Photoreflectance evidence of the N-induced increase of the exciton binding energy in an $In_xGa_{1-x}As_{1-y}N_y$ alloy

M. Geddo[a)]
INFM-UdR Pavia, Via Bassi 6, I-27100 Pavia, Italy and Dipartimento di Fisica della Università di Parma, Viale delle Scienze 7a, I-43100 Parma, Italy

G. Guizzetti
INFM-Dipartimento di Fisica "A. Volta," Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy

M. Capizzi and A. Polimeni
INFM-Dipartimento di Fisica, Università di Roma, Piazzale A. Moro 2, I-00182 Roma, Italy

D. Gollub and A. Forchel
Universität Würzburg, Technische Physik, Am Hublaund 97074, Würzburg Germany

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The binding energy of the heavy-hole ground-state exciton in $In_{0.25}Ga_{0.75}As_{1-y}N_y/GaAs$ single quantum wells ($y=0$, 0.011) was experimentally derived by photoreflectance measurements. We measured a binding energy of 6.6 and 8.5 meV for the N-free and the N-containing sample, respectively. The observed increase of the exciton binding energy can be accounted for by an increase of the exciton reduced mass of about 30% upon N introduction into the $In_xGa_{1-x}As$ lattice, consistently with recent experimental results and in agreement with earlier theoretical predictions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1594279]

In recent years $In_xGa_{1-x}As_{1-y}N_y/GaAs$ heterostructures[1] have attracted much interest owing to the surprising N-driven evolution of their electronic parameters which make these compounds GaAs-compatible highly efficient emitters in the 1.3–1.55 μm wavelength range. Nitrogen incorporation in $In_xGa_{1-x}As$ leads to a large bowing of the band gap for increasing N concentration and strongly modifies the hydrostatic pressure and temperature dependence of the band gap of the host material. These effects have been the subject of a large number of experimental and theoretical papers[2] and have been accounted for in terms of a highly localized perturbation of the lattice potential due to the N atoms. In a perturbative approach,[3] the N perturbation is reduced phenomenologically to the interaction between the level of an isolated N atom and the conduction band minimum (CBM). A comprehensive detailed theoretical model based on symmetry breaking considerations[4] predicts a sizable localized character of the CBM and the appearance of cluster states in the band gap.

The same theoretical models predict a significant increase of the electron effective mass. These predictions have been validated by different experimental techniques, with quite different results for In-containing and In-free alloys.[5–11] In the case of $In_xGa_{1-x}As_{1-y}N_y/GaAs$ quantum wells (QWs), band structure calculations[12] indicate that the electron effective mass increases up to ~30% upon N introduction for $y=0.02$. Recent calculations for similar heterostructures suggest an increase in the exciton binding energy in N-containing samples, as well.[13]

In this letter, the optical response of $In_xGa_{1-x}As_{1-y}N_y/GaAs$ single QWs was observed in N-free (or blank) and N-containing samples by exploiting the phase-sensitive detection and the derivative-like nature of the photoreflectance (PR) technique. A detailed analysis of the PR line shape has led to an accurate determination of the nature and the energy location of density of states critical points and has allowed us to separate the exciton and band-to-band components of the PR features associated to the main heavy-hole transition. We estimated a ~30% increase in the exciton binding energy upon 1% N insertion, in agreement with the predictions of recent calculations concerning the effect of N insertion in III–V alloys.[13] This is experimental evidence of the increase of the exciton binding energy in the perturbed host lattice. This increase can be accounted for by a ~60% increase of the electron effective mass, in agreement with an estimate obtained by measurements of the diamagnetic shift in the same samples.

The heterostructures investigated have been grown on GaAs substrates by solid source molecular beam epitaxy. They consist of a 500-nm-thick GaAs buffer, a 6-nm-thick $In_{0.25}Ga_{0.75}As_{1-y}N_y$ well ($y=0$, 0.011), and a 100-nm-thick GaAs cap layer. N_2 craking was obtained by using a radio frequency plasma source. The N concentration was determined by x-ray diffraction measurements. The blank and the nitrogenated structures have been singled out from a set of previously well characterized samples.[14,15] For our experiment we chose a sample with a relative low content of N ($y=0.011$) to avoid a PR signal degradation caused by the increased disorder of the crystalline structure, but suitable to produce a significant change in the electron effective mass (and, in turn, in the exciton binding energy).

