Optical investigations of GaInNAs/GaAs multi-quantum wells with low nitrogen content

H. D. Sun,[a] M. Hetterich,[b] and M. D. Dawson
Institute of Photonics, University of Strathclyde, Glasgow, G4 ONW, Scotland, United Kingdom

A. Yu. Egorov, D. Bernklau, and H. Riechert
Infineon Technologies, Corporate Research CPR 7, D-81730 Munich, Germany

(Received 11 March 2002; accepted for publication 9 May 2002)

The optical properties of GaInNAs/GaAs multi-quantum wells were investigated by photoluminescence excitation (PLE) spectroscopy, as well as by photoluminescence (PL), under various excitation intensities and at various temperatures. The PLE spectra demonstrated pronounced excitonic features and the corresponding transitions were identified. At low temperatures the PL spectra were sensitive to the excitation intensity. Under fixed excitation intensity, both the peak energy and the linewidth of photoluminescence showed anomalous temperature dependence, specifically an S-shaped temperature dependence of the peak energy and a N-shaped temperature dependence of linewidth in the PL spectra. The observed results are explained consistently in terms of the exciton localization effect due to the local fluctuations of nitrogen concentration. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1489716]

I. INTRODUCTION

Recently, dilute III-N-V alloys and superlattices have attracted a great deal of attention. The unusual large bowing coefficient due to N-incorporation has drawn strong interest to the investigation of its physical origin.[1] Meanwhile, this series of materials, especially the GaInNAs alloys, have shown favorable properties in the desired optical communication wavelength range around 1.3 μm.[2] Compared to GaInAsPInP materials currently in common use, GaInNAs/GaAs has several advantages. First, the optical properties of GaInNAs/GaAs have better thermal characteristics due to the introduction of N. This property has two-fold implications: (i) the larger conduction band offset and thus the stronger electron confinement give rise to better performance of lasers at high temperature, represented by a higher characteristic temperature T_0 for threshold current; and (ii) the band gap energy is less sensitively dependent on temperature, implying higher wavelength stability. The relative stability of both lasing threshold and operation wavelength is highly desirable for high performance optical-fiber communication systems employing dense wavelength-division multiplexing. Second, the fact that GaInNAs can be coherently grown on GaAs substrates allows growth of distributed Bragg reflector mirrors composed of high refractive index contrast AlAs/GaAs or GaAlAs/GaAs for the monolithic fabrication of vertical cavity surface emitting lasers (VCSELs). Indeed, both the edge emitting lasers and VCSELs based on GaInNAs/GaAs quantum wells have been extensively reported recently.[3–9] Despite great success in the demonstration of devices, the detailed investigation of the optical properties of the GaInNAs/GaAs system remains a major topic.[10–17] Understanding the emission mechanism in these materials is crucial for not only basic physical interest but also for device design. In this article, we report systematic studies on the optical properties of high quality GaInNAs/GaAs multi-quantum wells (MQWs) investigated by photoluminescence (PL) spectroscopy at various excitation intensities and temperatures and by photoluminescence excitation (PLE) spectroscopy. We made low temperature PLE measurements on a series of GaInNAs/GaAs MQWs with different well widths. Pronounced excitonic features are demonstrated in the PLE spectra. From these spectra, the excitonic transitions can be clearly identified. It is found that at low temperature the PL spectra were sensitive to the excitation intensity. Under fixed excitation intensity, both the peak energy and the linewidth of photoluminescence showed anomalous temperature dependence. All these observations can be explained in a consistent way by the exciton localization effect due to the local fluctuations of nitrogen concentration.

II. EXPERIMENT

The samples were grown by solid-source molecular-beam epitaxy on GaAs (001) substrates and *in situ* annealed at 750 °C. The fabrication process has been described elsewhere.[18] In brief, the GaInNAs/GaAs MQW structures consisted of $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ well layers and GaAs barrier layers with 5–10 periods. Nitrogen was provided by a radio frequency coupled plasma source. The mole fractions of N and In were determined by a combined analysis of high-resolution x-ray diffraction and precalibrated PL data. The MQWs were sandwiched between two five-period AlAs (2 nm)/GaAs (2 nm) superlattice cladding layers and finally capped with 10 nm GaAs. All samples were nominally undoped. To perform the measurement at various temperatures, the sample was mounted on the sample holder of a liquid He

[a]Author to whom correspondence should be addressed; electronic mail: handong.sun@strath.ac.uk
[b]Currently with Institute of Applied Physics, University of Karlstruhe, 76128 Karlstruhe, Germany.

