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Hydrogen-induced passivation of nitrogen in $GaAs_{1-y}N_y$

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Nitrogen isoelectronic impurities in $GaAs_{1-y}N_y$ are fully passivated by H irradiation from N dilute to the alloy limit. Photoluminescence measurements show that (i) for $y \leqslant 0.001$, exciton recombination lines in N-related complexes are fully quenched upon hydrogenation; (ii) for $y \geqslant 0.01$, the $GaAs_{1-y}N_y$ band gap blueshifts toward that of the N-free material with increasing H dose. Thermal annealings restore the optical properties $GaAs_{1-y}N_y$ had before hydrogenation. Finally, theoretical results on H equilibrium positions are reported and a mechanism for N passivation by H is given.

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The (In,Ga)(As,N)/(GaAs) system has been the subject of intense study[1,2] because of its potential applications in the telecommunication field.[3] These applications rely on a giant band-gap reduction, a reduced pressure and temperature dependence of the band gap, and an increase of the electron effective mass for increasing N content.[1] Surprisingly, it has been shown that H irradiation leads to a band-gap blueshift in $In_xGa_{1-x}As_{1-y}N_y$/GaAs quantum wells with $y \geqslant 0.01$.[4] It is well known that the introduction of hydrogen into semiconductors eliminates the shallow energy levels introduced by substitutional dopants through the formation of dopant-hydrogen complexes.[5] Hydrogen also modifies the electrical properties of a number of deep-level defects. The effect of hydrogen on isoelectronic impurities, that is, impurities that belong to the same group of atoms they replace,[6] has not been explored so well. Whenever the electronegativity and/or size of an isoelectronic impurity are quite different from those of the host atom, a highly localized potential results, giving rise to electronic levels in the lattice band gap as in GaP:N[7] or resonant with the host band states as in GaAs:N.[8] Hydrogen-induced passivation might be expected to be weak or absent in the case of isoelectronic impurities because the valences of both the impurity and host atoms are satisfied. However, our recent results for H in $In_xGa_{1-x}As_{1-y}N_y$ show that this viewpoint is naive.[4]

In this paper, we show that hydrogen and nitrogen atoms form complexes in pseudobinary $GaAs_{1-y}N_y$/GaAs heterostructures at all N concentrations investigated here. The main outcomes of the present work are as follows.

(i) In the N dilute limit ($y \leqslant 0.001$), a *full* quenching of the N-related luminescence lines occurs. This is the first evidence of the complete passivation of an isovalent impurity in a semiconductor;

(ii) In the alloy limit ($y \geqslant 0.01$), a strong blueshift of the band gap toward the value it has in GaAs occurs. This confirms previous results in $In_xGa_{1-x}As_{1-y}N_y$/GaAs quantum wells[4] and shows that they do not depend on In content and sample design;

(iii) At all N contents, the H-N complexes are dissociated by thermally annealing the samples. This results in a *nearly complete* recovery of the optical properties the $GaAs_{1-y}N_y$ had before hydrogenation. Moreover, an analysis of the activation energies for the release of the H atoms allows us to distinguish two different groups of N complexes in the dilute limit.

These results are consistent with infrared absorption measurements that show the formation of N–H bonds. Finally, we report calculations based on first-principle density-functional methods, which account for the results above by the formation of a N-H_n complexes, most likely leading to a passivation of N atoms.

