

**Abnormal broadening of the optical transitions in (Ga,As)N/GaAs quantum wells**S. Turcotte,<sup>\*</sup> J.-N. Beaudry,<sup>†</sup> R. A. Masut, and P. Desjardins*Département de Génie Physique and Regroupement Québécois sur les Matériaux de Pointe (RQMP), École Polytechnique de Montréal, Case Postale 6079, Succursale Centre-ville, Montréal, Québec, Canada H3C 3A7*G. Bentoumi and R. Leonelli<sup>‡</sup>*Département de Physique and Regroupement Québécois sur les Matériaux de Pointe (RQMP), Université de Montréal, Case Postale 6128, Succursale Centre-ville, Montréal, Québec, Canada H3C 3J7*

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We have measured the near band-gap absorption of structurally well characterized GaAs<sub>1-x</sub>N<sub>x</sub> quantum wells grown on GaAs(001) with  $x < 0.014$ . The spectra were reproduced by a model that includes electron-hole correlations. We find that the width of the excitonic and band-to-band optical transitions are more than twice larger than what is found in conventional III-V alloy heterostructures. This confirms the presence of strong nitrogen-configuration induced band-gap fluctuations reported previously by Bentoumi *et al.* [*Phys. Rev. B* **70**, 035315 (2004)] for bulk dilute GaAsN alloys.

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The large band-gap bowing observed in III/V dilute nitride semiconductors finds applications in a variety of optoelectronic devices, such as photovoltaic cells,<sup>1-3</sup> semiconductor lasers,<sup>4,5</sup> and heterojunction bipolar transistors.<sup>6</sup> However, these materials cannot be considered as conventional semiconductor alloys. Aside from the large bowing parameter, the incorporation of nitrogen in GaAs generates two non-parabolic conduction subbands instead of the parabolic one found in GaAs. Furthermore, in bulk layers, nitrogen-induced electronic perturbations imply that the absorption edge cannot be treated as is generally done in III-V semiconductors.<sup>7,8</sup> In particular, it has been found that in bulk GaAs<sub>1-x</sub>N<sub>x</sub>, nitrogen-configuration fluctuations broaden the absorption edge for  $x$  as low as 0.002 and that exciton resonances disappear for  $x > 0.005$ .<sup>8</sup>

As the sharpness of the near-edge optical transition in quantum confined heterostructures plays an important role in optical device operation, it is also of interest to examine the influence of nitrogen on the optical properties of quantum wells (QWs). Surprisingly, there have only been a few studies on the near band-gap absorption edge in GaAsN/GaAs QWs. Sun *et al.*<sup>9</sup> followed the temperature dependence of the absorption edge of QWs with  $x = 0.015$ . Takao *et al.*<sup>10</sup> measured the room-temperature absorbance of samples with  $x \geq 0.037$ . However, no attempt to analyze the optical transition broadening in QWs as a function of nitrogen content has been presented so far. In this paper, we analyze the broadening mechanisms of dilute GaAsN/GaAs(001) multiple quantum wells (MQWs) with a two-dimensional (2D) adaptation of a model developed for bulk epitaxial layers,<sup>8</sup> and we compare it to the broadening measured in bulk GaAsN epilayers and in QWs composed of conventional III-V alloys.

GaAs<sub>1-x</sub>N<sub>x</sub> MQWs in the composition range  $0.0005 \leq x \leq 0.014$  were grown using metal-organic vapor phase epitaxy on (001) oriented semi-insulating GaAs substrates. Trimethylgallium, tertiarybutylarsine, and dimethylhydrazine were used as gas sources for Ga, As, and N, respectively. The samples, which consist of seven GaAsN/GaAs bilayers capped with a GaAs layer, were grown at 550 °C. Further details on the growth procedure can be found in Ref. 11.

