Effects of Hydrogen on the Electronic Properties of Dilute GaAsN Alloys

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Nitrogen has profound effects on the electronic structure of GaAs, as only a few percent of N can drastically lower the band gap. It is, however, not recognized that the same amount of N can also qualitatively alter the electronic behavior of hydrogen: First-principles calculations reveal that, in GaAsN, a H atom bonds to N and can act as a donor in its own right, whereas in GaAs and GaN, H is amphoteric, causing passivation instead. At high Fermi energy and H concentration, a N complex with two H was found to have lower energy than the single-H configuration. By removing the effect of N, this electrically inactive complex restores the gap of GaAs.

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Not long ago, alloying semiconductors with large-lattice mismatch (10% or larger) was still considered impractical. With the recent advances in epitaxial growth [1,2], however, such alloys are not only today's reality but they also present unique opportunities not offered by conventional semiconductor alloys: for example, long-wavelength lasers [1,3] and high-performance solar cells [4,5]. The physics of these large-lattice-mismatched alloys is both challenging and fascinating, but needs to be explored further. For example, just a few atomic percent of nitrogen in GaAs is enough to cause drastic band-gap reduction [1,6,7] and other unexpected material [5] and defect [8] properties. The growth processes of the GaAsN alloys usually involve hydrogen [9], as in the case of metal organic chemical vapor deposition [10] or gas-source molecular beam epitaxy (MBE) [2,11]. The large difference in electronegativity between the anions (N and As) is expected to couple with the high chemical activity of H. This raises crucial questions about the behavior of H in GaAsN that theories of hydrogen in either conventional semiconductors [12] or in common-anion nitrides [13] are unable to answer.

Recent experimental results by Xin, Tu, and Geva [2,11] have shown that hydrogen incorporation increases with nitrogen concentration [N] in InGaAsN alloys grown by gas-source MBE. Based on Hall measurements, Xin *et al.* suggested that H acts as an isolated donor in InGaAsN and makes the as-grown undoped samples slightly *n* type. Annealing above 700 °C reduces the hydrogen concentration [H] and renders the samples *p* type. This behavior differs from the effect of hydrogen in other semiconductors where H acts as a passivation agent, but not as a source of doping in its own right. A second puzzling result emerged from experiments by Baldassarri *et al.* [14] and Polimeni *et al.* [15] which revealed that postgrowth hydrogenation of InGaAsN alloys can lead to a complete reversal of the drastic band-gap reduction caused by N, observed for various N and In concentrations in InGaAsN alloys. The authors of Refs. [14,15] attributed the InGaAs band-gap restoration to the binding of H to the N atom in a passivation process. However, there is no microscopic theory on the nature of these interactions; i.e., neither the atomic nor the electronic structures of the hydrogen donors and of the N-H complex responsible for the band-gap opening in GaAsN and InGaAsN alloys have been studied.

Using first-principles total-energy calculations, we study the atomic structure and stability of the various hydrogen-related configurations (see Fig. 1) and their effects on the electronic properties of GaAsN alloys. We find that monatomic H in dilute GaAsN acts as a donor for all Fermi level positions in the band gap. This is quite surprising, because in conventional semiconductors, monatomic H can exist in either donor or acceptor charge states depending on the Fermi energy position [12]. For complexes that involve two H atoms, we find that a $H_2^*(N)$ complex is more stable than an interstitial H_2 molecule because of the strong bonding between hydrogen and nitrogen. The formation of the $H_2^*(N)$ complexes leads to a complete removal of the band-gap reduction in GaAsN with respect to GaAs. These findings also apply to InGaAsN alloys, thus providing a qualitative explanation to the recent experimental observations.

The calculations were carried out based on the density functional theory [16] within the local density approximation (LDA) [17]. Details can be found in Ref. [18]. Supercells containing 64 host atoms and n H atoms ($n = 1, 2$) were used. Dilute GaAsN alloys were calculated by replacing 1 As by N in the 64-atom cell, corresponding to a N content of 3.125%. Convergence with respect to the supercell size was tested by comparing the results obtained with 32-, 64-, and 128-atom supercells.