Different $GaAs_{1-y}N_y$/GaAs heterostructures grown by solid source molecular beam epitaxy have been investigated. Nitrogen concentrations are $y=0$, 0.0001, and 0.001 (dilute limit) for 110-nm-thick $GaAs_{1-y}N_y$ epilayers, and $y=0.01$ (alloy limit) for a 310-nm-thick $GaAs_{1-y}N_y$ epilayer. The samples are lightly *p*-doped because of residual C in the growth chamber. Hydrogenation was obtained by ion-beam irradiation from a Kaufman source with the samples held at 300 °C. Low ion energy (100 eV) and current densities (~10 μA/cm^2), as well as a wide range of hydrogen doses (10^{14}–10^{19} ions/cm^2), have been used. Hydrogenated samples were annealed at temperatures $T_a = 300$, 330, and 400 °C for a duration time, t_a, ranging between 1 and 50 h. Photoluminescence (PL) was excited by the 515-nm line of an Ar^+ laser, dispersed by a single 1-m monochromator (spectral resolution 0.2 meV) and detected by a Ge detector or a photomultiplier with a GaAs cathode. Infrared absorption measurements were performed at liquid-He temperature by a Bomem DA3 spectrometer (spectral resolution 1 cm^{-1}) with an InSb detector. Nitrogen-hydrogen complexes have been investigated in the framework of the density-functional theory in the local-density approximation (LDA) by using 64-atom supercells, plane-wave basis sets, the special-point technique for **k**-space integration, and the exchange-correlation functional of Ceperley and Alder. Further details on the method are described in Ref. 9. In particular separable *ab initio* pseudopotentials[10] have been used in the case of the Ga and As atoms, and a soft pseudopotential has been used for the N atom.[11] A satisfactory convergence of the results has been achieved by using a plane-wave cutoff of 22 Ry. The vibrational frequencies of the H local modes have been evaluated in the harmonic approximation. One H atom is moved away from its equilibrium position while the other atoms of the supercell are frozen in the positions of the minimum energy configuration. The frequencies of the hydrogen local vibrational modes (LVM's) have then been estimated by fitting to a parabola the total energy values corresponding to the different H positions.[9]

Figure 1(a) shows the PL spectra at $T=10$ K of the as grown $GaAs_{1-y}N_y$ samples in the N dilute limit. When a small amount of N is incorporated in a sample, a number of sharp lines (linewidth ~0.5 meV) appear between 1.40 and 1.48 eV. This agrees with previous results obtained for N concentrations ranging from 10^{17} to 10^{20} cm^{-3}, which showed that N atoms tend to form pairs with different average distances, and eventually higher order clusters, whose electronic levels fall below the GaAs band edge.[12] The energy position and the linewidth of the narrow lines remain fixed despite an increase of one order of magnitude in the N concentration. This highlights the strongly localized character of the N isoelectronic traps, contrary to that of shallow impurities whose wave functions overlap at smaller concentrations. In Fig. 1(a), we identify the longitudinal optical (LO) phonon replicas of lines *a* and *b*, but an exact assignment of each line to a given N complex is made rather difficult by the strong dependence of the material optical properties on the growth conditions, as extensively reported in the literature.[12,13]

Hydrogenation at various doses, d_H, leads to a progressive and finally *complete* passivation of the N-related lines and of the broad luminescence band beneath them, as shown in Fig. 1(b) for the $y=0.001$ epilayer. The only two bands left in the $d_H = 100$ H_0 spectrum and separated by 36.7 meV are the LO-phonon replicas of the C-related free to bound transition, (e,C), at 1.4933 eV. These H-induced effects have never been reported before for any isoelectronic impurity, but for a weak reduction of the luminescence intensity of a few N-related lines in GaP:N.[14] Note that a 100% passivation of the impurity luminescence bands is hardly attainable even in the common case of H passivation of shallow impurities in GaAs or Si.[5] At high N doping ("alloy limit"), where the narrow luminescence lines related to N are no longer observed, N insertion in the lattice results in a redshift of the host band gap.[1] This redshift has been attributed to the interaction of an *isolated* N electronic level with the states of the host conduction band.[2,15] Hydrogen neutralizes the effects of nitrogen, as shown in Fig. 1(c) in the case of a $GaAs_{0.99}N_{0.01}$ epilayer. Here, the gap blueshifts by 170 meV toward the gap of the GaAs upon hydrogen irradiation, similarly to what reported for $In_xGa_{1-x}As_{1-y}N_y/GaAs$ quantum wells (QW's).[4] Therefore, H counterbalances the effects of N both in the dilute and alloy limits, suggesting a common nature of the N interaction with the host lattice in these two opposite limits.

