

Spectroscopic characterization of 1.3 μm GaInNAs quantum-well structures grown by metal-organic vapor phase epitaxy

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We report optical studies of high-quality 1.3 μm strain-compensated GaInNAs/GaAs single-quantum-well structures grown by metalorganic vapor phase epitaxy. Photoluminescence excitation (PLE) spectroscopy shows clearly the electronic structure of the two-dimensional quantum well. The transition energies between quantized states of the electrons and holes are in agreement with theoretical calculations based on the band anti-crossing model in which the localized N states interact with the extended states in the conduction band. We also investigated the polarization properties of the luminescence by polarized edge-emission measurements. Luminescence bands with different polarization characters arising from the electron to heavy-hole and light-hole transitions, respectively, have been identified and verify the transition assignment observed in the PLE spectrum. © 2005 American Institute of Physics. [DOI: 10.1063/1.1868866]

There has been intense interest recently in dilute-nitride III–V compound semiconductors and their related heterostructures.^{1–3} Apart from intriguing fundamental physical properties, these materials have been proposed for various optoelectronic devices. Ga_(1-x)In_xN_yAs_(1-y)/GaAs heterostructures, in particular, are considered advantageous over InP-based material systems for selected important devices in optical fiber communications. Various devices with attractive performance based on GaInNAs materials have been developed in the $\sim 1.3 \mu\text{m}$ wavelength range,^{4–7} and recently there have been substantial advances in the growth of 1.55 μm materials.⁸ Despite all this progress, growth of high-quality materials is still an important issue. Up to now, most of the GaInNAs material has been grown by molecular-beam epitaxy (MBE). For practical applications, the metal-organic vapor phase epitaxy (MOVPE) technique is generally preferred because of its advantages in controllable growth and large-scale production. Currently, most efforts on MOVPE growth are still focused on optimizing the growth conditions of the active quantum-well (QW) structures,^{9,10} although there are recent reports of high-performance edge-emitting diode lasers based on GaInNAs/GaAs QWs grown by MOVPE.^{11,12} Now that device-quality material grown by MOVPE is emerging, it is important to study the optical properties of this material to compare and contrast parameters and modeling in detail to the MBE case.^{13–18} In this letter, we investigate the detailed optical characterization of high-quality strain-compensated GaInNAs single-quantum-well (SQW) material grown by MOVPE, from a growth system proven to produce high-performance laser diodes.¹² In addition to the interband transitions between quantized QW states observed by photoluminescence excitation (PLE), po-

larized PL properties are also reported, which is important on the one hand to verify the transition assignments and modeling approach, and on the other hand for the development of devices such as polarization-insensitive semiconductor optical amplifiers.

The samples used in this study are grown by MOVPE in a horizontal-type reactor at low pressure (100 mbar) on epitaxially (001) GaAs substrates. The SQW structure consists of an 8.5 nm Ga_{0.65}In_{0.35}N_yAs_{1-y} QW sandwiched between two 1 nm GaN_{0.02}As_{0.98} strain-compensated layers and the GaAs barriers. The advantages of inserting such strain-compensated layers have been described in Ref. 19. Triethylgallium, trimethylindium, tertiarybutylarsine (TBA), and 1,1-dimethyl hydrazine (DMHy) were used as respective precursors for the sources of Ga, In, As, and N, to grow the GaInNAs layers. A 100 nm GaAs capping layer was grown at the QW growth temperature of 470 °C. All GaInNAs QW samples were *in situ* annealed at 650 °C for 10 min in AsH₃ ambient. The resultant samples exhibit a mirror-like surface and show clear interfaces between the layers, as observed by high-resolution transmission electron microscopy. The N composition in the QW is dependent on the gas-flow ratio of DMHy to TBA. For a SQW, it is hard to determine the N composition precisely. As can be seen later, we determine it by modeling the optical transition energies determined from PLE spectra. For general PL measurements, the samples were excited by a high-power diode laser (670 nm), and the PL signal was collected in conventional backscattering geometry. For polarized PL measurements, the excitation laser was directed perpendicular to the layer plane at the edge of the sample, and the PL signal was observed along the layer plane. A linear polarizer was used to analyze the polarization properties of the PL.

