Hydrogen-Mediated Nitrogen Clustering in Dilute III-V Nitrides

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First-principles calculation reveals multi-N clusters to be the ground states for hydrogenated N in dilute III-V nitrides. While hydrogenation of a single N, forming H_2^*(N), can relax the large strain induced by the size-mismatched N, formation of the clusters will relax the strain even more effectively. This suppresses the formation of H_2^*(N), the existence of which has recently been debated. More importantly, postgrowth dehydrogenation of the N-H clusters provides an explanation to the observed metastable bare N clusters in GaAsN grown by gas-source molecular beam epitaxy or metal-organic chemical vapor deposition.

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The large size mismatch between a substitutional N and its larger isovalent host anion can profoundly alter the electronic properties of III-V semiconductors. At low to intermediate N concentration [N], where [N] is below the alloy limit of about 1 at. %, a series of bound and resonant states appears near the conduction band minimum (CBM) [1–3]. The appearance of the bound and resonant states was attributed to the formation of nitrogen clusters. Understanding the origin of the N-cluster-induced bound states in dilute nitrides is important, not only because they serve as efficient radiative recombination centers for excitons but also because they could act as free-carrier traps that reduce the efficiency of solar cells made on GaAsN. Kent and Zunger have performed large-scale empirical pseudopotential calculations for the bare N clusters [4]. They showed that, in most cases, it is the *nearest-neighbor* N clusters that produce the bound states inside the band gap, seen by photoluminescence measurements [1–3]. In particular, a family of the [110] N chains produces successively the deeper bound states as each additional N is added. In contrast, the *non-nearest-neighbor* N pairs usually give resonant states above the CBM.

In spite of the study in Ref. [4], the fundamental question concerning the formation of the N clusters remains unanswered. In fact, the [110] chains are highly strained in the chain direction. It is precisely this strain that causes the bound states to appear inside the band gap. As such, the [110] N chains are expected to be unstable compared with other forms of N clusters. Indeed, our first-principles calculations showed sizable negative binding energies (meaning repulsive) of -0.13, -0.22, and -0.31 eV per N, respectively, for the [110] N dimer, trimer, and tetramer.

In this Letter, we will show that the formation of highly strained N clusters may be due to an unexpected effect, i.e., hydrogenation. Our first-principles calculations show that hydrogen can assist the formation of the [110] N chain clusters in GaAsN, thereby completely reversing the above binding energy trend in bare N clusters. In particular, hydrogenated monomers such as H_2^*(N) will cluster into the hydrogenated dimer, trimer, or tetramer with significant energy lowering from 0.35 to 0.5 eV per N. The reason is that hydrogenation can reduce the local strain near N_{As} and even more effectively for multi-N clusters. A detailed-balance study at a typical growth temperature of 420 °C shows that the hydrogenated N dimer H_2^{**}(2N) is the most abundant species under thermal equilibrium among the various hydrogenated N clusters, regardless of the H concentration. This explains for the first time why experiment has so far failed to detect the H_2^*(N) complex, which is the most stable hydrogenated N monomer [5].

Moreover, we expect that [H] should be significantly higher near the growth front than in the interior, resulting in a gradient in the H chemical potential, μ_H, being higher near the surface but lower inside, as revealed by recent experiments [6,7]. This, combined with our calculated energetics, suggests a dehydrogenation of the N clusters once the growth front has passed. Indeed, recent experiment showed that, upon rehydrogenation, the multi-N clusters are the ones first to be rehydrogenated [8]. Our proposal is in accordance with the fact that the high-concentration N is usually incorporated by gas-source molecular beam epitaxy (GSMBE) [3,9,10], metal-organic chemical vapor deposition (MOCVD) [1–3,11–14], or ion implantation [15,16]. The GSMBE or MOCVD involves a large number of hydrogen-containing molecules or radicals during the growth, whereas the ion implantation creates numerous vacancies. Binding N with vacancies can also reduce the large strain induced by the size-mismatched N. Thus, in contrast to the common role of hydrogen in semiconductors to passivate electronic states of impurities and defects [17] and the recovery of the band gap of GaAsN [18], our study here reveals the unexpected effect of H to assist the formation of the N clusters, which needs to be suppressed in order to use such large lattice-mismatched semiconductors for optoelectronic applications.

