

Effect of nitrogen on the temperature dependence of the energy gap in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ single quantum wells

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The electronic properties of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ single quantum wells have been investigated by photoluminescence and photoreflectance spectroscopy as a function of temperature. The introduction of nitrogen leads to a sizable slow down in the redshift of the ground state recombination energy with temperature. We explain the observed effects in terms of an anticrossing between states of the conduction band (CB) edge and a N-induced localized level resonant with the CB. The extent of this anticrossing, described by the matrix element V_{MN} , is derived from the temperature dependence of the exciton recombination energy in a wide compositional range. The measured functional dependence of V_{MN} on nitrogen concentration is compared with results reported in the literature.

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(InGa)(AsN)/GaAs heterostructures are of potential interest in the field of telecommunications, e.g., for the realization of devices emitting at 1.3 and 1.55 μm .¹ Most of the interesting properties of this system come from the modification of the band structure of the (InGa)As alloy due to incorporation of small amounts (a few percent) of nitrogen in the lattice. A dramatic redshift of the host material band gap is commonly found,^{1–5} as well as a large increase of the electron effective mass.^{6,7} These observations have been accounted for by assuming that N gives rise to a level E_N localized in real space² and degenerate with the states of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ conduction band (CB)—as expected for substitution of As with N atoms.⁸ The interaction between the CB states and E_N leads to a band repulsion, which is responsible for the observed band-gap shrinkage, and to an increase of the electron effective mass because of the mixed free/localized character of the electron wave function. In the framework of the perturbation theory, this mixing is described by the matrix element $V_{MN} = \int d\mathbf{k} d\mathbf{k}' \varphi_M^*(\mathbf{k}) U(\mathbf{k}, \mathbf{k}') \varphi_N(\mathbf{k}')$, where φ_M and φ_N are the single-particle states of the conduction band for free and N-localized electrons, respectively, and $U(\mathbf{k}, \mathbf{k}')$ is the Fourier transform of the N-impurity potential. As a result, the recombination energy of carriers confined in a (InGa)(AsN) quantum well (QW) can be written as²

$$h\nu = 1/2\{E_N + E_M - [(E_N - E_M)^2 + 4V_{MN}^2]^{1/2}\}, \quad (1)$$

where E_M is the energy of the (InGa)(AsN) unperturbed conduction sub-band. An estimate of V_{MN} has been obtained by pressure-dependent photoreflectance measurements^{2,9} and by optical absorption spectroscopy.¹⁰ The functional dependence of V_{MN} , E_M , and E_N on the nitrogen concentration,

derived for the $\text{GaAs}_{1-y}\text{N}_y/\text{GaAs}$ system within a two-band model, has been suggested to hold for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$, as well.¹¹

On the other hand, pseudopotential supercell calculations in $\text{GaAs}_{1-y}\text{N}_y$ show that nitrogen causes an interaction between Γ - and L -CB minima, which increases with N content,¹² as observed by ballistic electron emission spectroscopy¹³ and Raman scattering experiments¹⁴ in $\text{GaAs}_{1-y}\text{N}_y$ epilayers. Similar effects have been invoked in order to explain also the pressure dependence of the photoluminescence emission energy in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ epilayers.¹⁵

In this paper, we report on the effect of temperature T on the photoluminescence (PL) and photoreflectance (PR) of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ single QW's. Structures differing for the indium ($x=0.25$ – 0.41) and nitrogen ($y=0$ – 0.052) content have been studied. The thermal redshift of the ground-state transition energy has been measured from $T=10$ K to room temperature (RT). Its investigation in samples with and without nitrogen shows that the thermal redshift sizably decreases with increasing y . By the interaction model of Eq. (1) we (i) fully account for the thermal redshift in all samples; (ii) provide an estimate of the interaction energy V_{MN} between the $\text{In}_x\text{Ga}_{1-x}\text{As}$ CB edge and the N-localized level; (iii) find that the strength of the interaction potential decreases at high-indium content ($x=0.25$ – 0.41), thus suggesting short-range order effects in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloys.^{16,17}