The structural quality of the samples was ascertained with high-resolution x-ray diffraction (HRXRD) and transmission electron microscopy (TEM). The HRXRD measurements were carried out in a Philips diffractometer using Cu  $K\alpha_1$  radiation from a four-crystal Ge(220) Bartels monochromator that provides an angular divergence of 12 arc sec with a relative wavelength spread  $\Delta\lambda/\lambda = 7 \times 10^{-5}$ .  $\omega$ - $2\theta$  scans (where  $\omega$  is the angle of incidence and  $\theta$  the Bragg angle) were obtained with a detector acceptance angle of approximately 2°. Cross-sectional TEM analyses were carried out in a Philips CM30 microscope equipped with a LaB<sub>6</sub> electron source operated at 300 kV. The optical absorption experiments were performed with the samples mounted strain free and cooled to 6 K in a liquid-helium flow cryostat. The spectra were acquired using a Fourier transform spectrometer with a resolution better than 0.5 meV. For the sample with  $x = 0.0005$ , the MQW absorption edge could not be well separated from that of the GaAs substrate. We rather performed photoluminescence excitation (PLE) measurements, which gives the same information in the case of QWs near the band edge under thermal equilibrium conditions.<sup>12</sup> The PLE was excited with a tunable Ti:sapphire laser and detected with a 1-m double spectrometer equipped with a GaAs photomultiplier tube.

Figure 1 shows a cross-sectional TEM image of the sample with  $x = 0.014$ . The GaAsN/GaAs interfaces are sharp and the heterostructure is defect free. Furthermore, HRXRD spectra confirm the high structural quality of the samples. Figure 2 shows a typical rocking curve around the (004) planes of the samples. The main peaks and their satellites are well defined and surrounded by Pendellösung fringes that testify the good composition and thickness uniformity of the epilayers. The rocking curves were simulated using the Takagi-Taupin equations of the dynamical diffraction theory<sup>13</sup> under the assumptions that the layers are pseudomorphic with the GaAs substrate, the interfaces are abrupt, and continuum elasticity theory applies.<sup>14</sup> The HRXRD simulations, combined with the TEM images, allow the determination of the GaAsN well thicknesses and nitrogen compositions, which are reported in Table I.

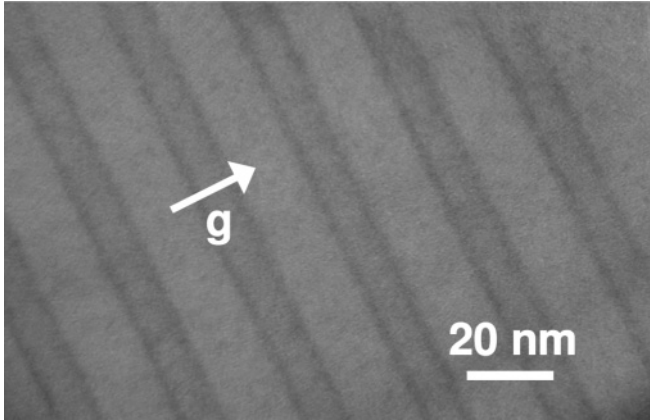


FIG. 1. Cross-sectional bright-field TEM image of sample GaAsN71 with  $x = 0.014$ , obtained near  $[1\bar{1}0]$  for  $g = [004]$ .

The absorption spectra for the samples with  $x \geq 0.0026$  are shown in Fig. 3, together with the PLE spectrum of the sample with  $x = 0.0005$ . A well-defined excitonic resonance is observed for the samples with  $x \leq 0.014$ , which indicates a higher  $e$ - $h$  wave function overlap in the case of QWs as compared to the bulk.<sup>8</sup> In order to extract quantitative information from the absorption spectra, electron-hole correlations must be taken into account. The strength of these correlations is controlled by the exciton binding energy  $R^*$ . For each direct transition between nondegenerate parabolic bands in 2D, the absorption coefficient  $\alpha(\hbar\omega)$  takes the form<sup>15</sup>

$$\alpha = \frac{C}{\hbar\omega} \left[ 2R^* F_1(\hbar\omega - E_X) + \int_{E_g}^{\infty} \frac{F_2(\hbar\omega - E)}{1 + e^{-2\pi/\sqrt{z}}} dE \right], \quad (1)$$

where only the dominant  $1s$  exciton state has been included. In Eq. (1),  $z = (E - E_g)/R^*$ ,  $E_X = E_g - R^*$ ,  $C$  is a constant which depends on the interband transition matrix elements, and  $F_1$  and  $F_2$  are line shape functions with unit surfaces. In GaAsN/GaAs(001) QWs, the splitting of the valence bands due to biaxial tensile strain shifts the  $lh$  and  $hh$  subbands, respectively, above and below the strain-free degenerate valence band. This effect, combined with the strain-induced anisotropy of the effective masses, makes the  $e_1$ - $lh_1$  a spatially