Figure 1 shows representative PL and PLE spectra for a sample that emits at a peak wavelength of 1340 nm at

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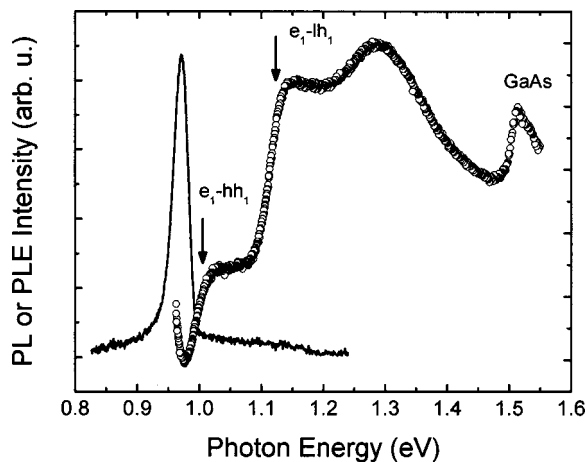


FIG. 1. Spectra of PL under excitation of 670 nm from the dispersed lamp and PLE of the GaInNAs/GaAs SQW measured at a temperature of 14.8 K.

300 K. The step-like features in the PLE spectrum represent the typical joint density of states of two-dimensional QW structures. In order to identify the electronic states, we calculated the band structure based on the band anti-crossing (BAC) model, in which the localized N states interact with the extended states in the conduction band,^{20,21} taking strain effects into account. The valence band structure in the QW is determined using a Luttinger–Kohn Hamiltonian.²² The band alignment between Ga_{1-x}In_xAs/GaAs systems is In content dependent, and therefore the ratio of band offset in conduction band to that in valence band with $x=35\%$ is chosen to be 0.8/0.2.²³ With respect to the alignment between GaNAs and GaAs, as there is still controversy on this issue, we follow the idea of BAC model and consider that N only influences the conduction band in GaNAs and the valence band is aligned with GaAs. As the N concentration in the well is not exactly known, we have calculated the N-content dependence of the interband transition energies. By comparing the modeled results and experiment, we deduced the N content to be 1.2%. With the assumption of the coupling strength between the localized N states and the extended states in the conduction band as (a typical) 2.45, the calculated first electron state–first heavy-hole state (e_1 - hh_1) and first electron state–first light-hole state (e_1 - lh_1) transition energies were in good agreement with the measurements, as denoted on the PLE spectrum (Fig. 1).

The PL properties have been investigated in detail by measurements under conditions of varying excitation intensity and temperature. Figure 2(a) shows the normalized PL spectra of the sample under the excitation power of $I_0=84$ mW at various temperatures. The PL peak energy as a function of temperature is plotted in Fig. 3, in which Varshni empirical equation $E(T)=E(0)-\alpha T^2/(T+\beta)$ which describes the temperature dependence of band gaps in semiconductors is also plotted. At high temperatures, the experimental PL energies agree very well with the Varshni equation. Least-squares fitting gives the fitting parameters α and β as 4.6×10^{-4} eV/K and 254.2, respectively. The energy of the e_1 - hh_1 transition observed in the PLE spectrum is denoted as a solid circle in the figure, which is very close to the extrapolation of Varshni formula to low temperature. Therefore, it is concluded that the main PL at high temperature originated in recombination from extended QW states (e_1 - hh_1 transition).