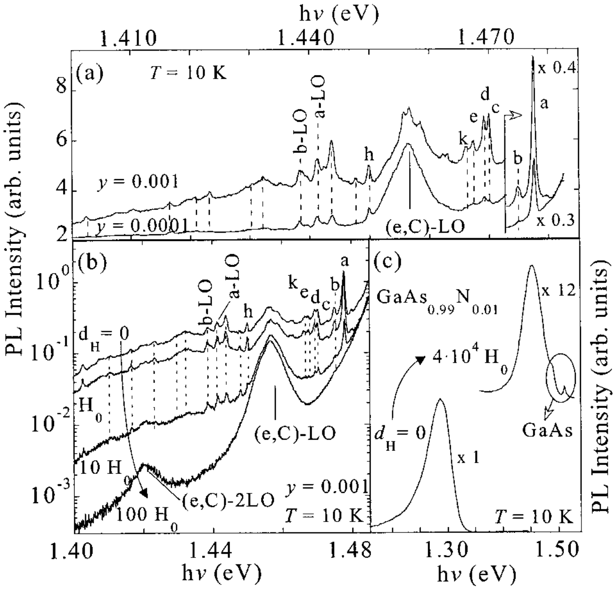

FIG. 1. (a) $T=10$ K photoluminescence spectra of two $GaAs_{1-y}N_y$ epilayers in the limit of dilute N concentrations. Letters label some of the PL lines discussed in the text. The LO-phonon replicas of lines *a* and *b* are indicated. (e,C)-LO is the phonon replica of the C-related free to bound transition. Laser power density $P=10$ W/cm^2. (b) $T=10$ K photoluminescence spectra of the $GaAs_{0.999}N_{0.001}$ epilayer after irradiation at different H doses, d_H. (e,C)-nLO are the phonon replicas of the C-related free to bound transition. Laser power density $P=10$ W/cm^2. $H_0 = 5\times10^{13}$ ions/cm^2. (c) Peak normalized photoluminescence spectra at $T=10$ K of the untreated (lower trace) and H irradiated (upper trace) $GaAs_{0.99}N_{0.01}$ epilayer (alloy limit). Normalization factors are given for each spectrum. Laser power density $P=20$ W/cm^2. $H_0 = 5\times10^{13}$ ions/cm^2.

Thermal annealing restores the electronic properties the samples had before hydrogenation. This rules out the possibility that N passivation by H is caused by N desorption from the samples as a consequence of the postgrowth hydrogen irradiation. Figure 2 shows the PL spectra of the $y=0.001$ sample hydrogenated at $d_H = 5\times10^{15}$ ions/cm^2 and annealed at $T_a = 330$ °C for different duration times. Most of the N-related lines, as well as the broad background beneath them, are progressively recovered for increasing t_a. In the alloy limit (not shown here) we observe a H release upon thermal annealing similar to that reported for $In_xGa_{1-x}As_{1-y}N_y/GaAs$ QW's.[16]

These results as well as those shown in Fig. 1 can be explained by the formation of bonds between H and N atoms, this formation being independent of N dilution (and In

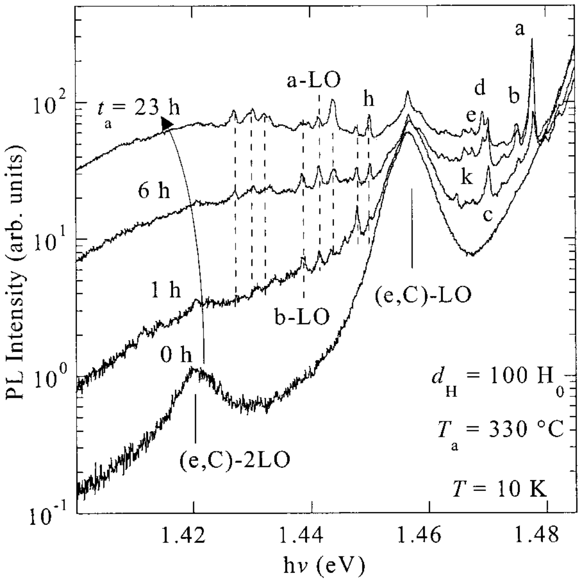

FIG. 2. $T = 10$ K photoluminescence spectra of the $GaAs_{0.999}N_{0.001}$ epilayer hydrogenated at $d_H = 100\ H_0$ for different thermal annealing times t_a (annealing temperature $T_a = 330\,°C$). $H_0 = 5\times10^{13}$ ions/cm^2. Laser power density $P = 10$ W/cm^2.