We performed calculations using the density functional theory within the local density approximation, as imple-

mented in the Vienna *ab initio* simulation package [19]. Ultrasoft pseudopotentials were employed to treat the ion-electron interactions. A plane wave basis set was used for the wave function expansion with a kinetic energy cutoff of 348 eV. We mimic isolated N-H complexes by using a supercell approach. Unless otherwise specified, all the calculations were done using a 216-atom cubic cell with a calculated GaAs lattice constant of 5.593 Å [20]. A $2 \times 2 \times 2$ grid was used for the k-point sampling, corresponding to 4 k points in the irreducible Brillouin zone. All the atoms were relaxed to minimize the Feynman-Hellmann forces to below 0.02 eV/Å.

Figure 1 shows the calculated structures for the three lowest-energy monomers α-H_2^*(N), β-H_2^*(N), and γ-H_2^*(N). The α-H_2^* is more stable than the β-H_2^* and γ-H_2^* by 0.16 and 0.04 eV per N, respectively. The α- and β-H_2^* have been studied previously [5,21], but the γ-H_2^* has not. The calculated 0.04 eV/N energy difference between α- and γ-H_2^* is rather small. Therefore, a slight elongation of the Ga-N bond (e.g., induced by the strain of a second nearby N) can make the latter more stable, as a larger Ga-N distance can better accommodate two bond-centered H.

We define the binding energy of a hydrogenated N cluster with respect to the hydrogenated ground-state monomer α-H_2^*(N) as

$$E_B = \{n_N E_{tot}[\alpha\text{-}H_2^*(N)] - E_{tot}[(n_N N)(n_H H)] + (n_H - 2n_N)(\mu_{H,mol} + \mu_H)\}/n_N, \quad (1)$$

where E_{tot} is the total energy of the supercell, n_H and n_N are the numbers of H and N in the cluster, respectively, and μ_H is the chemical potential of the H, referenced to $\mu_{H,mol}$ (half of the total energy for an H_2 molecule in the vacuum). In such a definition, a positive sign in E_B corresponds to binding.

Hydrogenated monomers bind to each other via minimization of their local strains. Figure 1 shows that in α-H_2^*(N) all three Ga-N bonds are strained, whereas in β-H_2^*(N) all three Ga-As bonds are strained. Therefore, it is energetically favored to cluster an α-H_2^*(N) and a β-H_2^*(N) together antiparallell to form a hydrogenated N dimer $(H_2^*)_2$(2N), as shown in Fig. 2(a), because such clustering reduces the number of strained bonds by 2. As a result, the Ga(1)-N(1) bond length in $(H_2^*)_2$(2N), $d_{Ga\text{-}N} = 1.96$ Å, is only 2% longer than that of bulk GaN, $d_{Ga\text{-}N} = 1.92$ Å. No other Ga-N bond ($d_{Ga\text{-}N} = 2.03$ Å) has been weakened in the process; therefore, formation of the $(H_2^*)_2$(2N) is favored by $E_B = 0.22$ eV per N.