However, with the decrease of temperature, the PL peak en-

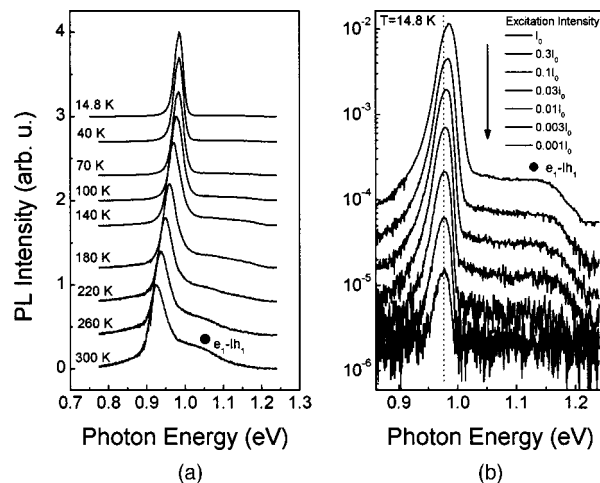


FIG. 2. Evolution of PL spectra with varying (a) temperature and (b) excitation power. The spectra in (a) have been normalized at the main peak and offset vertically for clarity. The dotted vertical line is a guide for the eye.

ergies deviate gradually from (are lower than) the Varshni equation. This implies that at low temperatures, the PL mechanism is not from the extended QW states but from localized states.²⁴

Figure 2(b) shows the PL spectra of the same sample measured at 14.8 K with differing excitation intensity. It is noted that the main PL peak shifts to higher energy as the excitation intensity increases. A similar phenomenon has also been observed in MBE-grown GaInNAs/GaAs multiple quantum wells (MQWs), and can be attributed to the saturation effect of localized states.²⁴ A striking feature in Fig. 2(b) is that with the increase of the excitation intensity there appears another emission band on the higher energy side denoted by a solid circle. It is also noted in Fig. 3 that the relative intensity of this new band increases with temperature. Based on these features, this new emission band may be attributed to the e_1 - lh_1 recombination. Although an earlier such observation was made by Kim *et al.*²⁵ in GaInNAs/GaAs MQWs, no further supportive evidence for such an assignment has been given. Here we provide direct evidence by a polarized PL measurement.

As is well known, in a compressively strained QW the luminescence from the electron to heavy-hole transitions is

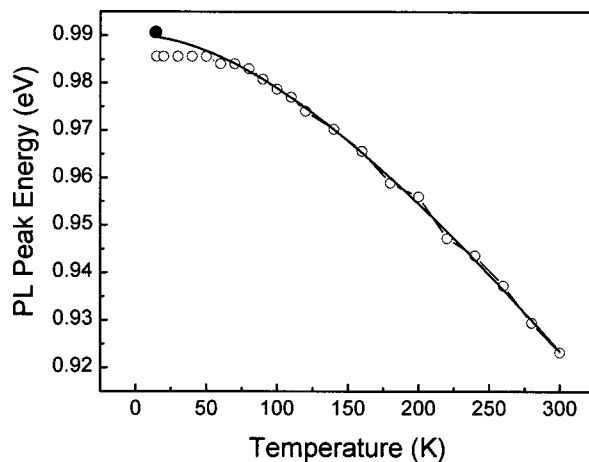


FIG. 3. Dependence of energy at the main PL peak on temperature. The solid curve is the fitting of Varshni equation. The solid circle represents the energy of e_1 - hh_1 transition determined by PLE spectrum at 14.8 K.

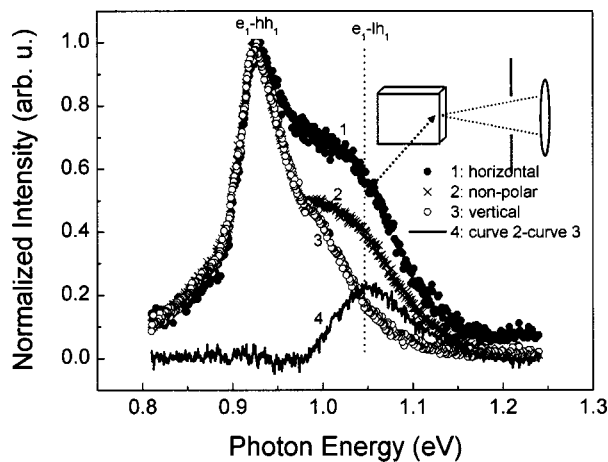


FIG. 4. Edge-emitted PL spectra of GaInNAs/GaAs SQW at 300 K. The experimental geometry is depicted in the inset. Curves 1 and 3 are measured with polarization perpendicular and in the layer plane. Curve 2 is the non-polarized PL. Curve 4 is the difference between curves 2 and 3, which represents the PL component polarized perpendicular to the layer plane (transition $e_1\text{-}lh_1$).