Because LDA underestimates the band gap, in this study it is necessary to apply a correction. It is known that LDA gives reasonably accurate atomic geometries, elastic properties, and heats of formation. Thus, LDA corrections to the defect formation energy arise [19] mainly because of the LDA errors in the occupied single-particle eigenvalues

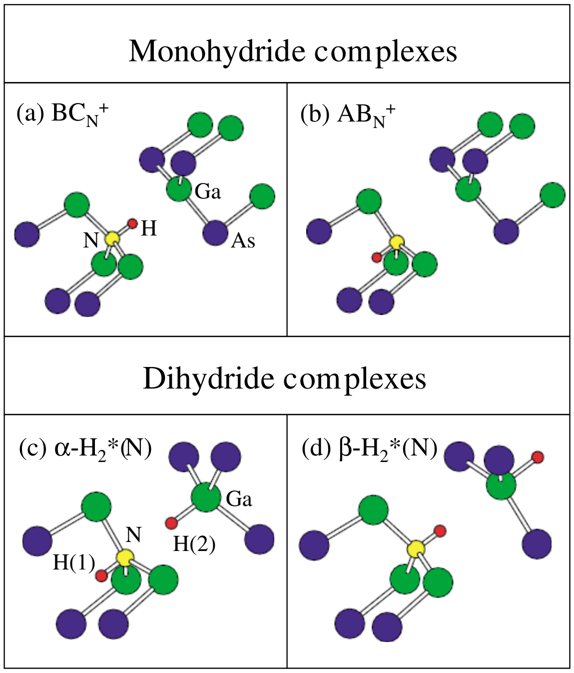

FIG. 1 (color online). Ball and stick models for the hydrogen and nitrogen complexes in GaAsN. Configurations involving one H include (a) the bond-center site next to N (BC_N) and (b) the antibonding site (AB_N). Complexes involving two H include (c) α-H_2^*(N) and (d) β-H_2^*(N).

associated with the defect. One can thus project the defect state onto a set of bulk states which form a complete basis, and subsequently correct the LDA errors based on the GW quasiparticle calculations for the bulk states [20]. In this study, we derive the projections by calculating the pressure coefficient of the defect levels and decomposing it in a two-band (valence + conduction band) approximation [21].

The calculated formation energy per hydrogen, used to predict the stability of the various configurations, is defined as

$$E_f = \frac{1}{n}[E_{\rm tot}({\rm host} + n{\rm H}, q) - E_{\rm tot}({\rm host}) - n\mu_{\rm H} + q\varepsilon_{\rm F}], \tag{1}$$

where $E_{\rm tot}({\rm host} + n{\rm H}, q)$ and $E_{\rm tot}({\rm host})$ are the total energies for a configuration with n H atoms in the host (either GaAsN or GaAs) at a charge state q, and for the pure host, respectively; $\mu_{\rm H}$ is the chemical potential of the hydrogen reservoir (which we choose to consist of H_2 molecules in free space at $T = 0$); and $\varepsilon_{\rm F}$ is the Fermi energy measured with respect to the valence band maximum (VBM).

First, we discuss monatomic H. We have studied the donor (+), neutral (0), and acceptor (−) charge states in the various monohydride configurations: namely, the bond-center sites next to N (BC_N) and far away from N (BC_{As}), the N and Ga antibonding sites (AB_N and AB_{Ga}), and the tetrahedral interstitial sites. Our results show that BC_N is the lowest energy configuration for all charge states. Other configurations are at least 1 eV higher in energy except for AB_N (see below). In the positively charged BC_N^+ configuration [Fig. 1(a)], the H atom strongly binds to the N atom with a H-N bond length of 1.05 Å. The Ga atom is displaced along the [111] direction to the basal plane formed by its three nearest neighbor As atoms. The Ga-H distance is 2.41 Å, 53% longer than the 1.58 Å expected from their respective atomic radii. The N atom is displaced along the opposite $[\overline{111}]$ direction. In the positively charged AB_N^+ configuration [Fig. 1(b)], the H atom at the antibonding site strongly binds to the N atom with a N-H bond length of 1.05 Å. In this case, similar to the BC_N^+ case, both N and Ga are displaced away from each other to their respective basal planes.