One can further eliminate the two Ga-bonded H in Fig. 2(a) to form a strained Ga-Ga bond, as we recently showed that the Ga-H bond is generally weak [22]. This leads to our second hydrogenated N dimer H_2^{**}(2N) in Fig. 2(b), which resembles somewhat the H_2^{**} in Si [23]. However, while the formation of H_2^{**} from an H_2^* in Si and GaAs is *always* endothermic, the formation of the H_2^{**}(2N) from two α-H_2^*(N) in GaAsN is surprisingly exothermic with $E_B = 0.35$ eV per N. Hence, at $\mu_H = 0$, H_2^{**}(2N) is also more stable than $(H_2^*)_2$(2N) by 0.15 eV per N. At first glance, this is surprising, because the formation of a weak Ga-Ga bond is usually not favored. However, by forming this bond, two weak Ga-H bonds are eliminated, and the two released H can also form a strong bond to become a free H_2 molecule. In addition, the formation of the Ga-Ga bond reduces the space at the N(1) site in Fig. 2(b), which is desirable for smaller atoms such as nitrogen. We find that the Ga-N bonds around the N(1) atom in H_2^{**}(2N), $d_{Ga\text{-}N} = 1.96$ and 2.01 Å, are significantly less strained than those in α-H_2^*(N). If one replaces the N(1) by an As, for example, such a strain reduction would be impossible, and the resulting structure is 1.26 eV higher in energy than the α-H_2^*(N). On the other hand, replacing N(2) by As costs only 0.41 eV with respect to the α-H_2^*(N). The calculated H vibrational modes for H_2^{**}(2N) are 3240 and 3203 cm^{-1}.

From the N dimers in Fig. 2, there are two open-ended paths to build larger clusters. In path 1, one adds additional H_2^*(N) units to $(H_2^*)_2$(2N) to form $(H_2^*)_3$(3N), $(H_2^*)_4$(4N), etc., to longer $(H_2^*)_n(nN)$ chains. In path 2, one adds one H_2^*(N) to H_2^{**}(2N), to form $H_2^* H_2^{**}$(3N)

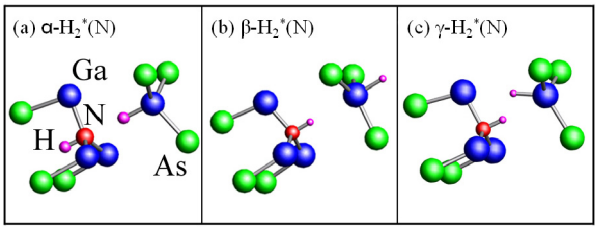

FIG. 1 (color online). Hydrogenated N monomers: (a) α-H_2^*(N), (b) β-H_2^*(N), and (c) γ-H_2^*(N).

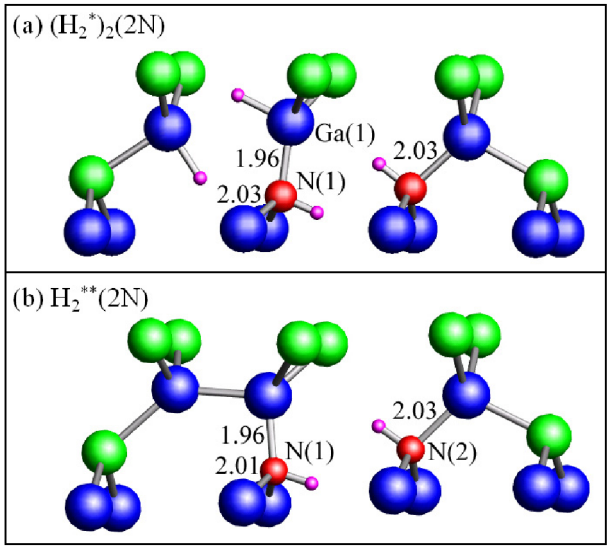

FIG. 2 (color online). Hydrogenated N dimers: (a) $(H_2^*)_2$(2N) and (b) H_2^{**}(2N).