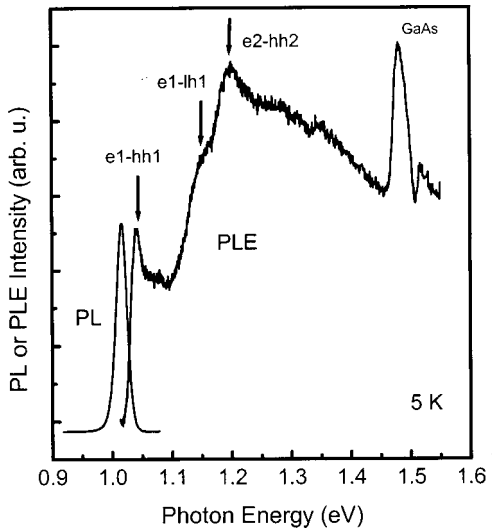

FIG. 1. PL and PLE at 5 K spectra of a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ MQW with well width of 9 nm.

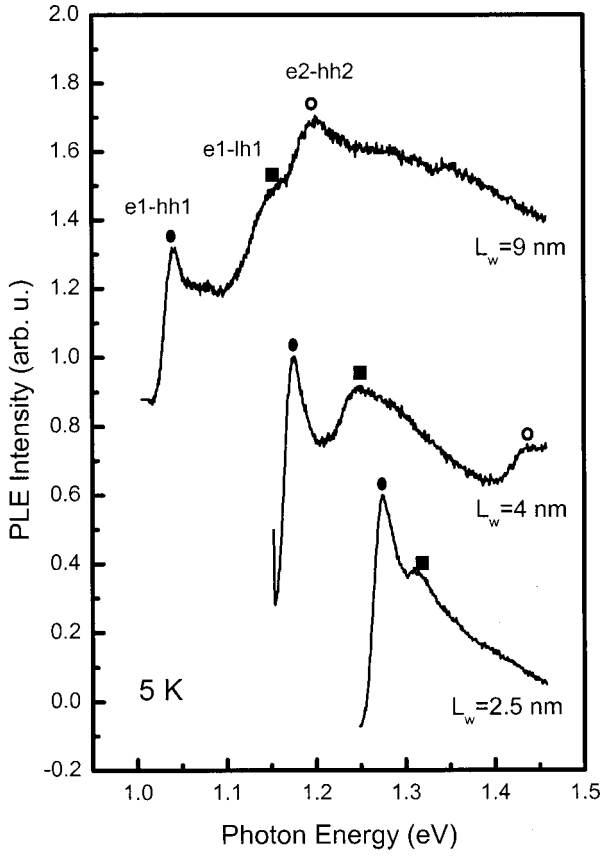

FIG. 2. PLE spectra at 5 K of three $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ MQWs, the well widths of which are denoted for each curve. The positions of three optical transitions: e1–hh1, e1–lh1 and e2–hh2 are marked by a closed circle, a closed square and a open circle, respectively.

cooled flow cryostat with suitable optical access for PL and PLE spectra. For the PL measurements, the samples were excited by a high power diode laser (670 nm), and the PL signal was collected in conventional back scattering geometry. The excitation intensity was adjusted by calibrated neutral density filters. The luminescence signal was dispersed by a 0.46 m grating monochromator and detected by a thermoelectrically cooled Si/InGaAs detector using standard lock-in techniques. The PLE signal is detected by the same system, but the light source was replaced by a 250 W tungsten halogen lamp combined with a 0.27 m grating monochromator and suitable filters.[11]

III. RESULTS AND DISCUSSION

Figure 1 shows typical spectra of PL (excited by the diode laser) and PLE (detected at $\lambda_{det}=1223$ nm) taken at 5 K for a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}/GaAs$ structure with well width of 9 nm. As can be clearly seen, the PLE spectrum shows clear features of optical transitions due to different quantized energies of quantum wells and a strong excitonic feature dominates the lowest transition energy. The latter property is the direct evidence of the formation of excitons. In a previous paper, we have assigned the features in the PLE spectrum as the transitions of e1−hh1, e1−1h1, and e2−hh2, respectively, as deduced from polarized PLE measurements and comparison with theoretical fitting.[11] The comparison of theoretical calculation and experimentally determined transition energies provides important information. A type-I alignment for the hhs with a strained conduction-band offset ratio of about 80% and an approximately flat band alignment for the 1hs were obtained.[11]

