phys. stat. sol. (b) **228**, No. 1, 287–291 (2001)

Electronic Structure of Heavily and Randomly Nitrogen Doped GaAs near the Fundamental Band Gap

YONG ZHANG[1]) (a), S. FRANCOEUR (a), A. MASCARENHAS (a), H. P. XIN (b), and C. W. TU (b)

(a) National Renewable Energy Laboratory, 1617 Cole Blvd. Golden, CO 80401, USA

(b) Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA 92093, USA

(Received June 21, 2001; accepted July 12, 2001)

Subject classification: 71.55.Eq; 78.55.Cr; S7.14

On increasing the nitrogen doping concentration in GaAs, states associated with isolated, paired and clustered (i.e., more complex configurations) nitrogen atoms sequentially appear, with their energy levels being resonant for the isolated center and most of the pairs and becoming bound for a couple of pairs and clusters. At a nitrogen mole concentration of $x \sim 0.1\%$, the shallow nitrogen bound states have merged with the GaAs band edge, which effectively gives rise to a band gap reduction, but the deeper nitrogen bound states persist as discrete levels. We study the behavior of nitrogen at this "transition" concentration, using various techniques (photoluminescence under selective excitation, electroreflectance, and Raman scattering), in order to gain insight into the large band gap reduction observed at all nitrogen concentrations. The validity of a few existing models proposed for explaining the large band gap reduction will be briefly discussed.

Introduction Isolated nitrogen in GaAs is well known to form a resonant state 150–180 meV above the GaAs conduction band edge [1–4]. Nitrogen pairs are found to form either resonant or bound states, depending on their configurations [4]. In addition to these nitrogen impurity states which appear at rather low nitrogen doping levels, deeper and also nitrogen related bound states have been observed more recently at somewhat higher nitrogen doping level ($[N] > 10^{18}\,cm^{-3}$) [5, 6]. Some of these newly observed bound states persist as discrete levels up to a nitrogen doping level near 0.1%. These bound states are more likely to be associated with nitrogen clusters [6, 7] than nitrogen pairs [5]. On further increasing nitrogen concentration, only a broad emission band, with its peak energy red-shifting proportionally to the nitrogen concentration, can be observed in a photoluminescence measurement [8]. The large band gap reduction in $GaAs_{1-x}N_x$ due to the nitrogen incorporation has been observed for nearly a decade [9], and its scaling rule has recently been accurately measured as $\delta E_g(x) = \beta x^{\alpha}$ (eV), with scaling exponent $\alpha = 0.667$ ($\approx 2/3$) and $\beta = 4.1$ [10]. The existence of such a scaling rule supports the impurity band model [11] in which the formation of an impurity band of nitrogen pair bound states is the primary mechanism for the large band gap reduction. However, there exist several other controversial views over this issue [12–14]. In this paper, we report a spectroscopy study on a $GaAs_{1-x}N_x$ sample with $x = 0.1\%$. At this composition, we are able to simultaneously investigate the behavior for two types of nitrogen induced states: those forming a continuous spectrum and those remaining as discrete states. We would like to point out that even those nitrogen induced

[1]) Corresponding author; Phone: +01 303 384 6617; Fax: +01 303 384 6655; e-mail: yzhang@nrel.gov

 0370-1972/01/22811-0287 $ 17.50+.50/0

states belonging to the continuous spectrum do not behave like extended states in GaAs. At least to some extent, they remained spatially localized.

Sample and Experiment The $GaAs_{1-x}N_x$ sample was grown by gas-source molecular beam epitaxy on a semi-insulating (001) GaAs, using a rf nitrogen radical beam source with a mixture of N_2 and Ar in a ratio of 1:9. The growth temperature was 420 °C and the growth rate was 0.8 μm/h. The epilayer thickness is nominally 4000 Å, with a 2000 Å GaAs buffer. The N concentration was determined by high-resolution X-ray rocking curve measurement and theoretical dynamical simulation to be 0.1%. Photoluminescence (PL) spectra were taken at 10 K, using both above band gap and near band gap selective excitation. Electroreflectance (ER) was measured at 80 K.

Results Figure 1 shows a PL spectrum (using above band gap excitation) and an ER spectrum. The dominant PL peaks appears at energies significantly lower than the band gap. Note that even ER was measured at 80 K, the band gap shift between 80 and 10 K is expected to be minimal (a few meV). In addition to the multiple peaks in the low energy region, there is a weak PL peak at 1.473 eV which is very close to the band gap. In fact, this peak is also close to the energy of a transition labeled as NN_A in Ref. [5]. A comparison of the PL and ER spectrum indicates the coexistence of discrete and continuously distributed states introduced by nitrogen doping.

