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Vibrational spectroscopy of hydrogenated $GaAs_{1-y}N_y$: A structure-sensitive test of an $H_2^*(N)$ model

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The N- and H-vibrational modes in hydrogenated $GaAs_{1-y}N_y$ alloys have been studied by infrared absorption spectroscopy. Data for samples containing both H and D show that the dominant defect complex seen in the infrared spectrum of hydrogenated $GaAs_{1-y}N_y$ contains two weakly coupled N-H stretching modes. This conclusion is inconsistent with the predictions of theory for an $H_2^*(N)$ defect that has been proposed recently to explain the properties of H in $GaAs_{1-y}N_y$ and $In_xGa_{1-x}As_{1-y}N_y$ alloys.

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The III-N-V alloys, especially $GaAs_{1-y}N_y$ and $In_xGa_{1-x}As_{1-y}N_y$, have been the subject of tremendous recent interest because of a large reduction of the band-gap energy that occurs for N concentrations of the order of a few percent.[1–3] Quaternary alloys of $In_xGa_{1-x}As_{1-y}N_y$ with band-gap energies *less* than that of GaAs can be grown lattice matched to GaAs, making the use of these alloys attractive for a wide variety of applications that includes long-wavelength lasers for telecommunications[1,4] and multijunction solar cells.[1,5] Hydrogen is a common impurity in semiconductors that can be introduced intentionally or, as is often the case, unintentionally during crystal growth and processing.[6,7] The hydrogenation of $GaAs_{1-y}N_y$ and $In_xGa_{1-x}As_{1-y}N_y$, unlike for most other semiconductors, gives rise to a remarkable increase of the band-gap energy, eliminating the reduction in energy caused by N.[8–10] This effect of H can be reversed by a thermal anneal at a temperature near 500 °C. Several groups have performed calculations that find that a hydrogen dimer known as H_2^* is stabilized by N in GaAs and GaP.[11–14] Furthermore, the formation of this defect $H_2^*(N)$ has been proposed to be the cause of the increase of the band-gap energies of $GaAs_{1-y}N_y$ and $In_xGa_{1-x}As_{1-y}N_y$ upon hydrogenation.[11–14] Until now, there have been no experimental data that test the microscopic defect models that have been proposed to explain the surprising effect that H has on the band-gap energies of dilute III-N-V alloys. In the present paper, we report the results of an infrared (IR) absorption study of N- and H-containing defects that are produced in $GaAs_{1-y}N_y$ by hydrogenation.

A nitrogen impurity on the group-V site is isoelectronic in III-V semiconductors and has been of long interest. For example, N introduces a localized potential that binds excitons in GaP:N.[15] H has been found to interact with N in GaP and GaAs and affects the luminescence of N-bound excitons.[9,10,16] H-stretching modes of N-H centers in GaP and in GaAs have been observed[17,18] and a few attempts at assignments have been made.[11,12,17–19] Of particular interest is an assignment made by Clerjaud *et al.* who suggested a trigonal H_{AB}-N-H_{BC} structure, in which both the antibonding and bond-centered H atoms are bonded to the same N atom, to explain their vibrational data.[17,18]

Several groups have performed theoretical calculations that show that a trigonal H_{AB}-N-H_{BC} defect with both H atoms bonded to N is unstable in GaP and GaAs and that an $H_2^*(N)$ defect with one H atom bonded to N and a second H atom bonded to Ga would form spontaneously.[11–14,19] Two configurations are predicted (Fig. 1), $\alpha-H_2^*(N)$ and $\beta-H_2^*(N)$, with the former having been found to be slightly lower in energy (~0.1 eV/H atom).[11–14] The vibrational properties of both $H_2^*(N)$ configurations also have been predicted.[11,12,19] For the $\alpha-H_2^*(N)$ defect in either GaAs or GaP, theory finds frequencies near 3150 and 2000 for N-H_{AB} and Ga-H_{BC} stretching modes, respectively, and a frequency near 1000 cm^{-1} for N-H_{AB} wagging. For the $\beta-H_2^*(N)$ defect in GaP, theory also finds a high frequency for N-H_{BC} (3147 cm^{-1}), and frequencies of 1683 and 852 cm^{-1} for the stretching and wagging modes of Ga-H_{AB}. Two groups argued that the vibrational lines seen by Clerjaud *et al.* are due to N-H centers with a single H atom,[12,19] while another suggested that these lines are due to $H_2^*(N)$.[11] The assignment to a center with a single H atom seems preferable

