

Investigation of phase-separated electronic states in 1.5 μm GaInNAs/GaAs heterostructures by optical spectroscopy

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We report on the comparative electronic state characteristics of particular GaInNAs/GaAs quantum well structures that emit near 1.3 and 1.5 μm wavelength at room temperature. While the electronic structure of the 1.3 μm sample is consistent with a standard quantum well, the 1.5 μm sample demonstrate quite different characteristics. By using photoluminescence (PL) excitation spectroscopy at various detection wavelengths, we demonstrate that the macroscopic electronic states in the 1.5 μm structures originate from phase-separated quantum dots instead of quantum wells. PL measurements with spectrally selective excitation provide further evidence for the existence of composition-separated phases. The evidence is consistent with phase segregation during the growth leading to two phases, one with high In and N content which accounts for the efficient low energy 1.5 μm emission, and the other one having lower In and N content which contributes metastable states and only emits under excitation in a particular wavelength range. © 2005 American Institute of Physics. [DOI: 10.1063/1.1836856]

I. INTRODUCTION

Considerable attention has been paid recently to dilute nitride alloy III-V semiconductors due to the novel physics and potential for practical application shown by these materials. The incorporation of a small amount of nitrogen gives rise to unusual physical properties favorable for optoelectronic devices. GaInNAs/GaAs heterostructures, in particular, have been considered to be advantageous over InP-based material for optoelectronic devices in optical fiber communications¹⁻³ and various devices operating near 1.3 μm wavelength based on GaInNAs/GaAs quantum wells (QWs) have been extensively demonstrated.⁴⁻⁷ It is also highly desirable to extend the operating wavelength of this material system towards the 1.55 μm optical fiber communications window. However, achieving this goal is challenging because further reduction in band gap requires the increase of In and/or N content risking serious degradation of material quality and substantial decrease in photoluminescence (PL) efficiency. Although there have been some reports on the demonstration of diode lasers emitting at $\sim 1.5 \mu\text{m}$,^{8,9} until now very few and limited reports have been made on the optical properties of GaInNAs/GaAs heterostructures in this longer wavelength range¹⁰⁻¹² and the optical emission mechanisms have never been fully investigated. Previously, there have been studies on the electronic state structures in 1.3 μm GaInNAs/GaAs QWs by various spectroscopic techniques, in which the basic electronic state structures were discussed consistently in terms of interband transitions between quasi-two-dimensional QW states.¹³⁻¹⁸ The optical emission mechanisms were attributed to localized states at

low temperature, but at high temperatures the PL is associated with extended QW states.¹⁹⁻²² With the further increase of N content, the microstructure of GaInNAs materials may change considerably due to the large miscibility between N and As, and especially decomposition as a result of phase segregation may be enhanced. Therefore the electronic state structure and the PL mechanisms may change accordingly.

In this paper we investigate the electronic states and PL characteristics of GaInNAs/GaAs heterostructures grown by molecular beam epitaxy (MBE) which emit at $\sim 1.52 \mu\text{m}$ at room temperature. We utilize selective PL and PL excitation (PLE) spectroscopy to show evidence that the $\sim 1.5 \mu\text{m}$ emission in these particular samples originates from In-rich quantum dots (QDs) as a result of strong phase separation. Although PL from QDs has been observed in $\sim 1.3 \mu\text{m}$ GaInNAs/GaAs QWs by scanning near-field magnetophotoluminescence spectroscopy,²³ these QD levels only account for the localized states in the lower energy range of two-dimensional (2D) QW states, and the properties of devices fabricated from such material should be still governed by the QW electronic structure. By contrast, in our samples there are no links between the long-wavelength emission and the electronic states of QWs, and the macroscopic PL properties are governed by QDs. Our measurements are not intended to imply that all 1.5 μm GaInNAs quantum wells will show dominant dotlike characteristics, and indeed we have recently measured other structures grown elsewhere showing clear 2D QW states.²⁴ However, we present this data to show that spontaneously generated quantum dot effects can be important in this material system, and their presence may be promoted for specific requirements.

