydrogen, Fig. 2 shows that the formation energy of H_N is lower than that of V_N^+ for all Fermi-level positions within the band gap. Substitutional hydrogen is stable exclusively in the 2+ charge state, H_N^{2+} . For E_F at the CBM, the formation energy of H_N^{2+} is 1.1 eV, i.e., 0.3 eV lower than that of V_N . This formation energy corresponds to an equilibrium concentration of $2 \times 10^{15} \text{ cm}^{-3}$ at $T=500$ °C. Note that this estimate is based on equilibrium with H_2 ; in reality, equilibrium is more likely with an adsorbed species on the surface, which lowers the formation energy and raises the solubility. Substitutional hydrogen is therefore a plausible cause of unintentional n -type conductivity in InN. Note that even in molecular beam epitaxy, hydrogen concentrations exceeding 10^{18} cm^{-3} have been found.¹¹

H_N^{2+} gives rise to three almost degenerate local vibration modes, with calculated frequencies close to 540 cm^{-1} . Comparing with values of 570 and 590 cm^{-1} for the highest longitudinal and transversal optical phonons in InN,²⁵ we expect strong coupling with bulk modes that will make experimental observation of the H_N^{2+} local vibration modes very challenging.

Hydrogen has only one electron, so it seems counterintuitive that H could act as a double donor. In order to understand its electronic structure, we can start from the nitrogen vacancy. Removing a nitrogen atom from InN leaves four In dangling bonds (DBs), occupied with three electrons. In the near-tetrahedral environment of the wurtzite structure, these DBs combine into a fully symmetric a_1 state located in the band gap and occupied by two electrons, plus three almost degenerate states located at 2 eV above the CBM. The electron that would occupy the lowest of these three states is transferred to the CBM, resulting in the positive charge state of the nitrogen vacancy (V_N^+), as shown in Fig. 3. This is indeed consistent with the results of our first-principles calculations (Fig. 2), which show that the neutral charge state of V_N is not stable for any position of E_F in the band gap. Since in the positive charge state the a_1 state in the gap is occupied by two electrons, V_N^+ is stabilized by an inward relaxation of the four surrounding In atoms, maximizing their bonding. For E_F close to the VBM, the vacancy is stable in the 3+ charge state (V_N^{3+}). In this case, the a_1 state is empty and V_N^{3+} is stabilized by a strong outward relaxation of the surrounding In atoms, strengthening the bonds with their remaining nitrogen neighbors.

When hydrogen is placed on the nitrogen site, the hydrogen $1s$ state combines with the a_1 state from V_N^+ , resulting in a bonding state at 6.5 eV below the VBM, and an antibonding state at 6 eV above the CBM. The electron that would occupy this antibonding state is transferred to the CBM, turning substitutional hydrogen into a double donor (H_N^{2+}). Note that the three almost degenerate V_N states remain unaltered and constitute the nonbonding states in Fig. 3.

To complete our investigation of potential donors, we address interstitial hydrogen, which is stable exclusively in

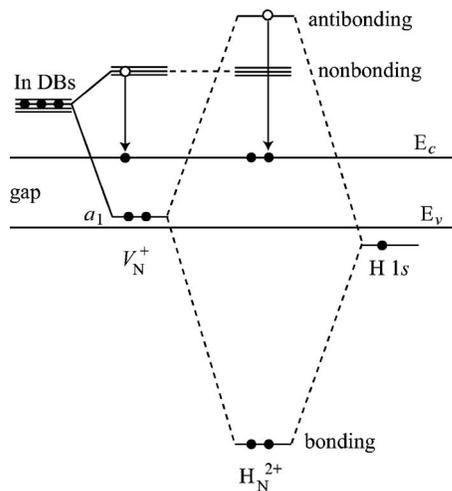


FIG. 3. Schematic illustration of the electronic structure of substitutional hydrogen H_N^{2+} in InN. The a_1 state of V_N^+ and the hydrogen $1s$ state combine into bonding/antibonding states. The bonding state is identified as a multi-center bond involving H and the four In neighbors. The antibonding state located in the conduction band will be unoccupied.

the positive charge state (Fig. 2). The calculated frequencies of the local vibrational modes are 3050 cm^{-1} for the stretching mode (including anharmonicity) and 626 cm^{-1} for the wagging modes. The formation energy of H_i^+ is lower than that of either H_N^{2+} or V_N^+ . However, in order to address the overall stability of interstitial and substitutional hydrogen, one also has to consider their migration barriers. The calculated migration barrier of interstitial hydrogen is 1.1 eV and corresponds to H breaking a bond with N and forming a bond with a nearest neighbor N. Using the calculated vibrational frequency as an attempt frequency, we estimate that H_i^+ will become mobile at temperatures around 100°C . Although H_i is mobile at relatively modest temperatures, this does not necessarily imply that it easily diffuses out of the InN samples. Present InN films exhibit a high electron accumulation on the surface that is associated with the pinning of Fermi level at $\sim 0.8\text{ eV}$ above the CBM due to intrinsic surface states.^{26–28} The associated band bending creates a potential barrier that impedes outdiffusion of positively charged impurities. We therefore expect that a significant concentration of interstitial hydrogen can be trapped inside the material and contribute to the n -type conductivity.

Substitutional hydrogen, H_N^{2+} , can migrate via three distinct processes: (1) assisted by a nitrogen vacancy, where H jumps to a nearby V_N , leaving a vacancy behind; (2) by dissociating into a nitrogen vacancy and a hydrogen interstitial: $H_N^{2+} \rightarrow H_i^+ + V_N^+$, or (3) by a concerted exchange with a nearest-neighbor N atom. The activation energy for the vacancy-assisted process (1) is the sum of $E^f(V_N^+)$ (1.4 eV for E_F at the CBM) and the barrier for the exchange process $H_N^{2+} \leftrightarrow V_N^+$ (estimated to be higher than 1 eV), resulting in a barrier of at least 2.4 eV. The activation energy for the dissociation process (2) is 1.6 eV, based on the sum of the binding energy $E_b = E^f(H_i^+) + E^f(V_N^+) - E^f(H_N^{2+}) = 0.5\text{ eV}$ and the migration barrier of H_i^+ (1.1 eV). The calculated energy barrier for the concerted exchange mechanism (3), finally, is 2.2 eV. Using our calculated vibrational frequency of

540 cm^{-1} for H_N^{2+} as an attempt frequency and an activation energy of 1.6 eV, we estimate that substitutional hydrogen is stable up to at least 300°C (and subject to the same barriers to outdiffusion as discussed for H_i above). Therefore, substitutional H is also a potential cause of unintentional n -type conductivity in InN, and overall more stable than interstitial H.

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