We have investigated a number of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ single QW's grown by solid source molecular beam epitaxy with indium (nitrogen) concentrations $x=0.25$ ($y=0.011$), $x=0.32$ ($y=0.027$), $x=0.38$ ($y=0.042, 0.052$),

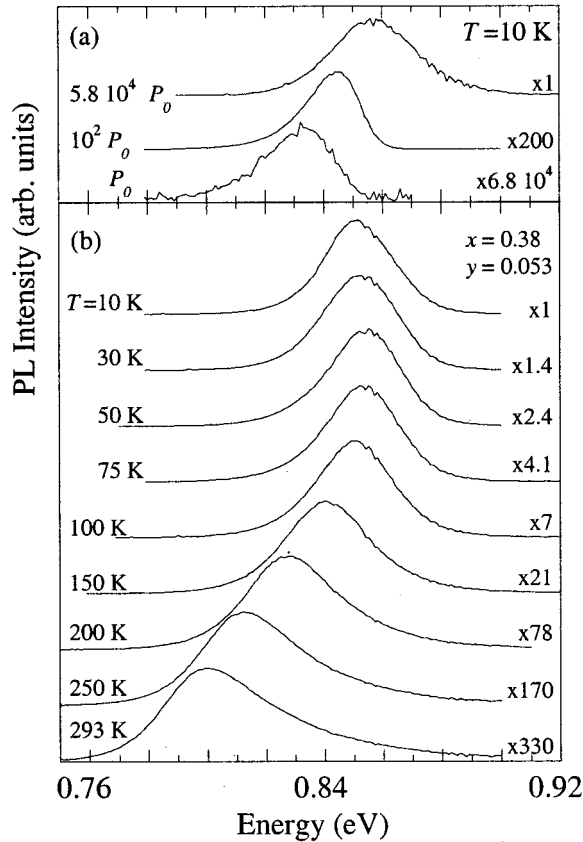


FIG. 1. (a) Peak-normalized photoluminescence PL spectra of a sample having $x=0.38$, $y=0.052$, and $L=8.2$ nm for different laser-power densities ($P_0=2.5$ mW/cm²). Normalization factors are given for each spectrum. (b) PL spectra recorded at different temperatures for a same level of laser-power density ($P=30$ W/cm²). Normalization factors are given for each spectrum.

and $x=0.41$ ($y=0.022, 0.031$). The N concentration has been determined by a combined analysis of x-ray diffraction and optical data. For each subset of quantum wells having the same indium content and well width L , but differing for the nitrogen concentration, a reference sample without nitrogen (blank) has been grown. L ranges from 6.0 to 8.2 nm. All samples have a 100-nm-thick GaAs-capping layer. PL was excited by the 515-nm line of an Ar⁺ laser, dispersed by a $\frac{3}{4}$ -m double or a 1-m single monochromator, and detected by an (InGa)As photodiode or a cooled Ge detector. PR measurements were performed at near normal incidence in the temperature range from $T=90$ K to RT. The probe source was a 100-W-halogen lamp, the excitation source was a He-Ne laser (power 2 mW) chopped at 220 Hz.

Figure 1(a) shows PL spectra at $T=10$ K as a function of the laser power P for the QW with the highest nitrogen content ($x=0.38$, $y=0.052$, and $L=8.2$ nm). At low P , the PL line shape is asymmetric, with a low-energy tail of localized-exciton (LE) states. This tail is present in other (InGa)(AsN) QW's and epilayers^{9,18–20} and in a large number of semiconductor alloys.^{21,22} The complexes giving rise to the LE states are likely due to In-N clusters, as proposed for (InGa)N/GaN QWs (Ref. 23) and for (InGa)(AsN)/GaAs heterostructures.^{9,20} N clusters, indeed, give rise to spatially local-