PR measurements were performed at near-normal incidence in the 0.8–1.6 eV range, with spectral resolution of 1 meV. The standard experimental apparatus operated with a 100 W halogen lamp as probe source. The excitation source was provided by a 2 mW He–Ne laser, mechanically

a)Electronic mail: geddo@fisicavolta.unipv.it

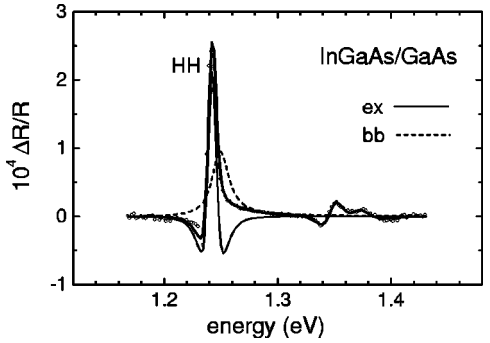

FIG. 1. Photoreflectance spectrum at 90 K of the blank sample. Decomposition into exciton (continuous line) and band-to-band (dashed line) contribution to the $1HH-1E$ feature is reported. Thick line indicates the best fit to the experiment (open circles).

chopped at a frequency of 220 Hz. The sample was mounted in thermal contact with the cold finger of a microminiature Joule–Thompson refrigerator that allows measurements in the 80–300 K temperature range.

Photoreflectance spectra taken at 90 K in the blank sample and the N-containing sample are shown in Figs. 1 and 2, respectively. Consistently with previously published photoluminescence and PR results,[14,15] we attribute the PR features at lower energy (which dominate in both spectra) to the optical response of the heavy-hole to conduction band transitions ($1HH-1E$) in the $In_xGa_{1-x}As_{1-y}N_y$ well. PR signals coming from higher excited state transitions as well as from the GaAs band gap of the buffer and/or cap layers were also detected in both spectra. The doublet (splitting: 26–30 meV) in Figs. 1 and 2 at higher energy than the $1HH-1E$ transition has been included in the best fitting procedure since it affects the determination of transition energies for the $1HH-1E$ structure. The nature of this doublet, as well as of the higher energy structures, is beyond the scope of the present manuscript (it will be the object of an analysis to be published elsewhere). Tentatively, the high energy doublet might be attributed to the light-hole transition ($1LH-1E$) and to $2HH-2E$ transition on the basis of the results reported in Ref. 16 for a 9-nm-thick $In_{0.28}Ga_{0.72}As$ well. However, contributions from weaker forbidden transitions, e.g., the $2HH-1E$ or $1HH-2E$ cannot be excluded.

An inspection of Figs. 1–2 shows that: (i) A rigid redshift affects the exciton transitions of the N containing sample, due to the well known[1–4] band gap reduction which characterizes III–V materials in the dilute N solution limit. (ii) The broadening parameter Γ of the $1HH-1E$ transition detected in the blank sample increases roughly by a factor of 2 in the N containing sample (from 10 to 23 meV). A similar behavior has been reported[14,15] for the line width of the *HH* free-exciton PL spectrum and accounted for by the increased disorder in the well produced by N introduction. (iii) The line shape of the $1HH-1E$ transition looks quite asymmetric (this must be related to the presence of a sizable band-to-band component) in both spectra, in particular in the spectrum of the N-containing sample.

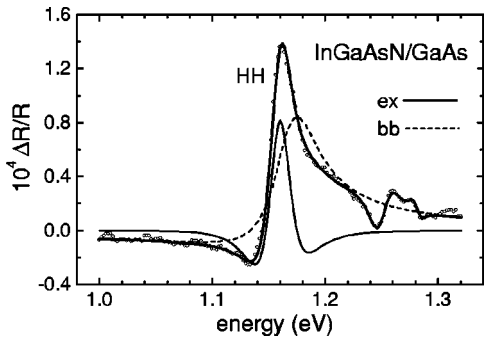

FIG. 2. Photoreflectance spectrum at 90 K of the N-containing sample. Decomposition into exciton (continuous line) and band-to-band (dashed line) contribution to the $1HH-1E$ feature is reported. Thick line indicates the best fit to the experiment (open circles).

Here we focus on the PR features of the $1HH-1E$ transitions where the extremely favorable signal-to-noise ratio allows to distinguish between exciton and band-to-band contributes to the experimental line shape. We should mention here that H irradiation, in a suitable dose, can be used to improve PR signal-to-noise ratio.[17] When attempting to interpret the optical response on the basis of the line shape models characteristic of modulation spectroscopy we found that a band-to-band contribution has to be added to the excitonic contribution in order to reproduce satisfactorily the experimental results. The deconvolution of the best fit into band-to-band (dashed lines) and exciton (solid lines) components displayed in Figs. 1–2 highlights the spectral weight gained by the *HH* band-to-band component after N insertion.