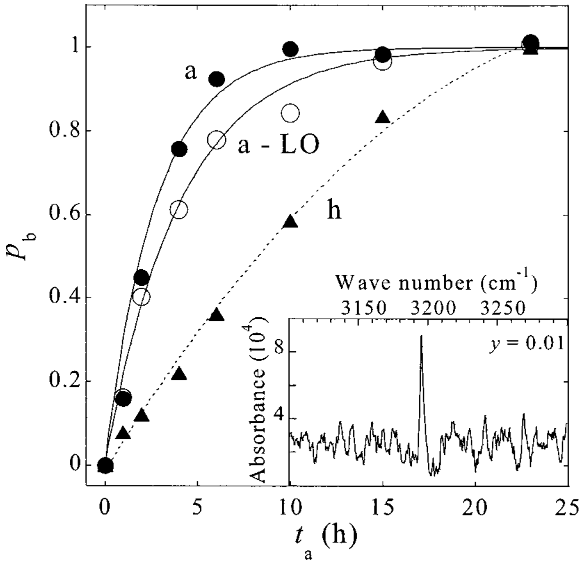

FIG. 3. Annealing duration (t_a) dependence of the percentage of broken H–N bonds, p_b, for the same sample shown in Fig. 2. The triangles, full circles, and open circles refer to luminescence lines *h*, *a*, and *a*-LO, respectively. The continuous lines are a fit of Eq. (1) to the data ($E_a = 2.15$ and 2.17 eV for line *a* and its phonon replica, respectively). The dashed line through line *h* data is a guide to the eye. Inset: Infrared absorption spectrum at $T = 4.2$ K for an hydrogenated 310-nm-thick $GaAs_{0.99}N_{0.01}$ epilayer. The peak at 3195 cm^{-1} is due to a N-H stretch mode. The hydrogen dose is 2×10^{18} ions/cm^2.

presence). Consistent with this picture, a LVM appears at 3195 cm^{-1} in the hydrogenated samples, as shown in the inset of Fig. 3 for the $GaAs_{0.99}N_{0.01}$ epilayer [PL spectrum shown in Fig. 1(c)]. A LVM at 3101 cm^{-1} has been found in $In_xGa_{1-x}As_{1-y}N_y$ ($0 \leqslant x \leqslant 0.06$) and has been attributed to N–H bonds.[17] A NH_2 complex has been invoked, previously to account for a mode observed at 2947 cm^{-1} in GaAs:N.[18] Later on we will discuss on a more quantitative ground how a H–N bond may lead to N passivation.

Now we analyze in more detail the results of the annealing experiments for the samples with low-N content. Different lines recover their intensity at *different rates*, suggesting the presence of N–H complexes with different bond strengths. The percentage of broken bonds of the same type, p_b, versus annealing time t_a at a given T_a is estimated by the ratio between the PL intensity $I(t_a)$ of each line and its saturation value $I_{sat}(t_a \rightarrow \infty)$. If one assumes that H-N complexes dissociate irreversibly (that is, without H recapture), p_b is given by[19]

$$p_b = I(t_a)/I_{sat} = 1 - \exp\{-\nu_a t_a \exp[-E_a/(k_B T_a)]\}, \quad (1)$$

where ν_a is the attempt frequency (set equal to the frequency found here for the N-H local vibrational mode) and E_a is the activation energy for the dissociation of the H-N complex. Some of the lines shown in Fig. 2, such as line *a*, are very rapidly recovered and their intensity saturates after a few hours of annealing. Figure 3 shows the p_b data for different lines. The best fit of Eq. (1) to the p_b data gives an activation energy of 2.15 eV for line *a*. The very close value ($E_a = 2.17$ eV) found for the *a*-LO line supports its assignment to a phonon replica of line *a*. A similar behavior is found for the lines emitting from 40 to 55 meV below the GaAs band edge (*b*, *b*-LO, *c*, *d*, *e*, and *k* lines). The E_a values of these lines range from 2.10 to 2.20 eV, values similar to that found in the alloy limit for the release of H in $In_xGa_{1-x}As_{1-y}N_y$ quantum wells.[16] In contrast, lines emitting below 1.45 eV (except *a*-LO and *b*-LO lines) do not reach a saturation value even after a 25-h annealing at $T_a = 330\,°C$. This is shown in Fig. 3 for line *h*. The slower intensity recovery for these deeper complexes suggests a higher E_a, whose exact value, however, cannot be estimated because of the absence of a well defined $I_{sat}(t_a \rightarrow \infty)$. An increase of E_a for these N complexes emitting at lower energy can be accounted for by clusters or chains with an increasing number of N atoms.[2] In this framework, H can either be caged in clusters with a large number of N atoms or be recaptured by long N-atom chains. In both cases, the formation of a stronger bond or a multistep dissociation process may lead to higher effective E_a's. Although further investigations are needed, we believe that these results may serve as a guideline to the microscopic characterization of the numerous N-related luminescence lines observed so far in $GaAs_{1-y}N_y$/GaAs heterostructures at low N doping.[12]