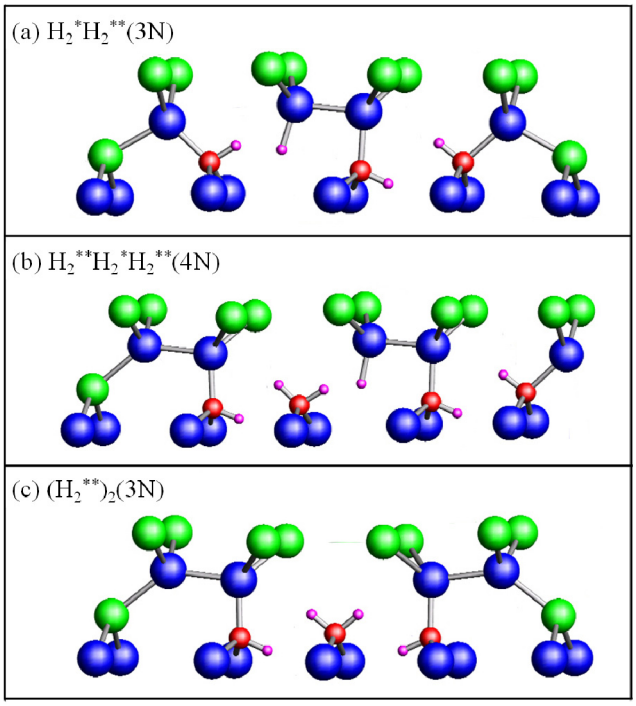

FIG. 3 (color online). Hydrogenated N clusters: (a) $H_2^*H_2^{**}$(3N), (b) $H_2^{**}H_2^*H_2^{**}$(4N), and (c) $(H_2^{**})_2$(3N).

[Fig. 3(a)], another H_2^{**}(N) to the $H_2^*H_2^{**}$(3N) to form $H_2^{**}H_2^*H_2^{**}$(4N) [Fig. 3(b)], and eventually to a periodic [110] chain with $H_2^*H_2^{**}$ as the basic unit. Note that one can alter the chain sequence in path 2 by inserting $H_2^{**}H_2^{**}$ twins, in which two consecutive H_2^{**} share one common N. Figure 3(c) shows the core of the twin as $(H_2^{**})_2$(3N). Interestingly, hydrogen in GaAsN can exist only as chains, not as the platelets seen in Si [24]. This is because the N atoms associated with the platelet would cause too much in-plane strain. The calculated E_B for the various clusters are shown in Fig. 4: In path 1, all the E_B are independent of μ_H. In path 2, while the relative E_B within the path is still independent of μ_H, the absolute E_B will increase if $\mu_H < 0$. Note that, in all the cases, N clusters are fully passivated by H without any electronic state in the band gap.

To determine the relative concentrations of the N-H complexes, we have performed a detailed-balance calculation. We used a typical experimental N concentration, 1 at. % at $T = 420\,^\circ$C, and the binding energies in Fig. 4 to calculate the concentrations for the various N-H complexes as a function of [H], shown in Fig. 5. Note that H_2^{**} and $H_2^*H_2^{**}$ (the basic building unit in path 2) dominate over the entire [H] range. On the other hand, the concentration of the H_2^* is never significant.

Figure 5 is a thermal equilibrium picture. Its validity thus depends on the diffusivity of N at growth temperature, which for GaAsN varies between 420 and 650 °C [3]. Anion diffusion usually takes place either via an anion vacancy (V_{As}) mechanism or an anion interstitial kickout mechanism. Assuming the former, we have calculated the barriers for V_{As} diffusion and for the hopping of an N to its nearest neighbor V_{As} to be 2.0 and 2.45 eV, respectively. These results suggest an appreciable N diffusion at $T \geq 700\,^\circ$C. In the presence of hydrogen, however, these diffusion barriers are considerably lowered. For example, in H_2^*, where one of the four Ga-N bonds is cut, our calculations show the energy barrier for displacing N to the nearest neighbor V_{As} is reduced by 0.54 eV to 1.9 eV. A recent study on V_N diffusion in GaN also showed a similar reduction of the barrier by 0.58 eV by hydrogen [25]. It is possible that the interstitial kickout mechanism can result