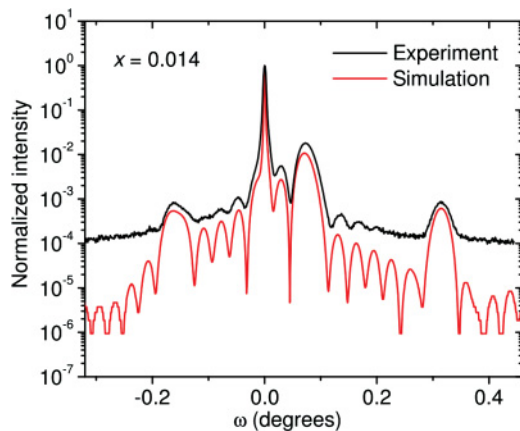


FIG. 2. (Color online) Measured (black) and simulated (red) HRXRD rocking curves around the (004) planes of sample GaAsN71 with  $x = 0.014$ .

TABLE I. Nitrogen composition and width of the MQWs with seven bilayers.

Sample	Nitrogen composition $x$	Well width $L_z$ in nm ( $\pm 0.3$ nm)
GaAsN68	0.0005	10.8
GaAsN69	0.0026	10.8
GaAsN70	0.0074	10.0
GaAsN71	0.014	8.4

direct transition (type I) while the  $e_1$ - $hh_1$  transition is spatially indirect (type II).<sup>16</sup> The direct  $e_1$ - $lh_1$  transition thus dominates the near-gap absorption edge. Indeed, the spectra presented in Fig. 3 do not show any evidence of multiple transitions due to strain-induced valence-band splitting. Therefore, it is more appropriate to use the following empirical function for the absorption coefficient:

$$\alpha = \frac{1}{\hbar\omega} \left[ A_1 V(\hbar\omega - E_X) + A_2 \int_{E_g}^{\infty} \frac{G(\hbar\omega - E)}{1 + e^{-2\pi/\sqrt{z}}} dE \right], \quad (2)$$

where  $A_1$  and  $A_2$  are constants,  $V$  is a Voigt function with Lorentzian and Gaussian FWHM  $\Gamma_{XL}$  and  $\Gamma_{XG}$  centered at an energy  $E_X$ , and  $G$  is a Gaussian line shape with FWHM  $\Gamma_G$ . As shown in Fig. 3, Eq. (2) gives excellent fits to the experimental data with the optimized parameters listed in Table II, strong evidence for a type I transition in these QWs with low nitrogen content. Equation (2) does not take into account the effects of the strong band nonparabolicity that occurs in GaAsN.<sup>17,18</sup> The values of  $E_X$ ,  $R^*$ , and  $\Gamma_{XL}$  are thus approximative. In contrast, the values of  $E_g$  and  $\Gamma_G$  are determined with a good degree of precision since they depend on the position and extent of the continuum edge transition. Indeed, the values of  $E_g$  shown in Table II indicate that  $\partial E_g / \partial x = -15$  eV, a value close to what was found for bulk samples in the same composition range.<sup>8</sup>

In conventional ternary III-V semiconductors, optical transition broadening is dominated at low temperature by

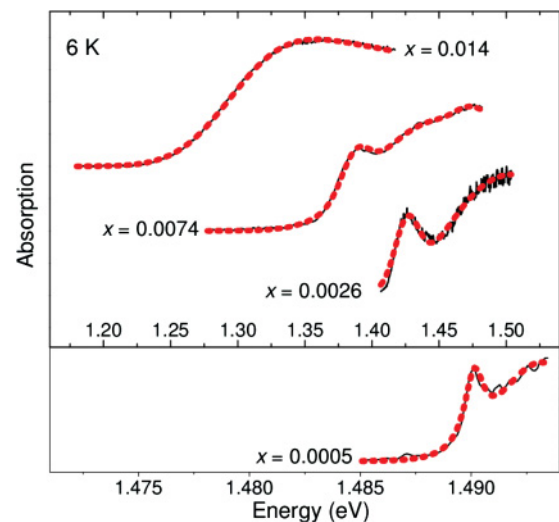


FIG. 3. (Color online) Absorption spectra of the GaAs<sub>1-x</sub>N<sub>x</sub> MQWs with  $x \geq 0.0026$  and PLE spectrum for the sample with  $x = 0.0005$ . The solid lines correspond to the experimental data and the red dots to the best fits using Eq. (2).