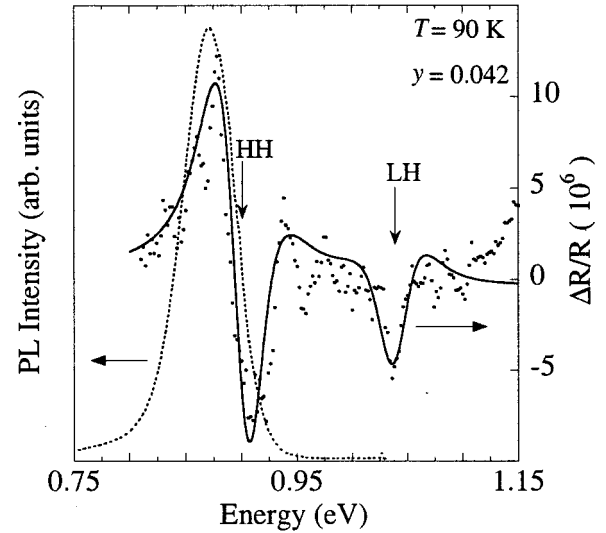


FIG. 2. Photoluminescence PL (left axis, dotted line) and photoreflectance PR (right axis, full dots) spectra of a sample with $x=0.38$, $y=0.042$, and $L=6.5$ nm at $T=90$ K. The continuous line is a simulation of the PR spectrum by the model of Ref. 24. Vertical arrows indicate the energies of the heavy (HH) and light (LH) hole exciton as determined by the simulation procedure. For PL spectrum, laser-power density $P=18$ W/cm².

ized fluctuations in the potential energy and to capture centers for excitons. For increasing P , the PL peak energy blueshifts due to carrier filling of LE states. Finally, at high power a new component adds to the spectrum on the high-energy side, which we attribute to free exciton recombination in the In_xGa_{1-x}As_{1-y}N_y quantum well. A similar behavior has been observed in all samples containing nitrogen. The presence of localized excitons can be inferred also from the temperature dependence of the PL spectra shown in Fig. 1(b). In fact, the blueshift of the PL peak energy observed as T increases up to 75 K should be attributed to a progressive carrier detrapping from LE states. However, we find that in low-N samples ($y<0.042$) LE states contribute sizably to PL spectra at low temperature only ($T<60$ K).

Figure 2 shows the PL (dotted line) and PR (full dots) spectra at 90 K for a sample with high-N content ($y=0.042$). The continuous line is a simulation of the PR data based on the model of Ref. 24. In PR, two transitions are observed and attributed to heavy- (HH) and light- (LH) hole excitons. The energy difference ΔE between the PL peak and the HH free exciton energy determined by PR is 27 meV, thus indicating a sizable contribution of LE states to the PL spectrum. This energy offset reduces to 16 meV for $T>200$ K. In other samples with medium-nitrogen content ($y=0.027$), ΔE is smaller (see inset in Fig. 3) and the temperature dependence of the transition energy as measured by PL and PR is the same over all the common T range. This is shown in Fig. 3 by the full squares (PL data) and dots (PR data). In the same figure, the temperature dependence of the exciton energy as measured by PR in the N-free blank is also shown by open dots (the data of the blank have been offset by -0.165 eV for ease of comparison with the N-containing sample). The rate of thermal redshift of the exciton transition