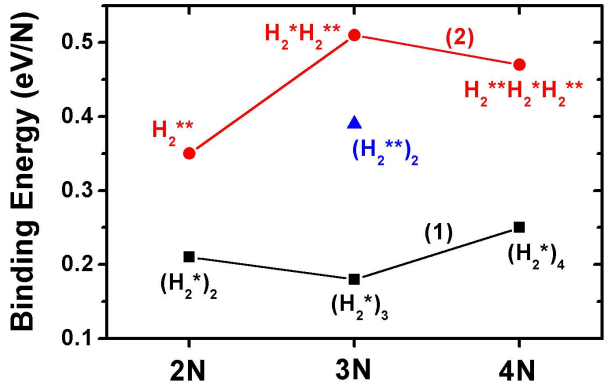

FIG. 4 (color online). Binding energy of the various N-H clusters with respect to α-H_2^*(N), calculated using Eq. (1). For path 2, μ_H is set to zero.

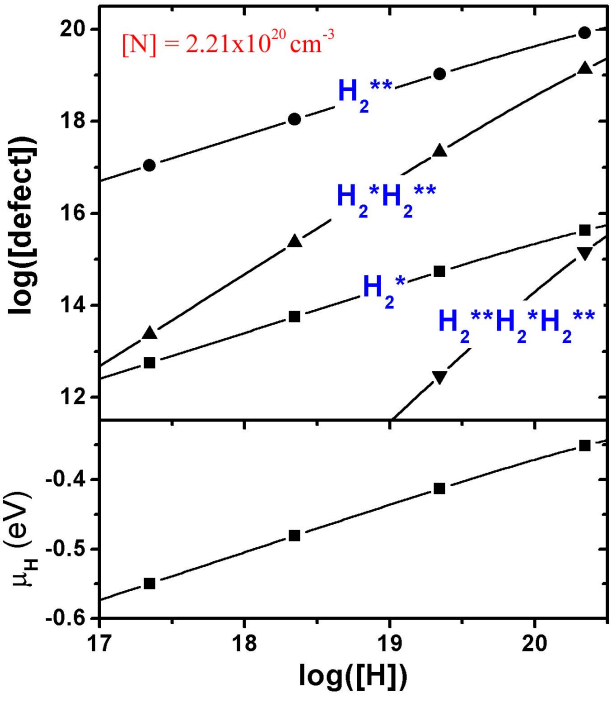

FIG. 5 (color online). (Top) Concentration of the various N-H clusters and (bottom) system H chemical potential under thermal equilibrium as a function of the hydrogen concentration H at the conditions of [N] = 2.21×10^{20} cm^{-3} and $T = 420\,^\circ$C.

in even lower barriers. In other words, H-assisted N diffusion is highly likely over the growth temperature range.

In the GSMBE or MOCVD growth of GaAsN using the H-rich ligands, it is typical that there is a high [H] (and, hence, high μ_H) at the growth front, but lower [H] (and, hence, lower μ_H) in the interior of the sample [6,7]. This suggests that the presence of nearest-neighbor N clusters in dilute III-V nitrides could be a consequence of postgrowth H desorption from the multi-N-H complexes. Figure 5 shows that, as [H] decreases, the number of hydrogenated N clusters also decreases [26]. Because the barrier to further dissociate substitutional fourfold-coordinated N atoms from the clusters is significantly larger than that of the onefold-coordinated H, bare N clusters are left behind. Our model suggests that these freeze-in N clusters should be more prone to rehydrogenation than isolated N_{As}. Indeed, recent experiments showed that, upon rehydrogenation of GaAsN, it is the N clusters that first disappear in the photoluminescence spectra [8].

In summary, first-principles study reveals the rich structures of a ground-state cluster phase of the N-H complexes in dilute III-V nitrides grown under the H-rich environment. We find that the relaxation of the nitrogen-induced strain is responsible for the stability of the clusters. The dominance of the cluster phase may explain the absence of IR modes from the most stable monomer $H_2^*(N)$. Furthermore, we suggest that a postgrowth dehydrogenation of the N-H clusters provides an energetic origin for the observation of metastable N clusters in GaAsN, whose presence could be harmful to the optoelectronic properties of GaAsN.

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