The AB_N^+ configuration has a formation energy that is 0.37 eV higher than BC_N^+, mainly because the electron charge density of the host at the BC_N^+ site is higher than that at the AB_N^+ site. Thus, the Coulomb binding energy for H^+ at the BC_N site is larger. This is in contrast to pure GaN, where H^+ prefers the AB_N site [22]. The Ga-N bond length is 2.05 Å in GaAsN, which is 7% longer than that in GaN of 1.92 Å. Because of the longer host Ga-N bond, the BC-site H^+ is less strained in GaAsN. Reduced strain energies are also responsible for the stabilization of the BC_{N0} and BC_N^- configurations in GaAsN.

The lowest formation energies for each charge state are plotted in Fig. 2 as a function of ε_F. Thus, as long as [H] is less than [N] (typically a few atomic percent for dilute alloys), *monatomic H in GaAsN exists only in the donor charge state*, with the (+/−) level above the conduction band minimum (CBM). These results are in clear contrast to those in GaN and GaAs, the parent compounds, where H is an amphoteric impurity, being positively charged in

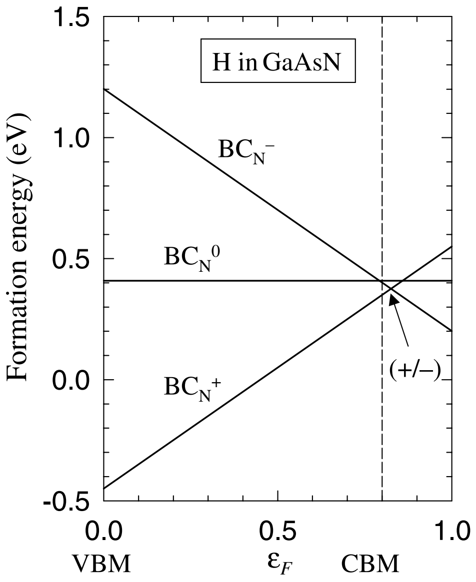

FIG. 2. Formation energies of monatomic H in GaAsN as a function of the Fermi energy ε_F. Only the lowest energy BC_N configuration is shown for each charge state: (+), (0), and (−). The vertical dashed line indicates the calculated band gap of GaAsN.

p-type samples and negatively charged in n-type samples [12,22,23]. The difference can be explained by the exceptionally large bowing effect of N that lowers the CBM of GaAsN [1,6,7] below both the CBM of GaAs and GaN, as well as below the H $(+/-)$ level. In the case of InGaAsN, the presence of indium lowers the CBM even further below that of GaAsN. Hence, we expect that the hydrogen $(+/-)$ level will be even further above the CBM. In general, when the host CBM level is very low [24], monatomic H can behave exclusively as a donor, as has been proposed for ZnO [25] and InN [13]. However, a similar behavior due solely to an alloying effect has not been suggested before.

An interesting question regarding H in p-type InGaAsN is whether it will induce compensation or passivation. Passivation occurs when an electrically neutral acceptor-donor complex is formed, while compensation implies that most donors are spatially separated from the acceptors. Compensation further implies that when hydrogen is removed by annealing, Hall mobility will *increase* as the number of ionized impurity scattering centers is reduced. This differs from what has normally been observed in elemental and III-V semiconductors, where a *decrease* in the Hall mobility upon annealing suggests the removal of hydrogen from H-passivated acceptor complexes [26]. Because the H^+-N binding energy of 1.0 eV is considerably larger than typical H^+-acceptor binding energies (e.g., 0.4 eV for Be-H^+), it is, therefore, entirely possible that, in dilute GaAsN and InGaAsN, H compensates instead of passivating the acceptors. Indeed, in the case of Ref. [11] in which Be is used as the dopant, the measured Hall mobility shows such an anomaly and increases upon annealing.