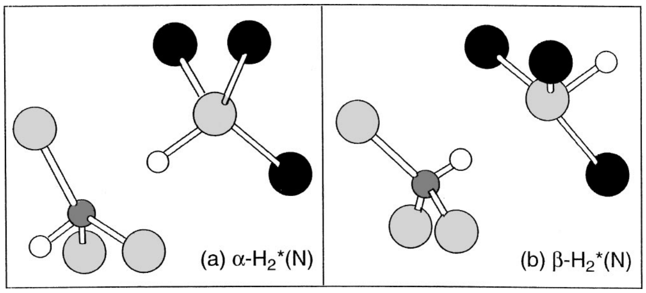

FIG. 1. The (a) $\alpha-H_2^*(N)$ and (b) $\beta-H_2^*(N)$ complexes in GaAsN or GaPN.

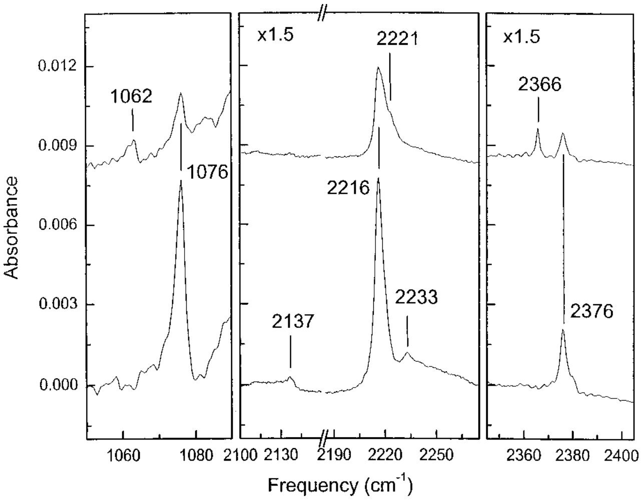

FIG. 2. Vibrational spectra showing the D modes for $GaAs_{0.992}N_{0.008}$ samples measured at 4.2 K with a resolution of 1 cm^{-1}. The lower spectra are for a sample deuterated with a dose of 2×10^{18} D^+/cm^2. The upper spectra are for a sample treated with both H (2×10^{18} H^+/cm^2) and D (2×10^{18} D^+/cm^2).

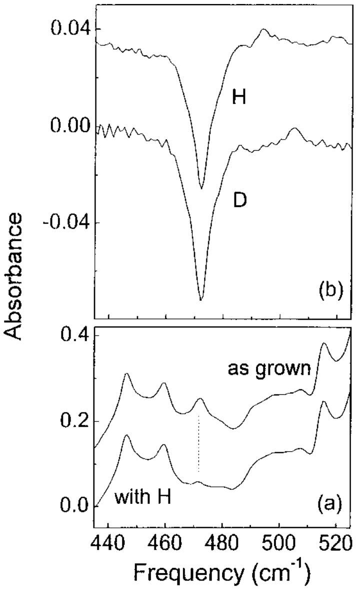

FIG. 3. Vibrational spectra showing the N mode for $GaAs_{0.992}N_{0.008}$ samples measured at 4.2 K with a resolution of 2 cm^{-1}. Spectra for an as-grown sample and a sample hydrogenated with a dose of 2×10^{18} H^+/cm^2 are shown in (a). Difference spectra for hydrogenated and deuterated (with dose 2×10^{18} D^+/cm^2) samples are compared in (b).

because the N-H centers seen by Clerjaud *et al.* were found to be electrically active,[17,18] which is inconsistent with $H_2^*(N)$ configurations which are predicted to be electrically inactive.[11–14,19]

In the present paper, vibrational lines different from those studied previously[17,18] are reported for hydrogenated and deuterated $GaAs_{1-y}N_y$ alloys. The samples used for our experiments were slightly *p*-doped $GaAs_{1-y}N_y$ epilayers, 300-nm thick and with $y=0.008$, that were grown on undoped GaAs substrates by solid source molecular beam epitaxy. A few additional samples, 670-nm thick and with $y=0.002$, were also studied. Hydrogenation or deuteration was performed with a Kaufman ion source with the samples held at 300 °C. The ion energy was 100 eV and current densities of ~ 10 $\mu A/cm^2$ were used. IR absorption spectra were measured over the range 350 to 4000 cm^{-1} with a Bomem DA.3 Fourier Transform spectrometer. Photoluminescence (PL) measurements were performed with the 515-nm line of an Ar^+ laser, a grating monochromator, and a cooled Ge detector.