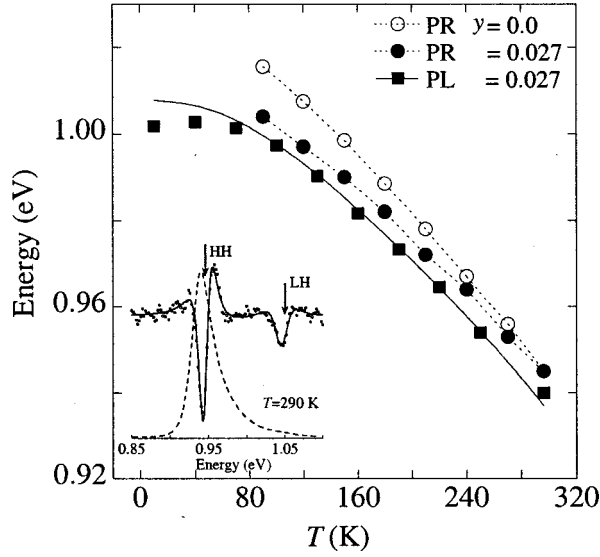


FIG. 3. Dependence on temperature of the transition energy for a sample having $x=0.32$, $y=0.027$, and $L=6.0$ nm as measured by photoluminescence PL (full squares) and photoreflectance PR (full dots). The transition energy of the corresponding blank as measured by PR is shown by open dots. The continuous line is the best fit of the interaction model to the data, as discussed in the text [see Eq. (2)]. Dotted lines are a guide to the eye. Inset: PL (dashed line) and PR (open dots) spectra of the same sample at room temperature. Vertical arrows indicate the energies of the heavy- (HH) and light- (LH) hole exciton as determined by the simulation procedure of Ref. 24 (continuous line).

energy is slower in the $y=0.027$ QW than in the blank. In general, a decrease of the thermal redshift with increasing y is found in all investigated samples (not shown here) and also observed in other (InGa)(AsN) based samples.^{4,20,25}

We now discuss in more detail the thermal properties of the N-containing QWs. In the framework of the interaction model,² N gives rise to a localized level. The energy E_N of this level should not vary much with T , as observed for deep centers²⁶ and strongly confining nanostructures.²⁷ In turn, the electronic level resulting from the interaction between E_N and the CB edge bears part of the T insensitivity of E_N . Therefore, the temperature dependence of the exciton recombination energy may provide a simple experimental tool for estimating the interaction matrix element V_{MN} , which determines the degree of mixing between N-localized and CB-extended states. This simple approach is alternative to the use of optical measurements in epilayers at very high pressure^{2,9} and optical absorption in a free-standing sample.¹⁰ By assuming that E_N is temperature independent, we can rewrite Eq. (1) and obtain the variation of the exciton energy at different T 's:

$$h\nu_P(T) = 1/2\{E_N + E_M(T) - [(E_N - E_M(T))^2 + 4V_{MN}^2]^{1/2}\}. \quad (2)$$

In the limit of $V_{MN}=0$ (i.e., $y=0$), Eq. (2) gives the temperature dependence of the recombination energy of N-free QW's. For increasing V_{MN} (or y), the term in square brackets

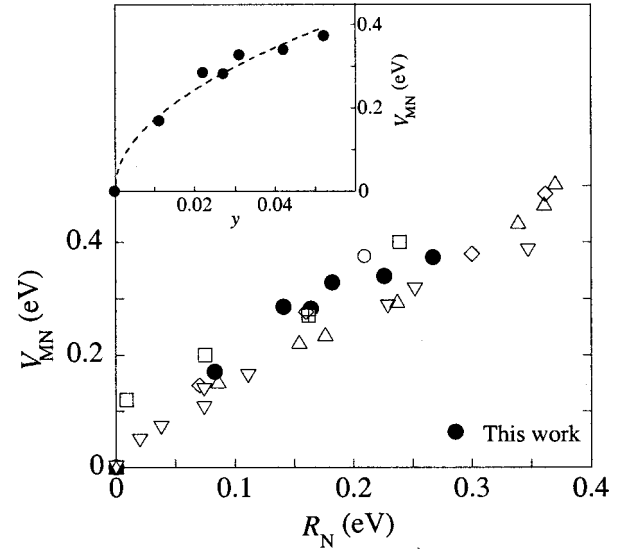


FIG. 4. Interaction potential, V_{MN} , vs the N-induced band gap redshift R_N at RT (full dots). Data reported in the literature are shown by open symbols. $\square$, Ref. 2; ∇ , Ref. 9; $\boxplus$, Ref. 10; $\triangle$, Ref. 29; $\circ$, Ref. 30; $\diamond$, Ref. 31. Inset: Dependence of V_{MN} on N concentration for the samples studied in this paper. The dashed line is a fit of $V_{MN} = C_{MN}\sqrt{y}$ to the data ($C_{MN} = 1.7$ eV).