Figure 2 shows the PL spectra obtained under selective excitations. For any excitation energy below the band gap, we always observe a sharp transition, labeled as NN′, at 1.1–1.3 meV below the excitation energy. NN′ most of time is found to be followed by a TA phonon replica of 8.6 meV. Besides this moving peak, we also observe a few other peaks (NN_B, NC, and NN_D) whose peak positions remain stationary on varying the excitation energy. Here NN_B and NN_D are labeled as in Ref. [5], but they are reasonably to be interpreted as excitons bound to nitrogen clusters as for NC, although the exact configurations are not known at this time. A similar N

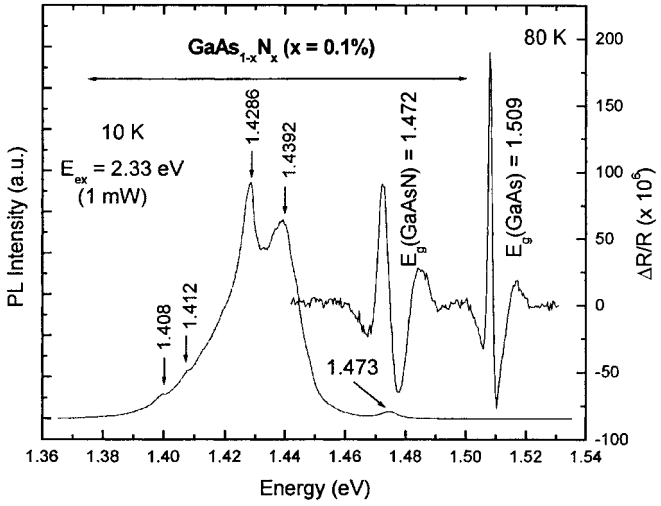

Fig. 1. Photoluminescence (left) and electroreflectance (right) spectrum

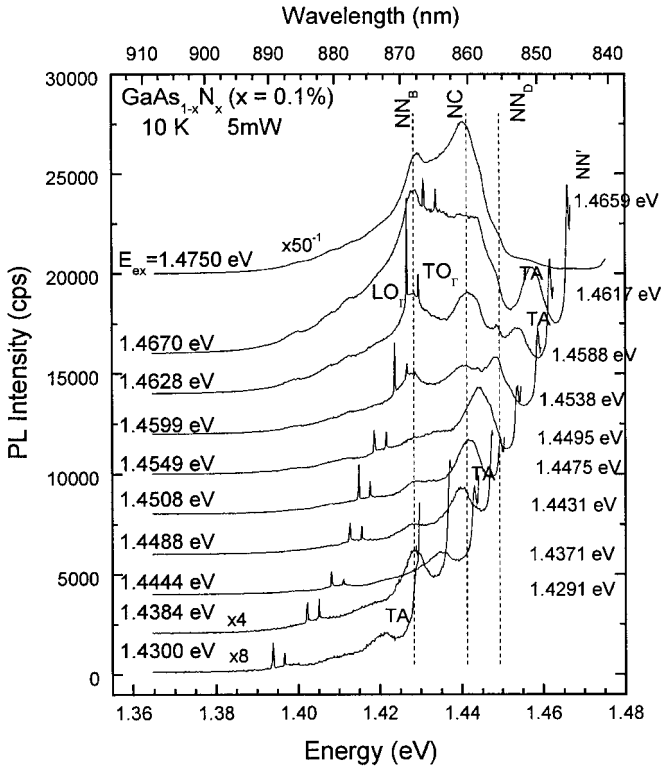

Fig. 2. Selective excitation PL spectra with different excitation energies indicated on the left. The peak energies for the NN′ transition are shown on the right. The spectra are vertically shifted for clarity

cluster related transition has also been observed in GaP:N [15]. The tunable below band gap excitation or absorption reveals that the continuous spectrum actually extends into an energy region at least 40 meV below the band gap, which means that the energy spectrum of nitrogen induced states is comprised of closely spaced (thus, practically continuous) states and well separated discrete states. The continuous spectrum can be understood as nitrogen pair states under the random perturbation of nearby nitrogen atoms which do not form isolated clusters. Very similar phenomenon has been observed in GaP:N [15]. The red shift between the excitation energy and NN′ can be explained as follows: the excitons created at the excitation energy tend to transfer to nearby trapping centers of local energy minima within their radiative lifetime [16]. These observations lead to the conclusion that although the nitrogen induced states form a continuous spectrum energetically, they retain a certain degree of spatial localization. When the exciation energy is tuned just above the band gap, alongside with a large enhancement in the PL intensity (as shown in the topmost spectrum of Fig. 2), we find that not only the NN′ peak disappears but also the Raman lines (LO_Γ and TO_Γ) become invisible. In fact, the disappearence of the NN′ peak is indicative of that the states above the band gap are less localized than those below the band gap.