TABLE II. Values of the parameters used to fit the absorption coefficients with Eq. (2).  $\Gamma_{XL}$  was maintained fixed at 1 meV for all samples.  $\Gamma_G^{th}$  is the broadening expected for a conventional random alloy as given by Eqs. (3)–(5).

$x$	$E_x$ (eV)	$\Gamma_{XG}$ (meV)	$E_g$ (eV)	$R^*$ (meV)	$\Gamma_G$ (meV)	$\Gamma_G^{th}$ (meV)
0.0005	1.490	<1	1.493	4.9	1.9	2.8
0.0026	1.426	20.6	1.460	6.0	26.8	6
0.0074	1.388	23.6	1.400	9.8	32.7	11
0.014			1.298	5.9	33.1	17

compositional disorder on a microscopic scale.<sup>19–21</sup> For a zinc-blende random alloy, the 2D broadening is described by a Gaussian having a FWHM  $\Gamma_G$  given by<sup>20</sup>

$$\Gamma_G^{th} = 2\sqrt{2 \ln 2} \left[ \frac{a_0^3}{4\pi (a_B^{2D})^2 L_z} x(1-x) \right]^{1/2} \left| \frac{\partial E_g}{\partial x} \right|, \quad (3)$$

where  $a_0$  is the lattice constant,  $a_B^{2D}$  is the 2D exciton Bohr radius, and  $L_z$  is the QW width. The random alloy model has been applied to InGaAs/InAlAs MQWs lattice matched to InP, a technologically important system.<sup>20</sup> Most of the measured widths of the optical transitions of heterostructures with well widths similar to those of our samples were found to fall within 20% of those predicted by Eq. (3).<sup>20–22</sup>

The Bohr radius and band-gap shift with composition depends on the specific system studied. In order to compare the optical transition broadening in our samples to other ternary alloys, it is best to compare the measured values of  $\Gamma_G$  to the ones given by Eq. (3). In the case of a narrow QW with infinite confinement, the exciton Bohr radius  $a_B^{2D}$  equals half the bulk Bohr radius  $a_B^{3D}$ .<sup>23</sup> For QWs with finite confinement,  $a_B^{2D}$  can be estimated using a simple analytical method that introduces an effective dimensionality  $d_{\text{eff}}$  given by<sup>23,24</sup>

$$d_{\text{eff}} = 3 - \exp \left\{ -\frac{L_{\text{QW}}}{2a_B^{3D}} \right\}, \quad (4)$$

where  $L_{\text{QW}}$  is the effective width of the QW. The QW 1s exciton Bohr radius is then obtained from  $d_{\text{eff}}$  using

$$a_B^{2D} = \left[ 1 + \frac{d_{\text{eff}} - 3}{2} \right] a_B^{3D}. \quad (5)$$

In Eq. (4),  $L_{\text{QW}}$  should take into account the wave function spread into the barriers.<sup>24</sup> However, tight-binding calculations indicate that, for our relatively wide QWs, the electronic wave functions are well confined within the wells except for the sample with the lowest nitrogen content. We thus have set  $L_{\text{QW}} = L_z$ . It can be seen from Eqs. (4) and (5) that this approximation results in a lower bound for  $a_B^{2D}$  and thus a higher bound for the calculated values of  $\Gamma_G^{th}$ . We further have set  $a_B^{3D}$  equal to the bulk GaAs value, as it is not very sensitive to the low N content of the samples examined here.