Figure 2 shows the evolution of the PLE spectra of $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}/GaAs$ MQWs as a function of well width. The well width L_w for each sample is marked in the figure. It is interesting to note that the excitonic features for MQWs with different well widths are correlated to the quantum confinement effect. First, the excitonic transition energy of the quantized states in the quantum wells is very sensitive to the well width, indicating that as expected the operation wavelength of devices based on this material system can be effectively tailored by both the depth and width of the quantum wells. Second, the oscillator strength of the heavy hole exciton transitions largely increases as the well width decreases.[19]

As is shown in Fig. 1, the PL spectra showed a single peak with a full width at half maximum (FWHM) of about 21.2 meV. The PL peak is positioned at the lower energy side of lowest absorption peak with a Stokes shift of 25.5 meV. This indicates that the PL emission is associated with the recombination of the lowest heavy-hole exciton states of the quantum wells. Investigation of the lineshapes showed that the PL peak is asymmetric with a low energy tail. These features are a typical indication of the exciton localization effect.[20] In general, the localization effect in quantum wells may result from the local fluctuations of both well width and alloy composition in the wells. We have measured a series of samples with the same composition but with various well widths from 2.5 to 9 nm. The PL properties of the full set of samples are summarized in Table I. We found that both the Stokes shift and the linewidth of PL show no clear correlation with the well width. This implies that the main reason for the exciton localization in our samples is not dominated by the fluctuation in well width, because otherwise the linewidth and Stokes shift would increase as the well width decreases. Therefore the localization effect is attributed mainly

TABLE I. PL properties of various samples at 5 K under the excitation power of 84 mW.

Sample No.	Well width (nm)	FWHM (meV)	Stokes shift (meV)
12393	2.5	19.0	23.0
12394	4	16.1	22.6
12313	7	19.2	31
12395	9	21.2	25.5

to the fluctuation in the alloy composition in the well layers. Because of the very large bowing coefficient induced by N-incorporation, it is expected that the local fluctuation of N concentration gives rise to a big difference in local potential and thus a strong localization effect. Moreover, for the strained quantum wells, the local fluctuation of nitrogen concentration also implies the spatial distribution of strain. All these effects are expected to affect the PL properties of $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}/GaAs$ MQWs.[13,17]

In order to further investigate the PL properties, we performed PL measurements under various excitation intensities at low temperature for all samples. In Fig. 3, we show the PL spectra at 5 K normalized by their peak intensity under average excitation power from 0.084 to 84 mW for a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}/GaAs$ MQW with a well width of 9 nm. One can see that the PL peak energy blueshifted about 9 meV as the excitation power increased from 0.84 to 84 mW.

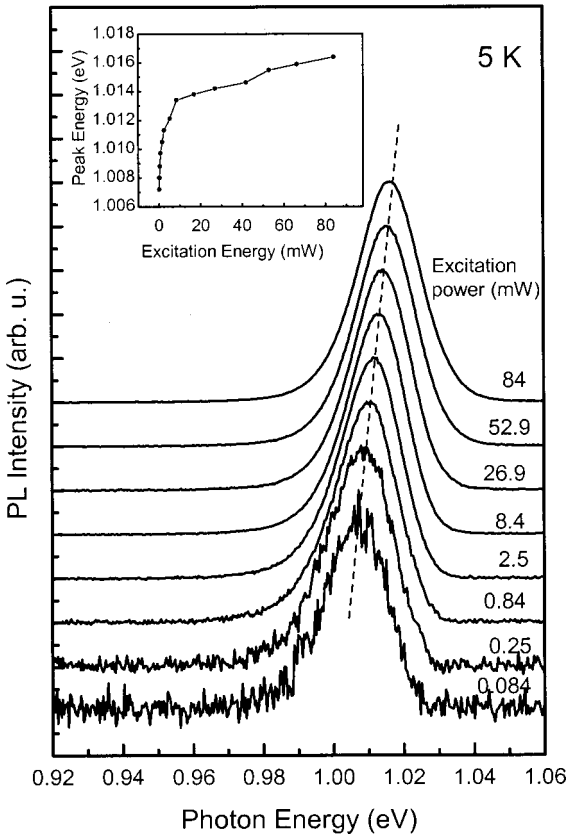

FIG. 3. PL spectra of a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ MQW with well width of 9 nm measured at 5 K under different excitation power. The dashed line is guide to the eye. The inset of the figure shows the peak energy as a function of excitation power.