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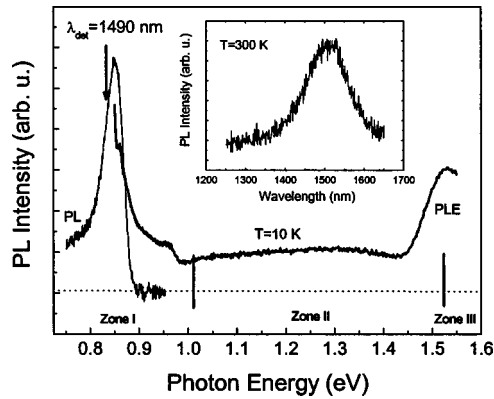


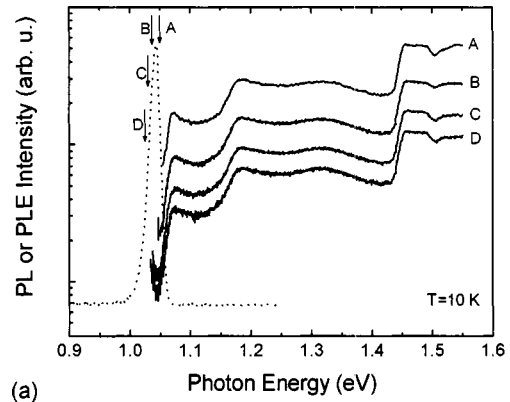
FIG. 1. Typical spectra of PL and PLE of the 1.5 μm GaInNAs/GaAs quantum well at 10 K. The horizontal dot line is the base for PL and PLE spectra. The inset shows the PL spectrum measured at 300 K.

II. EXPERIMENT

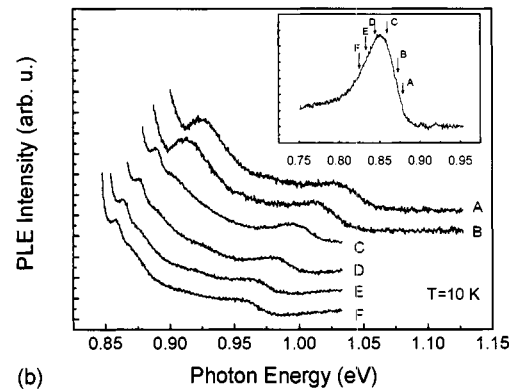
The 1.5 μm GaInNAs/GaAs “quantum well” samples in this study were grown by gas source molecular beam epitaxy on an (001) GaAs substrate. The single “QW” structure consisting of ~ 8 nm GaInNAs well and GaAs barriers was grown at 400–420 $^{\circ}\text{C}$. Before the growth of QWs, a 400 nm GaAs buffer layer was deposited at a temperature of 580–600 $^{\circ}\text{C}$. Finally the QW structure was covered with a 155 nm GaAs capping layer grown at 580 $^{\circ}\text{C}$. The detail of the growth process is similar to that of our reference, 1.3 μm Ga_{0.72}In_{0.28}N_{0.0114}As/GaAs structures^{15,25} except for the compositions. In this case the plasma power was increased to 275 W and the pressure was adjusted to 125 mTorr in order to incorporate more N into the QWs. As will be detailed later, the studied 1.5 μm QW material is highly inhomogeneous and the precise compositions are difficult to determine. However, the nominal compositions of In and N were estimated to be 38%–40% and 2%–3%, respectively. For the temperature dependent 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 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 excitation source was replaced by a 250 W tungsten halogen lamp and 0.27 m grating monochromator combination and suitable filters.

III. RESULTS AND DISCUSSION

The PL properties were investigated from 10 to 300 K under excitation by a 670 nm diode laser. Shown in the inset of Fig. 1 is the PL spectrum measured at 300 K for the 1.5 μm sample subjected to detailed studies. It demonstrated a single PL peak at ~ 1520 nm, very close to the desired 1.55 μm fiber communication wavelength. Figure 1 shows the typical spectra of PL and PLE taken at 10 K, where the PL was obtained under excitation at 670 nm from the dispersed lamp system, and the PLE was recorded at a detection wavelength of 1490 nm (0.832 eV). The PL shows a single peak at 0.851 eV (1457 nm) with full width at half maximum of 56



(a)



(b)

FIG. 2. PLE spectra with different detection energies for two different GaInNAs/GaAs QWs: (a) 1.3 μm structure and (b) 1.5 μm structure.