The hydrogenation (or deuteration) of $GaAs_{1-y}N_y$ gives rise to new H- (or D-) vibrational lines. Figure 2 shows spectra for several D vibrational lines that were seen for a deuterated $GaAs_{0.992}N_{0.008}$ sample. Similar H-vibrational spectra, shifted to higher frequency by a factor approximately equal to $(m_D/m_H)^{1/2}$, were seen for hydrogenated samples with $y=0.008$ and $y=0.002$. The frequencies of these absorption lines are listed in Table I. The intensity of the principal D modes shown in Fig. 2 is consistent with a concentration of deuterated defects equal to the N concentration in the sample and an absorption strength that is typical of local vibrational modes.[20,21] (A line at 2015 cm^{-1} in hydrogenated samples and lines at 2233 and 798 cm^{-1} in deuterated samples were consistently seen. We found no corresponding lines in samples containing the alternative hydrogen isotope.)

The high frequencies of the absorption lines at 3195 and 2967 cm^{-1} are characteristic of the stretching modes of H strongly bonded to a light element such as N (or O) and are at much higher frequencies than might be expected for Ga-H stretching which has a typical frequency near 1800 cm^{-1}.[22] The line at 1447 cm^{-1} has a frequency somewhat smaller than is characteristic of an N-H bending mode in an ammonia molecule (1627 cm^{-1}), suggesting an assignment to an N-H wagging mode.[23] Similarly, the vibrational lines at 2376 and 2216 cm^{-1} shown in Fig. 2 for a deuterated sample have frequencies characteristic of N-D stretching, and the 1076 cm^{-1} line has a frequency near that of N-D bending in ammonia. Furthermore, the frequency ratio $r=\omega_H/\omega_D$ is sensitive to the atom to which the H is attached and, for all of the modes in Table I for which both H and D lines have been

TABLE I. Vibrational frequencies (in units cm^{-1}) for the H and D modes seen in hydrogenated and deuterated $GaAs_{0.992}N_{0.008}$. The frequency ratio $r=\omega_H/\omega_D$ is given for those modes for which corresponding H and D lines were found. Weak lines are indicated by a (*w*).

ω_H	3195		2967	2868(*w*)	2015	1447	
ω_D	2376	2233(*w*)	2216	2137(*w*)		1076	798
r	1.345		1.339	1.342		1.345	

identified, is close to 1.34. This value for r is very similar to what has been observed previously for N-H modes in semiconductors[24] and is smaller than has been observed previously for Ga-H stretching modes with $r = 1.39$.[22,25]

The nature of the high frequency H and D modes is revealed further by spectra measured for samples that contained both H and D. We focus on the D-vibrational lines at 2376 and 2216 cm^{-1} (Fig. 2). For a sample containing H and D, two additional D-stretching lines appear at a reduced separation compared to the lines in the sample containing only D. One line is clearly resolved and appears at 2366 cm^{-1}. A second line appears as a shoulder at 2221 cm^{-1}. (Spectra for the H-stretching region for the sample that contained H and D show a new H-stretching line at 3192 cm^{-1} that is the isotopically shifted partner of the 2366 cm^{-1} line. A line isotopically shifted from the shoulder at 2221 cm^{-1} was not clearly seen in the H-stretching spectrum because of the poor signal to noise ratio at the expected frequency position due to absorption arising from the small concentration of oil vapor and organic contamination that is present in our spectrometer.) The appearance of two new lines with reduced separation upon the introduction of H and D strongly suggests that the D-stretching lines at 2376 and 2216 cm^{-1} are due to a single defect complex and that this complex contains two coupled D atoms. In this case, for the corresponding defects that contain both H and D, the stretching modes are dynamically decoupled to produce the new lines shifted toward the average position of the coupled modes. Similar considerations are presumed to apply to the corresponding H-stretching modes at 3195 and 2967 cm^{-1}.

There is also a weak line present in the D spectrum at 2137 cm^{-1}. This frequency is 15 cm^{-1} less than twice the frequency of the 1076 cm^{-1} line. These frequency positions suggest that the presence of the weak line at 2137 cm^{-1} is due to a Fermi resonance interaction[20] between the second harmonic of the 1076 cm^{-1} line and the 2216 cm^{-1} line from which it derives its intensity. The Fermi resonance interaction requires that the modes be weakly coupled and, therefore, that the 1076 and 2216 cm^{-1} lines belong to the same defect complex. Similar considerations apply to the H-stretching spectra where strong lines at 1447 and 2967 cm^{-1} are seen along with a weak line at 2868 cm^{-1}. The frequency of the 2868 cm^{-1} line is at 26 cm^{-1} less than twice the frequency of the 1447 cm^{-1} line, suggesting that the weak 2868 cm^{-1} line is due to a Fermi resonance interaction between the second harmonic of the 1447 cm^{-1} line and the strong 2967 cm^{-1} line of the complex.