The data points in Fig. 4 show the ratio  $\Gamma_G/\Gamma_G^{th}$  for our samples. It also shows the values of  $\Gamma_G/\Gamma_G^{th}$  obtained in bulk GaAsN layers as reported in Ref. 8 and presents a direct comparison of dilute nitride 2D and 3D systems with QWs of conventional alloys where the random model is verified. The value of  $\Gamma_G/\Gamma_G^{th}$  for the sample with  $x = 0.0005$  is

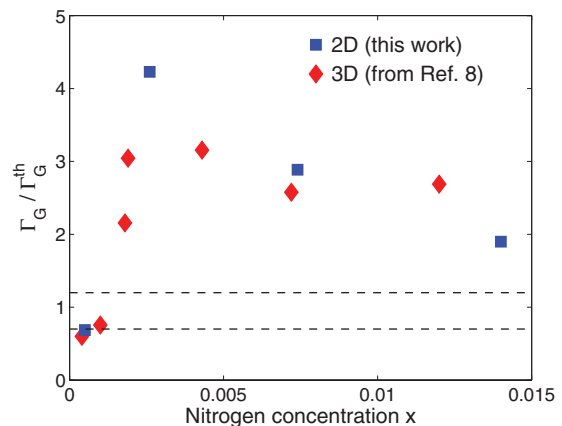


FIG. 4. (Color online)  $\Gamma_G/\Gamma_G^{th}$  as a function of nitrogen concentration  $x$ . The blue squares correspond to the values for the samples presented in this work and the red circles to values obtained from bulk epitaxial layers (Ref. 8). The dashed lines delimit the range of values measured in InGaAs MQWs (Refs. 20–22).

smaller than 1. This is not surprising since, for this sample, we underestimated the wave function leakage into the barriers and thus the exciton volume. For the other samples, we find that  $\Gamma_G/\Gamma_G^{th}$  reaches a value of four for the sample with  $x = 0.0026$  and then decreases. It is difficult to ascertain whether this effect is significant or not. Nevertheless, the large values of the ratio  $\Gamma_G/\Gamma_G^{th}$  (larger than 2) is a clear indication that the broadening of the optical transitions in dilute nitrides with  $x \geq 0.0026$  is much larger than in conventional random alloys and thus that other broadening mechanisms are present. Further, even though  $\Gamma_G$  is more than twice higher in some of our MQW samples than in bulk GaAsN layers with comparable nitrogen content, the ratio  $\Gamma_G/\Gamma_G^{th}$  reaches similar values for  $x \geq 0.0074$  in both 2D and 3D dilute nitride systems.

Optical transition broadening in MQWs can also arise from fluctuations in well width. The TEM image shown in Fig. 1 indicates that  $\Delta L_z \approx 0.3$  nm for the sample with  $x = 0.014$ . This would amount to a change in the transition energy of  $\Delta E \approx 5$  meV. From the convolution of independent normal distributions, it can be assumed that the observed broadening  $\Gamma'$  is given by  $\Gamma' = (\Gamma_G^2 + \Delta E^2)^{1/2}$ . Since  $\Gamma_G \gg \Delta E$ , its value would be reduced by at most 3% if well thickness fluctuations were accounted for. It follows that neither compositional nor structural disorder can explain the optical transition broadening we observe in our GaAsN samples.

Another broadening mechanism can arise from anisotropic N-N interactions, which have been predicted for very low concentrations.<sup>25,26</sup> Further, *ab initio* calculations performed within the generalized-gradient approximation have revealed that the band gap of ordered GaAsN depends markedly on nitrogen atomic configuration in a composition range that encompasses that of our samples.<sup>8</sup> We thus propose that the observed abnormal broadening of the optical transitions in our MQWs is induced by N-N configuration variations that occur on the scale of the exciton Bohr radius. The sharp rise of  $\Gamma_G$  observed close to  $x = 0.002$  can then be interpreted as a transition from isolated to interacting nitrogen atoms. At this concentration, the average distance between

nitrogen atoms is  $\sim 2$  nm, a distance that would correspond to the onset of strong N-N interactions in dilute GaAsN alloys.

In conclusion, we have measured the width of the near band-gap optical transition in a series of GaAsN/GaAs multiple quantum wells with nitrogen concentration in the range  $0.0005 \leq x \leq 0.014$ . We find that, for  $x \geq 0.0026$ , the optical transitions are significantly broadened with respect to what is measured in conventional III-V alloys where compositional disorder dominates. A similar increase in the width of the

optical transitions was also observed in bulk GaAsN epitaxial layers. We thus confirm that large band-gap fluctuations are induced by nitrogen-nitrogen interactions at the atomic level.

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