tends to lower the ground-state energy and to reduce the thermal shift of $h\nu_P$, thus qualitatively accounting for the reduced temperature dependence found in (InGa)(AsN) QW's. The dependences of E_N , E_M , and V_{MN} on the nitrogen content of the well should be duly taken into account. Since E_N and E_M are not directly accessible by experiments, we use the dependences on N content calculated in Ref. 11 for $\text{GaAs}_{1-y}\text{N}_y/\text{GaAs}$ (all quantities are measured in eV): namely, $E_M(y) = E_c^0 - 1.55y$ and $E_N(y) = E_N^0 - 2.52y$. E_c^0 is the minimum of the conduction-band energy of the host matrix without N. $E_N^0 = (1.675 \text{ eV})$ is the energy of an isolated-N state.¹¹ All energy levels are measured with respect to the valence band maximum. We set $E_c^0(T)$ equal to the T dependence of the exciton recombination energy experimentally determined in the QW's without nitrogen and use V_{MN} as a free parameter in the best fit of Eq. (2) to the experimental dependence of the exciton energy on temperature in N-containing QW's. This dependence is measured by the PL peak energy provided that localization effects can be disregarded (PR data have been used whenever this does not happen).

The continuous line in Fig. 3 shows a best fit of Eq. (2) to the data of the $y=0.027$ QW ($V_{MN}=0.282$ eV). The deviation of the theoretical data from the experimental points observed for $T < 100$ K is due to an increasing contribution of localized excitons to the low-temperature PL spectra. The same fitting procedure has been successfully applied to all samples considered in this work, thus providing V_{MN} values for different In and/or N concentrations.

It should be noticed that Γ -L intermixing effects in the CB induced by nitrogen^{12,15} cannot account for the observed temperature dependence of the (InGa)(AsN) band gap. In fact, the L minimum of the CB redshifts with increasing

temperature faster than the Γ minimum does.²⁸ Therefore, a level resulting from the mixing of Γ and L states should exhibit a *larger* redshift than a Γ state alone, contrary to what is observed.

All values of V_{MN} obtained by fitting Eq. (2) to the experimental $h\nu_p(T)$'s have been plotted in Fig. 4 vs R_N , namely, the energy difference at RT between $h\nu_p$ in N-free and N-containing samples. Data from the literature^{2,9,10,29,30} are also shown, as well as those obtained by a recent analysis³¹ of the temperature dependence of the band gap in $\text{GaAs}_{1-y}\text{N}_y$ epilayers. The agreement between estimates of V_{MN} obtained by different techniques in samples with different indium concentrations is rather good. This indicates that R_N and V_{MN} are correlated since they are a different measure of the same effect, i.e., the interaction of nitrogen with the CB states of the (InGa)As host lattice. The inset in Fig. 4 shows the V_{MN} values for our samples ($x=0.25-0.41$) as a function of the N concentration. The dashed line is a fit of $V_{MN}=C_{MN}\sqrt{y}$ to the data. The best fit value of C_{MN} is 1.7 eV quite smaller than the values (2.3–2.7 eV) found in (InGa)(AsN) samples with indium concentration varying between 0 and 0.08.^{2,9,10,29-31} This finding is consistent with theoretical predictions of atomic ordering effects,^{16,17} which lead to a N-induced band gap lowering in (InGa)(AsN)

smaller than in Ga(AsN) (Ref. 16) (also predicted for II-VI quaternary alloys in Ref. 32).

In conclusion, the influence of nitrogen on the band structure of single $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ QW's with high x (0.25–0.41) has been investigated by studying the temperature dependence of the PL and PR line shape and peak position. At low temperature ($T<60$ K), the PL spectra are mainly due to recombination of excitons localized most likely in In-N clusters. A comparison of the thermal properties of QW's with and without nitrogen has been performed in the framework of the band-anticrossing model. This provides an estimate of the interaction energy V_{MN} between the states of the unperturbed CB edge and a localized level introduced by nitrogen. By comparing the dependence of V_{MN} on y found here with previous findings in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ epilayers with zero or low-indium content ($x=0.08$), we provide an experimental support to short-range ordering effects recently predicted to take place in (InGa)(AsN).

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