The experiments in Refs. [2,11] also showed that the total hydrogen concentration [H] is higher than the free-electron concentration in as-grown unintentionally n-doped InGaAsN. This implies that hydrogen is also present in inactive states such as interstitial H_2 molecules or H_2^* complexes [27]. Furthermore, our calculations show that the formation of $H(BC_N^+)$ has only a minor effect on the band gap. Hence, a defect other than active H^+ has to be responsible for the large band-gap opening (of several tenths of an eV) observed in the postgrowth hydrogenation experiments [14,15]. To identify this defect, we have studied a number of $H_2^*(N)$ complexes that involve two hydrogen atoms adjacent to a nitrogen. Table I shows that the α-$H_2^*(N)$ complex [Fig. 1(c)] has the lowest formation energy, $E_f = -0.07$ eV/H. In this complex, H(1) is at the antibonding site, similar to $H(AB_N^+)$ in Fig. 1(b), with a N-H bond length of 1.05 Å. H(2) is at the bond-center site with a Ga-H bond length of 1.54 Å. No chemical bond is formed between H(2) and N as the N-H separation of 2.06 Å is 93% longer than the 1.07 Å expected from their respective atomic radii. The β-$H_2^*(N)$ complex [Fig. 1(d); $E_f = 0.01$ eV/H] is slightly higher in energy than the α-$H_2^*(N)$ complex by about 0.1 eV/H. The N-H(1) bond length is 1.05 Å, and the Ga-H(2) bond length is 1.60 Å. Here, both the N and Ga atoms assume the planar configuration, raising the strain energy of the β structure with respect to the α structure. The α-$H_2^*(N)$ complex is also strongly favored by as much as 0.3 eV/H over the interstitial H_2 molecule ($E_f = 0.23$ eV/H). In contrast, in GaAs the interstitial H_2 molecule is considerably more stable.

TABLE I. Formation energies (in eV per H) of the double-H complexes in GaAsN and GaAs. H_2(Ga) and H_2(V) refer to H_2 molecules at the tetrahedral interstitial site next to Ga and anions (one of which is N for GaAsN), respectively. H_2^{AB} refers to a complex where both H atoms are at the antibonding sites.

Conf.	α-H_2^*	β-H_2^*	H_2(Ga)	H_2(V)	H_2^{AB}
GaAsN	-0.07	0.01	0.23	0.46	0.26
GaAs	0.72	0.67	0.28	0.38	0.92

The formation energy of $H(BC_N^+)$ increases as the Fermi energy ε_F increases (Fig. 2). A study of detailed balance between H^+ and H_2^* suggests that the relative concentration $[H^+]/[H]$ decreases with [H], whereas $[H_2^*]/[H]$ increases. Interestingly, however, the absolute $[H^+]$ increases with [H] instead of decreasing. As a result, the Fermi energy also increases with [H]. At $[H] = 10^{19}$ cm^{-3}, the calculated $[H^+]$ of 10^{16} cm^{-3} agrees with the experimental free-electron concentration of 7×10^{15} cm^{-3} [11]. This suggests that a majority of the single H are ionized so the $(+/-)$ level is indeed shallow. At higher [H] comparable to [N], however, the role of H is shifted towards restoring the GaAs band gap by H_2^*. An analysis of the density of states near the band edges (not shown) suggests that, while N incorporation lowers the CBM of GaAs of 0.6 eV for 3.125% N, H_2^* formation pushes the CBM back up completely—an observation that holds for every [N] being studied: 1.5625%, 3.125%, and 6.25%, respectively. This remarkable effect can be qualitatively understood via a three-step process schematically shown in Fig. 3:

First, the bonding of a hydrogen to N leads to large atomic displacements along the [111] direction, breaking one of the Ga-N bonds. This *eliminates* one of the nitrogen-derived GaAsN CBM states [7], creating a N dangling bond (DB)-like state in the valence band and a Ga DB-like state near the GaAsN CBM. Second, the binding of H(1) to the N DB-state creates a N-$H(1)^B$ bonding state deep in the valence band and a N-$H(1)^A$ antibonding state in the GaAs conduction band. Because of their spatial proximity, some interaction between the N-$H(1)^A$ state and the reactive Ga DB-like state can be expected. Third, the binding of H(2) to the Ga DB-like state creates a bonding Ga-$H(2)^B$ state below the VBM and an antibonding Ga-$H(2)^A$ state inside the conduction band of GaAs. The net result of the process depicted in Fig. 3 is that one GaAsN CBM state is completely removed by the formation of one $H_2^*(N)$ complex.

As H is gradually introduced during postgrowth hydrogenation [14,15], the concentration of $[H_2^*]$ increases,

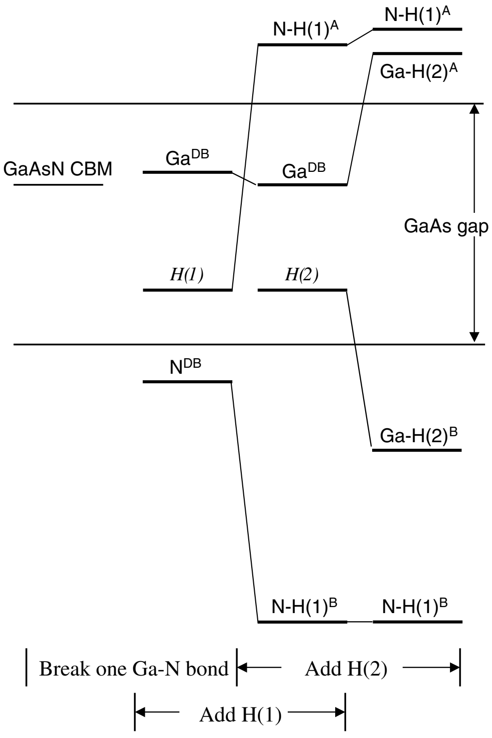

FIG. 3. A schematic plot of the effect of the α-H_2^*(N) complexes on the band gap of GaAsN. In step one, we break one of the Ga-N bonds. A Ga DB-state and a N DB-state emerge at the expense of one GaAsN CBM state. In step two, H(1) is added to the AB side of N, forming the N-H(1)^B and N-H(1)^A states. In step three, H(2) is added next to the Ga, forming the Ga-H(2)^B and Ga-H(2)^A states.

whereas the concentration of nonhydrogenated N decreases. The band gap also increases because the N-induced gap reduction is proportional to the concentration of nonhydrogenated N. This process approaches completion when [H] is larger than [N], which leads to the exposure of the original GaAs band gap. The same conclusion can also be straightforwardly applied to InGaAsN alloys, which have an even lower CBM than GaAsN.

In summary, we have studied the electronic effects of hydrogen in GaAsN and InGaAsN with a few percent of nitrogen. We find that nitrogen alloying qualitatively alters the electronic behavior of monatomic hydrogen to become *only* a donor, despite the fact that in GaAs or GaN hydrogen is amphoteric, existing in either donor or acceptor states. At higher hydrogen concentrations, it is energetically more favorable to form self-compensated, charge neutral H_2^*(N) complexes. The formation of these complexes completely eliminates the band-gap reduction caused by nitrogen. Our results provide an explanation to the recent puzzling experimental observations.

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