The line shape models used in the fitting procedure are those of excitonic[18] or band-to-band[19] transitions in confined systems. Moreover the first derivative of a gaussian profile has been used for the dielectric function in order to take into account the inhomogeneous broadening[18] related to thickness and composition fluctuations of the QWs.

The experimental line shapes have been fitted in terms of the Aspnes formula[20]

$$\Delta R/R = \mathrm{Re}[Be^{i\varphi}(h\upsilon - E + i\Gamma)^{-n}], \tag{1}$$

which is generally used to reproduce electroreflectance and photoreflectance spectra near a critical point in bulk semiconductors[20] as well as in confined systems[18,19,21] $h\upsilon$ is the photon energy of the probe beam and E is the critical point (CP) energy; B and Γ are the amplitude and the broadening parameter of the critical point, respectively; φ is the phase projection angle; n is an integer or half integer depending on the type of critical point. In the case of confined systems, exciton[18] and band-to-band[19] transitions have been satisfactorily fitted with values of the parameter n equal to 3 and 1, respectively.

Since best fits in terms of a single contribution were unsuccessful in both N-free and N-containing samples, two contributions were considered. The simultaneous presence of distinct bandgaps separated by 30–40 meV and due to N atoms occupying different environments has been reported in $In_xGa_{1-x}As_{1-y}N_y$ samples.[22,23] However, by no way we could fit our spectra in terms of two $n=1$ (or $n=3$) contributions so largely separated. Quite satisfactory fits have been obtained, instead, by using two closely spaced structures with $n=3$ and $n=1$ to reproduce the $1HH-1E$ signal. In the case of the higher energy signals, which are more noisy and could be almost equally fitted by using $n=1$ or 3, we choose the excitonic profile ($n=3$).

TABLE I. Energy and broadening of the $1HH-1E$ excitonic (ex) and band-to-band (bb) components as obtained by fitting Eq. (1) to the photoreflectance spectra. The fit-derived uncertainty in the energy separation of the $1HH-1E$ contributions is 0.5 meV.

Sample		E (eV)	Γ (meV)	ΔE (meV)
Blank	ex	1.2426	10	6.6
	bb	1.2492	8	
N-containing	ex	1.1587	24	8.5
	bb	1.1672	24	

In Table I the physical parameters Γ and E of both components for the $1HH-1E$ transition obtained from the best fit of the experimental line shape can be compared for the two samples. The energy separation between the CPs of the two contributions to the $1HH-1E$ PR features is an estimate of the exciton binding energy.

In the blank sample, the exciton binding energy determined from the splitting of the two contributions to $1HH-1E$ is 6.6 ± 0.5 meV, in excellent agreement with experimental and theoretical results.[24,25] In the N-containing sample this value increases to 8.5 ± 0.5 meV in qualitative agreement with the predictions of recent theoretical calculations.[13]

An estimate of the electron effective mass, m_e^*, can be obtained by assuming that the dielectric constant does not change sizably upon the introduction of a small concentration of N ($y=0.011$) in the lattice and by taking a value of $0.335\ m_0$, independent of N content, for the heavy hole effective mass, where m_0 is the free-electron effective mass.[13] In turns, this change of the HH exciton binding energy can be accounted for by a $60\%\pm15\%$ increase in the electron effective mass, m_e^*. This increase agrees pretty well with measurements of the diamagnetic shift in the same sample which leads to an increase of m_e^* equal to $\sim42\%$ (to be published elsewhere). It is also consistent with that (50%–100%) reported for m_e^* in similar QW structures on the basis of a fitting to the transition energy for HH transitions as measured by optical techniques[10,11] as well as with the theoretical increase predicted on the ground of an increased localized character of the electron wave function upon N introduction in the $In_xGa_{1-x}As$ lattice.[4]

Let's finally comment the possibility to detect a band-to-band component in addition to the exciton component in QW PR features. In $Al_xGa_{1-x}As/GaAs$ and $In_xGa_{1-x}As/GaAs$ QWs it has been well established that the nature of the transitions is essentially excitonic up to room temperature.[18] Nevertheless, in $Al_xGa_{1-x}Sb/GaSb$ heterostructures, it has been shown that exciton can be partially screened by an increase in the impurity concentration in the well, thus favoring the reappearing of a band-to-band character in the QW transitions.[26] Moreover, both exciton and band-to-band transitions have been observed at room temperature on a doped $GaAs/In_xGa_{1-x}As/Al_xGa_{1-x}As$ QW.[27] In both cases the reappearing of the band-to-band character of the transitions must be related to the presence of free carriers, due to nonintentional doping (the former) or intentional doping (the latter). In the present case, where there is no intentional doping, the possibility to reveal a band-to-band component in QW PR features could be related to the competition between free excitons and bound excitons (not detected with an absorption-like technique).