Discussions In recent papers [7, 10, 11, 15], we have pointed out and demonstrated the close similarity in various aspects between the heavily nitrogen doped III–V semiconductors and heavily n- or p-type doped semiconductors where one also observes a very large band gap reduction together with effects due to the random nature of doping [17]. Here we summarize three possible cases, which we have discussed previously at different occasions, for the impurity band formation in nitrogen doped III–V semiconductors. The first case is that bare electrons bound to nitrogen centers directly couple with each other. The second case is unique to the systems discussed here. Note that usually the experimentally significant is not the bare electron bound state but the exciton bound state. The impurity band formation may originate from the coupling between the exciton bound to nitrogen centers. This situation is in fact analogous to the case of the impurity band formation for the acceptor in semiconductors, recalling that the nitrogen bound exciton was classified as acceptor-like [18]. With the excitonic effect taken into account, the inter-center coupling may become more probable than fully relying on the coupling of the bare electron states, since the radius of the hole bound state of the bound exciton is significantly larger than that of the electron bound state. The third case is unique to the random distribution of impurities. In fact, this is a well discussed situation for the impurity band in literature [17]. Essentially, in a random system, the impurity centers can have closely spaced energy levels, but each center remains spatially localized, which effectively forms a continuous spectrum. All the three cases discussed here may occur in $GaP_{1-x}N_x$ and $GaAs_{1-x}N_x$, depending on the nitrogen concentration and on which center is considered. To theoretically model these systems, one faces two difficulties: the first is to accurately describe the very localized impurity potential, and the second is to properly simulate the random structure. For instance, the impurity potential used in a recent calculation [19] was able to match the energy of the resonant isolated nitrogen state reasonably well in its energy, but yielded nitrogen pair states that very poorly match experimental results, which makes the conclusion arrived questionable. Also, the supercell size used for simulating the random nitrogen doped GaAs was not quite sufficient for properly modeling the inter-pair interaction for a relatively low doping level of $x \sim 0.1\%$ [19]. Thus, it still remains to be confirmed both experimentally and theoretically whether the states just above the band edge are due to the impurity band formation of nitrogen pair states [7] or the GaAs host states being perturbed and pushed down [19].

Acknowledgements The work at NREL was supported by the U.S. DOE under contract No. DE-AC36-83CH10093 and by the NREL DDRD under program No. 0659.0004, and the work at UCSD was partially supported by Midwest Research Institute under subcontractor No. AAD-9-18668-7 from NREL.

References

[1] D. J. WOLFORD, J. A. BRADLEY, K. FRY, J. THOMPSON, and H. E. KING, in: Inst. Phys. Conf. Ser. No. 65, Ed. G. E. STILLMAN, The Institute of Physics, Bristol 1983 (p. 477).
D. J. WOLFORD, J. A. BRADLEY, K. FRY, and J. THOMPSON, in: Proc. 17th Internat. Conf. Physics of Semiconductors, Eds. J. D. CHADI and W. A. HARRISON, Springer-Verlag, New York 1984 (p. 627).
[2] X.-S. ZHAO, G.-H. LI, H.-X. HAN, Z.-P. WANG, R.-M. TANG, and R.-Z. CHE, Acta Phys. Sin. **33**, 588 (1984) [Chin. Phys. **5**, 337 (1985)].
[3] M. LEROUX, G. NEU, and C. VÈRIÉ, Solid State Commun. **58**, 289 (1986).

[4] X. Liu, M.-E. Pistol, L. Samuelson, S. Schwetlick, and W. Seifert, Appl. Phys. Lett. **56**, 1451 (1990).
X. Liu, M.-E. Pistol, and L. Samuelson, Phys. Rev. B **42**, 7504 (1990).
[5] T. Makimoto, H. Saito, T. Nishida, and N. Kobayashi, Appl. Phys. Lett. **70**, 2984 (1997).
T. Makimoto, H. Saito, and N. Kobayashi, Jpn. J. Appl. Phys. **36**, 1694 (1997).
[6] H. Güning, L. Chen, Th. Hartmann, P. J. Klar, W. Heimbrodt, F. Höhnsdorf, J. Koch, and W. Stolz, phys. stat. sol. (b) **215**, 39 (1999).
[7] Y. Zhang, A. Mascarenhas, J. F. Geisz, H. P. Xin, and C. W. Tu, Phys. Rev. B **63**, 85205 (2001).
[8] S. Francoeur, G. Sivaraman, Y. Qin, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **72**, 1857 (1998).
[9] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys. **31**, L853 (1992).
[10] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **63**, R161303 (2001).
[11] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **61**, 7479 (2000).
[12] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).
[13] E. D. Jones, N. A. Modline, A. A. Allerman, S. R. Kurtz, A. F. Wright, S. T. Tozer, and X. Wei, Phys. Rev. B **60**, 4430 (1999).
[14] T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. B **60**, R11245 (1999).
[15] Y. Zhang, B. Fluegel, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **62**, 4493 (2000).
[16] J. H. Collet, J. A. Kash, D. J. Wolford, and J. Thompson, J. Phys. C **16**, 1283 (1983).
[17] B. I. Shklovskii and A. L. Efros, Electronic Properties of Doped Semiconductors, Springer-Verlag, Berlin 1984.
[18] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).
[19] P. R. C. Kent and A. Zunger, Phys. Rev. Lett. **86**, 2613 (2001).