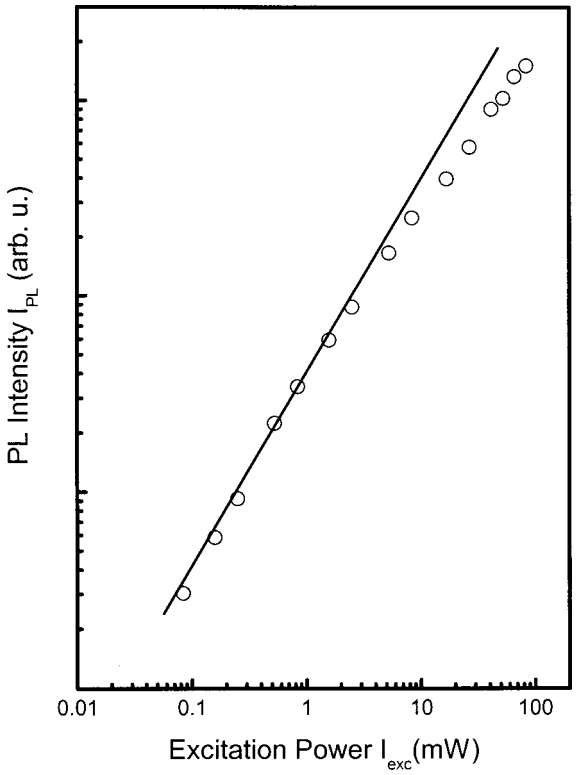

FIG. 4. Dependence of integrated PL intensity on the excitation power. The solid line represents the linear relation $I_{PL} \propto I_{exc}$.

As is well known, two factors may lead to blueshift with increased excitation: filling of band tail states and the screening of electric fields by high carrier density.[21] The latter, however, should be negligible in our samples. This is because (001) symmetry does not suffer from electric field normal to the QW plane owing to spontaneous and piezoelectric polarizations. Furthermore, even if there exist electric fields in local areas induced by composition fluctuations, this screening effect should be negligible because of the very low excitation density (the highest excitation density in our experiment is about 300 W/cm^2).

The inset of Fig. 3 shows the dependence of the peak energy of PL at 5 K on the excitation power. In the power range from 0.084 to 84 mW, the PL peak energy increases monotonically without saturation, indicating that in the whole range the PL is still from localized states. The rate of increase of peak energy with respect to excitation power was very fast at weak excitation and slowed down at higher excitation power. This behavior is totally consistent with the distribution of density of localized states. It is well recognized that the distribution of the localized states in a disordered system shows an exponential-like density of states.[22] This means that the filling of the localized states with higher energies needs more photogenerated carriers, consistent with the experimental observation.

Figure 4 shows the integrated PL intensity as a function of excitation power plotted in log–log scale. Under low excitation power the PL intensity has a nearly linear relation with the excitation power. However, under high excitation power it deviated from the linear relationship, and exhibits a sublinear relation. This suggests that the tail states with

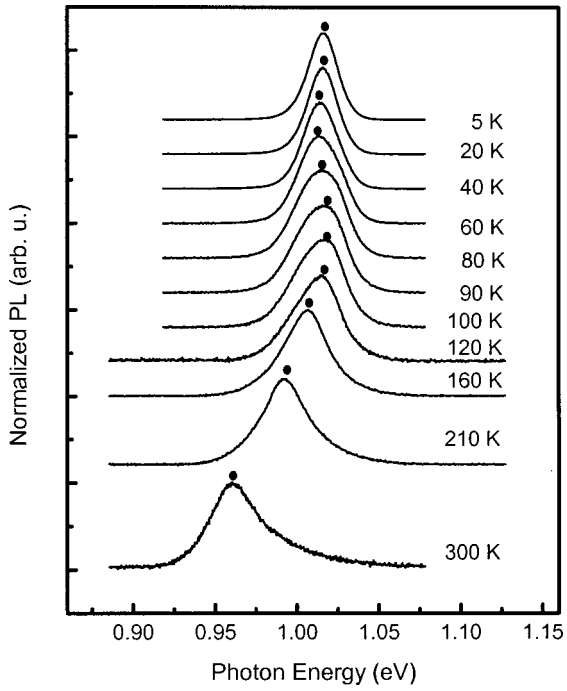

FIG. 5. Temperature dependence of PL spectra for a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ MQW with well width of 9 nm measured at an excitation power of 84 mW. Peak positions of individual spectra are indicated with close circles.