The behavior of the H and D lines reported here is remarkably similar to what was seen previously for the vibrational modes of the H_2^* defect in Si (which consists of H_{AB} and H_{BC} atoms, lying along a trigonal axis, bonded to nearest neighbor Si atoms).[26] For H_2^* in Si, the stretching vibrational modes of H_{BC} and H_{AB} are coupled and additional, dynamically decoupled modes are produced in samples that contain both H and D. Furthermore, the second harmonic of the wagging mode of H_{AB} shows a Fermi resonance interaction with the stretching mode. Therefore, it might be tempting to assign the lines seen in $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ to an $H_2^*(\mathrm{N})$ complex. However, in contrast to our experimental findings, both $\alpha-H_2^*(\mathrm{N})$ and $\beta-H_2^*(\mathrm{N})$ are expected to have one N-H mode near 3150 cm^{-1} and a second Ga-H mode between 1650–2100 cm^{-1}.[11,12,19] The presence of two high frequency N-H modes is inconsistent with the vibrational properties predicted for either configuration of $H_2^*(\mathrm{N})$. We have considered the possibility that both $\alpha-H_2^*(\mathrm{N})$ and $\beta-H_2^*(\mathrm{N})$ configurations might be produced in our samples to explain the observation of two high frequency modes. The vibrational spectra measured for samples that contained H and D and their interpretation, however, suggest that the principal D modes at 2376, 2216, and 1076 cm^{-1} all belong to a single defect and similarly for the corresponding H modes at 3195, 2967, and 1447 cm^{-1}. Furthermore, the corresponding H and D modes all have frequency ratios that are consistent with N-H vibrational modes.

A vibrational band at 471 cm^{-1} that can be seen by IR or Raman spectroscopies for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ was assigned previously to N on the As site.[27–29] Figure 3(a) shows that the nitrogen band at 471 cm^{-1}, initially present in as-grown $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ without H, disappeared when the sample was hydrogenated. The 471 cm^{-1} band is seen as a negative absorption peak in difference spectra [Fig. 3(b)], where the spectrum for the sample without H (or D) is subtracted from the spectrum of the sample with H (or D). When the 471 cm^{-1} band is removed by deuteration, a weak new absorption band at 505 cm^{-1} appears, seen as an upward-going feature in the spectrum. There also might possibly be a low-frequency mode in the hydrogenated sample at 495 cm^{-1}. This band, if present, is weak, making its unambiguous identification difficult.

The intensities of the N-related modes near 500 cm^{-1} and the H or D modes at higher frequency were studied for a series of isochronal (30 min.) anneals. For a deuterated $\mathrm{GaAs}_{0.992}\mathrm{N}_{0.008}$ sample, the absorption of the 471 cm^{-1} N band was restored by a 30 min anneal at 500 °C with the concomitant disappearance of the weak IR line at 505 cm^{-1} along with the D-vibrational lines listed in Table I. The band gap of $\mathrm{GaAs}_{0.992}\mathrm{N}_{0.008}$, as monitored by PL for the same sample, recovered in steps as the annealing temperature was increased up to a temperature of 500 °C where the band-gap energy of $\mathrm{GaAs}_{0.992}\mathrm{N}_{0.008}$ without D was fully recovered. We have also examined the introduction of the D-vibrational lines as a function of increasing D dose. For successive doses of 1×10^{17}, 1×10^{18}, and 2×10^{18} $\mathrm{D}^+/\mathrm{cm}^2$, all of the D lines increased in intensity together while the 471 cm^{-1} N band became successively weaker. All of these results show that the presence of the H and D lines reported here is correlated with the changes in the band-gap energy and intensity of the N mode.

In summary, the formation of an $H_2^*(\mathrm{N})$ defect has been proposed by several theoretical groups to explain the effect of hydrogenation on the band-gap energy of $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_{1-y}\mathrm{N}_y$ alloys.[11–14] The conclusion that the principal defect seen by IR spectroscopy for hydrogenated $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ contains two N-H stretching modes follows naturally from an interpretation of vibrational spectra measured for $\mathrm{GaAs}_{1-y}\mathrm{N}_y$ containing both H and D and is difficult to reconcile with the predictions of theory[11,12,19] for the vibrational properties of $H_2^*(N)$. The trigonal H_{AB}-N-H_{BC} configuration proposed by Clerjaud *et al.*[17,18] would provide a simple explanation for the vibrational data, although this configuration is inconsistent with theory.[11–14,19] Additional, alternative models are possible if defects with more than one N atom or symmetries lower than trigonal are considered. The results of our IR absorption study of the vibrational modes found in hydrogenated $GaAs_{1-y}N_y$ suggest that the fascinating behavior of H in the III-N-V alloys is not yet fully explained.