We now discuss the microscopic origin of the effects related to the N-H interaction. In GaN, the large electronegativity and small size of N has been shown to lead to the formation of H–N bonds in *p*-type material.[20,21] Here, the structural and vibrational properties of H-N complexes in $GaAs_{1-y}N_y$ have been investigated by first-principles theoretical methods. The stable configuration of the H-N complex has been found for a H^+_{BC} ion[22] located at a bond-

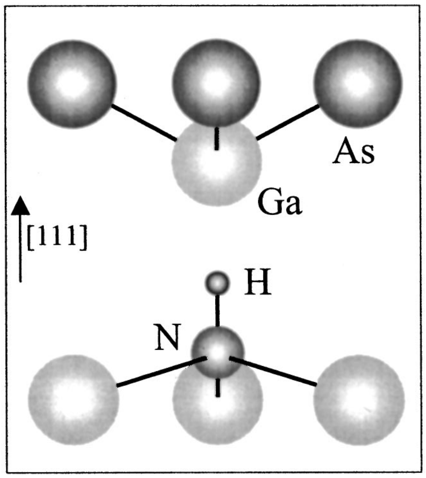

FIG. 4. Sketch of the Ga-H_{BC}^{+}-N complex.

centered (BC) site between Ga and N (see Fig. 4). In this Ga-H_{BC}^{+}-N complex, the H_{BC}^{+}-N and Ga-H_{BC}^{+} bond lengths are equal to 1.05 and 2.43 Å respectively. These values can be compared with the N–H bond length estimated in NH_3 (1.04 Å) and with the sum of the atomic covalent radii of Ga and H (1.58 Å). Such comparison points to a strong H_{BC}^{+}-N bond and negligible Ga-H_{BC}^{+} interactions, as confirmed by an analysis of the electronic charge density distribution (not shown here). In the Ga-H_{BC}^{+}-N complex, the Ga and N atoms relax outwards by 0.63 and 0.45 Å, respectively. The displacements of the four Ga atoms that are first neighbors of the N atom lead to a mean Ga-N distance equal to 2.39 Å, namely, the Ga–As bond length in GaAs. This suggests that the strain induced by the presence of N in the host material is on the average neutralized by the formation of the H-N complex. Furthermore, in the Ga-H_{BC}^{+}-N complex the chemical valence of each atom is fully satisfied. The N atom uses its five electrons to form four bonds with its three Ga neighbors and the H^{+} ion. The Ga atom has its three valence electrons involved in the formation of three Ga–As bonds. Thus, the above results suggest that electronic or structural effects induced by the presence of N on the properties of GaAs are neutralized by the formation of H-N complexes and provide a simple picture of the nitrogen passivation by hydrogen. Notice that additional H-containing complexes might be formed following the neutralization of acceptors in GaAsN. Finally, a vibrational frequency of 3172 cm^{-1} has been calculated for the stretching modes of the H_{BC}^{+}–N bond, in excellent agreement with the local vibrational mode at 3195 cm^{-1} observed by infrared absorption.

Summing up, the electronic properties induced by N in $GaAs_{1-y}N_y$/GaAs heterostructures are neutralized by H irradiation for all the N concentration investigated here. In the dilute limit, radiative recombination related to N complexes are fully quenched upon hydrogenation, providing evidence for strong interaction between H and N complexes. In the alloy limit, the redshift of the band gap upon N insertion is reversed by H irradiation. Evidence of H–N bonds is given by a sharp infrared absorption peak in hydrogenated samples. These results show that the charge distribution around N atoms maintains in the alloy limit the strongly localized character it has in the impurity limit. They also provide a guideline for theoretical models describing the role of N in III-V nitrides and its interaction with H. Finally, total energy calculations in *p*-type $GaAs_{1-y}N_y$ show that H has a stable equilibrium position at the bond center between N and Ga, which may explain the observed N passivation and recovery of the GaAs band gap in $GaAs_{1-y}N_y$:H.

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