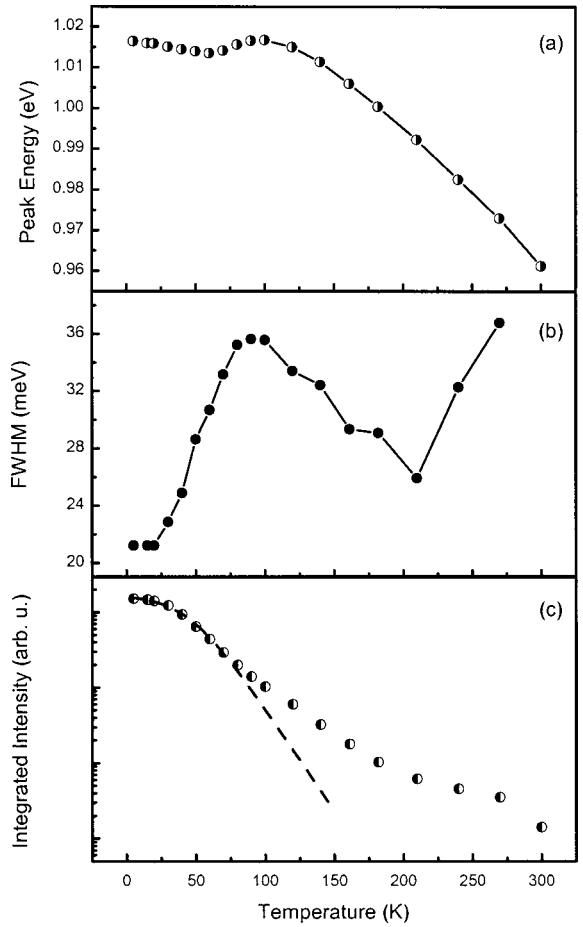

FIG. 6. Temperature dependence of peak energy (a), FWHM (b), and integrated intensity (c) of PL for a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$ MQW with well width of 9 nm measured at 84 mW. The dashed line is the fitting curve according to Eq. (1).

higher energy have lower emission efficiency. This is reasonable, because higher energy tail states should have higher mobility and therefore have more chance to encounter a nonradiative center.

We have systematically studied the temperature dependence of the PL spectra including the emission peak energy, integrated intensity, and the FWHM. The evolution of GaInNAs-related PL spectra over the temperature range from 5 to 300 K is shown in Fig. 5 for a $Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}$/GaAs MQW with well width of 9 nm at an excitation power of 84 mW. It is interesting to note that the temperature dependent PL of GaInNAs/GaAs MQWs exhibits an S-shaped property. Figure 6(a) shows the temperature dependence of the peak energy of PL. When the temperature increases from 5 to 60 K, the PL peak energy redshifts 2.9 meV. However, from 60 to 100 K the peak energy of PL blueshifts 3.2 meV. When the temperature is further increased above 100 K, the peak energy decreases again. This behavior differs remarkably from the temperature dependence of the band gap energy for a semiconductor, which decreases monotonically as the temperature increases following the Varshni or Bose–Einstein relation. The anomalous temperature dependence of PL has been also observed by other authors for GaInNAs/GaAs MQWs,[12,14,15] and was generally explained in terms of the competition between the transfer dynamics of localized carriers/excitons and the thermalization effect.[23] At the lowest temperature, the photogenerated carriers (excitons) are rapidly captured in their lifetime by the localized potential induced by the fluctuation of well width or alloy composition. In the localized states they are essentially immobile apart from phonon-assisted tunneling or hopping to adjacent localized states. Within the localization length, the excitons have a high probability to persist at low temperatures until they recombine radiatively.[24] The emission energy from the localized excitons is lower than the delocalized free excitons, which is the main origin of the low temperature Stokes shift. With the increase of the temperature, some of the localized excitons are thermally activated, and thus are mobile to some extent. In this case, some of these excitons may relax down into lower energy tail states. Thus the higher energy side emission is suppressed and a redshift of peak energy is produced as indicated from 5 to 60 K. However, with the further increase in temperature, the peak energy of the thermal equilibrium distribution of the localized excitons will increase and get close to the delocalized exciton energy. This process can explain the blueshift of peak energy of PL from 60 to 100 K. At still higher temperatures, the recombination of delocalized states dominates the PL, and the peak energy of PL will follow the delocalized exciton emission energy and will decrease as the thermal shrinkage of gap energy.