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[1] J. W. Ager III and W. Wlaukiewicz, Semicond. Sci. Technol. **17**, 741 (2002), and other papers in this special issue on III-N-V semiconductor alloys.

[2] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys. **31**, L853 (1992).

[3] W. G. Bi and C. W. Tu, Appl. Phys. Lett. **70**, 1608 (1997).

[4] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).

[5] S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, Appl. Phys. Lett. **74**, 729 (1999).

[6] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Heidelberg, 1992).

[7] B. Clerjaud, Physica B **170**, 383 (1991).

[8] A. Polimeni, G. Baldassarri H.v.H., M. Bissiri, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 201204(R) (2001).

[9] M. Bissiri, G. Baldassarri H.v.H., A. Polimeni, V. Gaspari, F. Ranalli, M. Capizzi, A. Amore Bonapasta, F. Jiang, M. Stavola, D. Gollub, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **65**, 235210 (2002).

[10] Recently, a similar increase of the band gap energy upon hydrogenation has also been reported for $GaP_{1-y}N_y$; A. Polimeni *et al.*, Phys. Rev. B **67**, 201303(R) (2003).

[11] A. Janotti, S. B. Zhang, and S.-H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).

[12] Y.-S. Kim and K. J. Chang, Phys. Rev. B **66**, 073313 (2002).

[13] A. Janotti, S. B. Zhang, S.-H. Wei, and C. G. Van de Walle, Phys. Rev. Lett. **89**, 086403 (2002).

[14] A. Amore Bonapasta, F. Filippone, P. Giannozzi, M. Capizzi, and A. Polimeni, Phys. Rev. Lett. **89**, 216401 (2002).

[15] D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Lett. **15**, 857 (1965).

[16] M. Singh and J. Weber, Appl. Phys. Lett. **54**, 424 (1989).

[17] B. Clerjaud, D. Côte, W.-S. Hahn, A. Lebkiri, W. Ulrici, and D. Wasik, Phys. Rev. Lett. **77**, 4930 (1996).

[18] B. Clerjaud, D. Côte, W.-S. Hahn, A. Lebkiri, W. Ulrici, and D. Wasik, Phys. Status Solidi A **159**, 121 (1997).

[19] P. Dixon, D. Richardson, R. Jones, C. D. Latham, S. Öberg, V. J. B. Torres, and P. R. Briddon, Phys. Status Solidi B **210**, 321 (1998).

[20] M. Stavola, in *Identification of Defects in Semiconductors*, edited by M. Stavola (Academic Press, Boston, 1999), p. 153.

[21] The integrated absorption of the D lines at 2376, 2216, and 1076 cm^{-1} shown in Fig. 2 and a concentration of deuterated complexes equal to the N concentration in the sample corresponds to an oscillating effective charge (Ref. 20) of $q \sim 0.7$ e.

[22] H. J. Stein, Appl. Phys. Lett. **57**, 792 (1990); H. J. Stein and J. C. Barbour, Phys. Rev. B **56**, 3813 (1997).

[23] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 295.

[24] M. G. Weinstein, C. Y. Song, M. Stavola, S. J. Pearton, R. G. Wilson, R. J. Shul, K. P. Killeen, and M. J. Ludowise, Appl. Phys. Lett. **72**, 1703 (1998).

[25] A few cautions about assignments should be noted. If a Ga-H mode were to have an unusually large anharmonic shift, say $\sim$400 cm^{-1}, then the ratio r would be reduced from its expected value. In this way, a Ga-H mode might give a value for r that mimics an N-H mode, and the line at 1447 cm^{-1} could possibly be due to Ga-H stretching rather that the more straightforward attribution to N-H wagging. Furthermore, the splitting of the corresponding 1076 cm^{-1} D-vibrational line observed for the sample containing both H and D (Fig. 2) is not consistent with the behavior seen for the wagging mode of H_2^* in Si and suggests further caution.

[26] J. D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).

[27] T. Prokofyeva, T. Sauncy, M. Seon, M. Holtz, Y. Qiu, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **73**, 1409 (1998).

[28] H. Ch. Alt, A. Yu. Egorov, Riechert, B. Wiedemann, J. D. Meyer, R. W. Michelmann, and K. Bethge, Appl. Phys. Lett. **77**, 3331 (2000).

[29] S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, and N. Karam, Appl. Phys. Lett. **78**, 748 (2001).