linearly polarized in the plane of layers, whereas the luminescence from electron to light-hole transitions is unpolarized.²³ This polarization nature cannot be distinguished by traditional PL measurements in backscattering geometry because the polarization of the as-observed PL is always in the layer plane. However, this can be achieved by observing the linear polarization of luminescence from a cleaved edge of a QW sample. We have used the geometry shown in the inset of Fig. 4 to determine the origin of the QW luminescence. Figure 4 shows the PL spectra of the sample detected without polarization selection, and detected with polarization parallel or perpendicular to the layer plane. The spectra have been normalized with respect to the low-energy emission band. It is interesting to note the change of relative weight of the two emission bands with the polarization direction. Without the polarization (curve 2), there are obviously two emission bands. When the polarization direction is in the vertical, that is, layer plane direction (curve 3), the high-energy band has been largely suppressed and the PL spectrum is dominated by the lower-energy band. This result implies that the low-energy band is polarized in the layer plane, while the high-energy band has a component that is polarized perpendicular to the layer plane. This is further confirmed by the PL spectrum when the polarization is in the horizontal direction. In this case, the relative weight of the high-energy band to the low-energy band is even higher. It should be pointed out that, in principle, the $e_1\text{-}hh_1$ transition should vanish in this case. In our experiment, we only observe the suppression of the PL band of $e_1\text{-}hh_1$ transition rather than it vanishing. This can be attributed to two reasons: (1) the extinction coefficient of polarization is not 100%, and (2) the response of the monochromator is anisotropic about polarization, with the vertical direction higher than horizontal direction. Nevertheless, it is apparent that the high-energy band has a component perpendicular to the layer plane. This component can be obtained by subtracting curve 2 by curve 3, as has been shown as curve 4. The energy difference of the two emission bands is ~ 120 meV, which is

in close consistence with the energy splitting between $e_1\text{-}hh_1$ and $e_1\text{-}lh_1$ transitions (123 meV) deduced by the PLE spectrum in Fig. 1. Therefore, the high-energy emission band can be safely assigned to $e_1\text{-}lh_1$ transition.

In summary, high-quality $1.3\ \mu\text{m}$ strain-compensated GaInNAs/GaAs QW samples grown by MOVPE have been studied in detail by optical measurements. The electronic structure has been investigated by PLE. The observed transition energies are consistent with theoretical calculations based on the BAC model. The polarization dependence of the PL observed in the direction of a cleaved edge has been used to identify the character of the optical transitions.