The origin of the localized states could be well width and/or strain fluctuations, as well as composition fluctuations (In- and N-rich cluster regions) mentioned by Xin *et al.*[28] The last effect is expected to be more pronounced in the N containing QWs, consistently with the simultaneous presence of nonuniform In and N concentrations.

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[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).
[2] For a review see: "Special issue: III–N–V semiconductors alloys" Semicond. Sci. Technol. **17**, 741 (2002).
[3] 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).
[4] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).
[5] E. D. Jones, N. A. Modine, A. A. Allerman, I. J. Fritz, S. R. Kurtz, A. F. Wright, S. T. Tozer, and X. Wei, Proc. SPIE **3621**, 52 (1999).
[6] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **61**, 7479 (2000).
[7] C. Skierbiszewski, P. Perlin, P. Wisniewski, W. Knap, T. Suski, W. Walukiewicz, W. Shan, K. M. Yu, E. E. Haller, J. F. Jeisz, and J. M. Olson, Appl. Phys. Lett. **76**, 2409 (2000).
[8] P. N. Hai, W. N. Chen, A. Buyanova, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **77**, 1843 (2000).
[9] J. Wu, W. Shan, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. P. Xin, and C. W. Tu, Phys. Rev. B **64**, 085320 (2001).
[10] M. Hetterich, M. D. Dawson, A. Yu. Egorov, D. Bernklau, and H. Riechert, Appl. Phys. Lett. **76**, 1030 (2000).
[11] Z. Pan, L. H. Li, Y. W. Lin, B. Q. Sun, D. S. Jiang, and W. K. Ge, Appl. Phys. Lett. **78**, 2217 (2001).
[12] S. Tomic and E. P. O'Reilly, Physica E (Amsterdam) **13**, 1102 (2002).
[13] K. Ryczko, G. Sek, and J. Misiewicz, Solid State Commun. **112**, 323 (2002).
[14] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Appl. Phys. Lett. **77**, 2870 (2000).
[15] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 195320 (2001).
[16] G. Sek, K. Ryczko, J. Misiewicz, M. Fischer, M. Reinhardt, and A. Forchel, Thin Solid Films **380**, 240 (2000).
[17] We have observed that the H irradiation of $In_xGa_{1-x}As/GaAs$ QW ($0.25<x<0.32$) increases the PR signal by a factor of 5 at 90 K and a factor of 2 at 300 K, thus permitting a more precise quantitative analysis of the signal.
[18] H. Shen, S. H. Panad, F. H. Pollack, and R. N. Sacks, Phys. Rev. B **37**, 10919 (1988); J. Glembocki and B. Shanabrook, in *Semiconductors and Semimetals*, edited by D. G. Seiler and C. L. Littler (Academic, Boston, 1992), Vol. 36, p. 221; F. H. Pollak, in *Handbook on Semiconductors*, edited by P. Balkansky (North-Holland, Amsterdam, 1994), Vol. 2, p. 527.
[19] Y. S. Tang, J. Appl. Phys. **69**, 8298 (1991).
[20] D. E. Aspnes, Surf. Sci. **37**, 418 (1973).
[21] L. Aigouy, T. Holden, F. H. Pollak, N. N. Ledentsov, W. M. Ustinov, P. S. Kop'ev, and D. Bimberg, Appl. Phys. Lett. **70**, 3329 (1997).
[22] P. J. Klar, H. Gruning, J. Coch, S. Shafter, K. Volz, W. Stolz, W. Heimbrodt, A. M. Kamal Saadi, A. Lindsay, and E. P. O'Reilly, Phys. Rev. B **64**, 121203(R) (2001).
[23] 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).
[24] R. C. Iotti and L. C. Andreani, Semicond. Sci. Technol. **10**, 1561 (1995).
[25] P. Bigenwald and B. Gil, Solid State Commun. **91**, 33 (1994).
[26] R. Ferrini, M. Geddo, G. Guizzetti, M. Patrini, S. Franchi, C. Bocchi, E. Mukhamedzhanov, A. Baraldi, and R. Magnanini, Phys. Rev. B **59**, 15395 (1999).
[27] M. Geddo, S. Di Lernia, and L. C. Andreani, Semicond. Sci. Technol. **12**, 1121 (1997).
[28] H. P. Xin, K. L. Kavanagh, Z. Q. Zhu, and C. W. Tu, Appl. Phys. Lett. **74**, 2337 (1999).