It is interesting to note the temperature dependence of the PL linewidth as shown in Fig. 6(b) and its correlation to the temperature dependence of peak energy. From 5 to 100 K, the value of FWHM increases monotonically from 21.2 to 35.6 meV. However, as the temperature increases from 100 to 210 K, the value of FWHM decreases from 35.6 to 25.9

meV. As the temperature further increases, the FWHM value increases again. This N-shaped temperature dependence can be well explained by the transfer and thermalization of localized states.[15] As we have pointed out, the temperature range from 5 to 100 K represents the transfer process of localized exciton states to delocalized state. At the lowest temperatures (5–20 K), the localized excitons follow the distribution of trapped localized excitons. Thus the linewidth of PL changes little with temperature. With the increase in temperature up to the thermalization point (~100 K), two processes occur. First, some of the trapped excitons gain enough energy to transfer to deeper localized states; second, due to the increased thermalization some localized excitons become mobile and occupy shallower localized states (higher energy tail states). Both of these two processes will broaden the PL linewidth. When the temperature is over the delocalization temperature, the emission is dominated by the recombination of delocalized states so that the carrier distribution and thus the linewidth narrows. With a further increase in the temperature, thermal broadening of the carrier distribution occurs and the linewidth increases accordingly.

Finally, we investigated the temperature dependence of integrated intensity of PL. This relationship is shown in Fig. 6(c). Between 5 to 300 K, the integrated intensity decreases remarkably. We found that the quenching of the PL intensity could not be described by an Arrhenius relation. However, from 5 to 100 K the temperature dependence of integrated PL intensity can be well described by

$$I_{\mathrm{PL}}(T) = I_0 / [1 + A \exp(T/T_0)], \tag{1}$$

where $I_{\mathrm{PL}}(T)$ is the integrated PL intensity at temperature T, T_0 a characteristic temperature, A a tunneling factor, and I_0 the integrated intensity at the low temperature limit. This shows that the PL quenching at temperature below 100 K is principally due to the transfer of the localized states. The least-square fitting gives rise to the characteristic temperature $T_0 = 16.06$ K, close to the reported value of Grenouillet *et al.*[12]

As can be seen, the quenching rate is much slower in the temperature range from 100 to 300 K. This means that the quenching in this temperature range has a different mechanism. In fact, above 100 K the PL intensity is dominated by the recombination of delocalized carriers, so the quenching process will be governed by nonradiative recombination channels. Bissiri *et al.* have studied photoluminescence efficiency of InGaNAs/GaAs single quantum well in a wide temperature range. They attributed the high thermal stability of PL intensity at high temperatures to the strain compensation effect due to nitrogen incorporation into highly strained InGaAs/GaAs QWs.[17]

Until now we have observed the close correlation among the temperature dependent peak energy, FWHM, and the integrated intensity of PL in a sample, and our full set of samples show similar properties. It should be pointed out that while some of our results have the same features as observed by others for GaInNAs/GaAs QWs, some authors have reported different features for the same material systems,[10,12,14–16] although all the observed phenomena about PL were explained in term of carrier/exciton localization effect. The reason may be attributed to different samples and excitation conditions (excitation wavelength and intensity) since the recombination dynamics of localized carriers should be dependent on the distribution of localized states. For example, the tunneling rate between the localized states is dependent on the localization depth and length; and the thermal equilibrium distribution of localized states should be excitation intensity dependent.