- ¹M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, *Jpn. J. Appl. Phys.* **35**, 1273 (1996).
- ²I. A. Buyanova, W. M. Chen, and B. Monemar, *MRS Internet J. Nitride Semicond. Res.* **6**, 2 (2001).
- ³P. J. Klar, *Solid State Chem.* **31**, 301 (2003).
- ⁴T. Kitatani, M. Kondow, S. Nakatsuka, Y. Yazawa, and M. Okai, *IEEE J. Sel. Top. Quantum Electron.* **3**, 206 (1997).
- ⁵S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, *Appl. Phys. Lett.* **74**, 729 (1999).
- ⁶M. C. Larson, M. Kondow, T. Kitatani, K. Nakahara, K. Tamura, H. Inoue, and K. Uomi, *IEEE Photonics Technol. Lett.* **10**, 188 (1998).
- ⁷H. D. Sun, G. J. Valentine, R. Macaluso, S. Calvez, D. Burns, M. D. Dawson, T. Jouhti, and M. Pessa, *Opt. Lett.* **27**, 2124 (2002); A. H. Clark, S. Calvez, N. Laurand, R. Macaluso, H. D. Sun, M. D. Dawson, T. Jouhti, and M. Pessa, *IEEE J. Quantum Electron.* **40**, 878 (2004); J. M. Hopkins, S. A. Smith, C. W. Jeon, H. D. Sun, D. Burns, S. Calvez, M. D. Dawson, T. Jouhti, and M. Pessa, *Electron. Lett.* **40**, 30 (2004).
- ⁸H. Y. Liu, M. Hopkinson, P. Navaretti, M. Gutierrez, J. S. Ng, and J. P. R. David, *Appl. Phys. Lett.* **83**, 4951 (2003).
- ⁹M. Kawaguchi, T. Miyamoto, E. Gouardes, T. Kondo, F. Koyama, and K. Iga, *Appl. Phys. Lett.* **80**, 962 (2002).
- ¹⁰J. Derluyn, I. Moerman, M. R. Leys, G. Patriarcho, G. Sek, R. Kudrawiec, W. Rudno-Rudzinski, K. Ryczko, and J. Misiewicz, *Appl. Phys. Lett.* **94**, 2752 (2003).
- ¹¹N. Tansu, A. Quandt, M. Kanskar, W. Mulhearn, and L. J. Mawst, *Appl. Phys. Lett.* **83**, 18 (2003).
- ¹²K.-S. Kim, S.-J. Lim, K.-H. Kim, J.-R. Yoo, T. Kim, and Y.-J. Park, 16th Annual Meeting of the IEEE Lasers & Electro-Optics Society Tucson, Arizona, 26–30 Oct. 2003, Post-deadline paper PD2.6.
- ¹³J. 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).
- ¹⁴M. Hetterich, M. D. Dawson, A. Yu. Egorov, D. Bernklau, and H. Riechert, *Appl. Phys. Lett.* **76**, 1030 (2000).
- ¹⁵H. D. Sun, M. D. Dawson, M. Othman, J. C. L. Yong, J. M. Rorison, P. Gilet, L. Grenouillet, and A. Million, *Appl. Phys. Lett.* **82**, 376 (2003).
- ¹⁶Z. Pan, L. H. Li, Y. W. Lin, B. Q. Sun, D. S. Jiang, and W. K. Ge, *Appl. Phys. Lett.* **78**, 2217 (2001).
- ¹⁷J. Y. Duboz, J. A. Gupta, Z. R. Wasilewski, J. Ramsey, R. L. Williams, G. C. Aers, and G. I. Sproule, *Phys. Rev. B* **66**, 085313 (2002).
- ¹⁸P. J. Klar, H. Grüning, W. Hembrodt, J. Koch, W. Stolz, S. Tomic, and E. P. O'Reilly, *Solid-State Electron.* **47**, 437 (2003).
- ¹⁹T. Jouhti, C. S. Peng, E. M. Pavelescu, J. Konttinen, L. A. Gomes, O. G. Okhotnikov, and M. Pessa, *IEEE J. Sel. Top. Quantum Electron.* **8**, 787 (2002).
- ²⁰W. Shan, W. Walukiewicz, and J. W. Ager III, *Phys. Rev. Lett.* **82**, 1221 (1999).
- ²¹E. P. O'Reilly and A. Lindsay, *Phys. Status Solidi B* **216**, 131 (1999); A. Lindsay and E. P. O'Reilly, *Solid State Commun.* **112**, 443 (1999).
- ²²J. C. L. Yong, J. M. Rorison, and I. H. White, *IEEE J. Quantum Electron.* **38**, 1553 (2002).
- ²³M. J. Joyce, M. J. Johnson, M. Gal, and B. F. Usher, *Phys. Rev. B* **38**, 10978 (1988).
- ²⁴H. D. Sun, M. Hetterich, M. D. Dawson, A. Yu. Egorov, D. Bernklau, and H. Riechert, *J. Appl. Phys.* **92**, 1380 (2002).
- ²⁵N. J. Kim, Y. D. Jang, D. Lee, K. H. Park, W. G. Jeong, and J. W. Jang, *Appl. Phys. Lett.* **83**, 3114 (2003).