IV. SUMMARY

In summary, optical studies have been performed for GaInNAs/GaAs MQWs with low nitrogen content using PLE and PL spectroscopy. At low temperature pronounced excitonic features have been observed in the PLE spectra, and the transitions between different quantum states could be identified. PLE spectra measured for MQWs with various well widths exhibited the quantum confinement effect of excitons. The PL properties have been investigated for various excitation intensities and at various temperatures. At low temperature a single peak PL with a FWHM value of about 20 meV was located at the near-band edge. It is observed that at low temperature, the PL peak energy increases with excitation power. The PL peak energy exhibits S-shape dependence while the FWHM exhibits N-shape dependence with temperature. The observed results is explained by exciton localization effect due to the local fluctuations of nitrogen concentration.

ACKNOWLEDGMENTS

This work was supported by EC Brite-Euram Project ''OPTIVAN'' and by UK LINK-OSDA project ''GAINS.''

[1] For a review, see, I. A. Buyanova, W. M. Chen, and B. Monemar, MRS Internet J. Nitride Semicond. Res. **6**, 2 (2001).
[2] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys. **35**, 1273 (1996).
[3] M. Kondow, T. Kitatani, S. Nakatsuka, M. C. Larson, K. Nakahara, Y. Yazawa, IEEE J. Sel. Top. Quantum Electron. **3**, 719 (1997).
[4] M. C. Larson, M. Kondow, T. Kitatani, K. Nakahara, K. Tamura, H. Inoue, and K. Oumi, IEEE Photonics Technol. Lett. **10**, 188 (1998).
[5] M. Kondow, Y. Kitani, K. Nakahara, and T. Tanaka, Jpn. J. Appl. Phys. **38**, L1355 (1999).
[6] T. Miyamoto, K. Takeuchi, F. Koyama, and K. Iga, IEEE Photonics Technol. Lett. **9**, 1448 (1997).
[7] S. Sato and S. Satoh, Electron. Lett. **35**, 1251 (1999).
[8] B. Borchert, A. Yu Egorov, S. Illek, M. Komainda, and H. Riechert, Electron. Lett. **35**, 2204 (1999).
[9] M. Fischer, M. Reinhardt, and A. Forchel, Electron. Lett. **36**, 1208 (2000).
[10] R. A. Mair, J. Y. Lin, H. X. Jiang, E. D. Jones, A. A. Allerman, and S. R. Kurtz, Appl. Phys. Lett. **76**, 188 (2000).
[11] M. Hetterich, M. D. Dawson, A. Yu. Egorov, D. Bernklau, and H. Riechert, Appl. Phys. Lett. **76**, 1030 (2000).
[12] L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vannuffel, A. Million, and A. Chenevas-Paule, Appl. Phys. Lett. **76**, 2241 (2000).
[13] I. Suemune, K. Uesugi, and W. Walukiewicz, Appl. Phys. Lett. **77**, 3021 (2000).
[14] A. Kaschner, T. Luttgert, H. Born, A. Hoffmann, A. Yu. Egorov, and H. Riechert, Appl. Phys. Lett. **78**, 1391 (2001).
[15] M.-A. Pinault and E. Tournie, Appl. Phys. Lett. **78**, 1562 (2001).
[16] S. Shirakata, M. Kondow, and T. Kitatani, Appl. Phys. Lett. **79**, 54 (2001).
[17] M. Bissiri, V. Gaspari, A. Polimeni, G. Baldassarri Hoger Von Hogersthal, M. Capizzi, A. Frova, M. Fischer, M. Reinhardt, and A. Forchel, Appl. Phys. Lett. **79**, 2585 (2001).

[18] A. Yu. Egorov, D. Bernklau, D. Livshits, V. Ustinov, Z. I. Alferov, and H. Riechert, Electron. Lett. **35**, 1643 (1999).
[19] S. Schmit-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).
[20] I. A. Buyanova, W. M. Chen, G. Pozina, J. P. Bergman, B. Monemar, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **75**, 501 (1999).
[21] E. Kuokstis, J. Zhang, M. Y. Ryu, J. W. Yang, G. Simin, M. Asif Kham, R. Gaska, and M. S. Shur, Appl. Phys. Lett. **79**, 4375 (2001).
[22] T. Tiedje and A. Rose, Solid State Commun. **37**, 49 (1980).
[23] Y. H. Cho, G. H. Gainer, J. B. Lam, J. J. Song, W. Yang, and W. Jhe, Phys. Rev. B **61**, 7203 (2000).
[24] C. Klingshirn, Phys. Status Solidi B **202**, 857 (1997).