meV. The peak at ~ 1.52 eV in the PLE curve is attributed to the band edge transition of the GaAs barriers, but at photon energies lower than the barrier band gap the PLE curve demonstrates interesting features. First, the PLE spectrum does not demonstrate a steplike profile expected and measured by us for other samples in this wavelength range²⁴ for the joint density of states of 2D semiconductor superlattices. Second, as we will discuss in detail later, the PLE features below the GaAs barrier band gap are sensitively dependent on the detection wavelength. This is contrary to what we have observed for the 1.3 μm structure which demonstrated typical QW electronic states¹⁵ as shown in Fig. 2(a) where the PLE spectra of the 1.3 μm reference structure at four different detection wavelengths are plotted. The relative positions of detection energies are denoted on the PL spectrum. One can see that the spectra remain the same in terms of both the shapes and the transition energies. This is consistent with the properties of QWs because the continuity in the joint density of states (JDOS) assures the effective carrier relaxation and the PLE spectrum closely replicates the JDOS. By contrast, in the 1.5 μm sample, the PLE spectra change sensitively with detection spectral position as shown in Fig. 2(b).

The above results imply that, contrary to the 1.3 μm sample, the electronic states contributing to the 1.5 μm PL emission may not be from the transitions of QW states, but show behavior expected of inhomogeneous ensembles of QDs.²⁶ In the following, we will discuss the spectroscopic properties on the basis of QD ensembles with variable distributed dot sizes and/or composition.

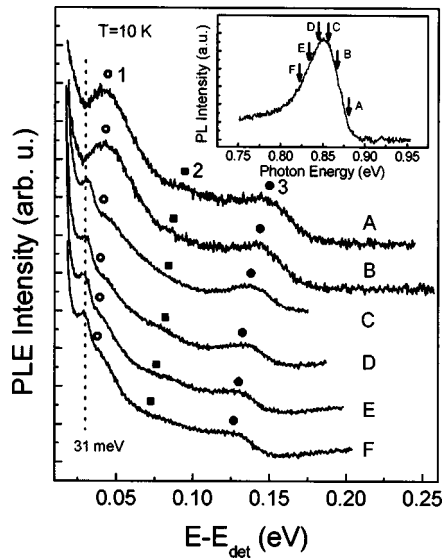


FIG. 3. PLE spectra plotted against the difference between the incident photon energy and the detection energy for the 1.5 μm structure. The inset shows the PL spectrum excited at 670 nm. The detection energy positions for the PLE spectra are marked.

In order to facilitate the explanation, we divide the PLE spectrum into three zones as shown in Fig. 1. The PLE signal in zone III is mainly due to the absorption of the GaAs barriers. Thus the excitation in this zone is nonresonant with respect to the transitions in the GaInNAs layers. Zone II has a relatively small and featureless PLE signal, while there are relatively stronger PLE signals and features apparent in zone I. We attribute these features to the excited states of QDs.²⁷ It should be pointed out that the partition of these zones is not absolute because the PLE spectra differ for different detection energies.

The behavior of the features in the PLE spectra in zone I is shown in Fig. 3, which shows the PLE spectra plotted against the difference between the incident photon energy and the detection energy. Spectra are shown for detection at different wavelength points in the PL peak shown in the inset. Although the spectra are modified by stray light, three features denoted by the open circles, solid squares, and solid circles, respectively, are identifiable, which we attribute to the transitions of the first, second, and third excited states of QDs, respectively.²⁷ It is noticeable that the excited state resonant energies increase with increasing detection energy. As PLE spectroscopy on a QD ensemble probes the absorption of a subensemble of similar QDs defined by the detection energy, the above behavior appears consistent with the quantum size effect. Besides the excited state transitions, another feature appears at about 31 meV in the PLE spectra. Since this peak is relatively sharp and does not move with the detection energy, it is reasonable to assign it as an LO-phonon feature. The enhanced relaxation by the involvement of LO-phonons surely modifies the shape of the absorption spectrum in an inhomogeneous QD ensemble because this process happens only selectively in QDs with particular size (in this case bigger dots) for which the energy difference between the ground and first excited states is close to the energy of LO phonons. This physical process has been ex-

tensively investigated in self-assembled QDs.^{28–31}

Since the sample was originally designed and grown based on two-dimensional structures, the formation of QDs is ascribed to a strong phase separation effect. In order to achieve long PL wavelength, both In and N contents are specified higher than for usual 1.3 μm structures. Due to the high In content and the big miscibility gap in mixed group V nitride-arsenides, the high strain energy may provide a tendency to strong composition separation, which would lead to the formation of QDs. Unlike self-assembled QDs, phase-separated QD states can be more conveniently identified by spectroscopic techniques rather than by direct observation through transmission electronic microscopy. A similar physical picture has been proposed in the ternary InGaN/GaN material system, where the highly efficient blue-green emission is attributed to the In-rich quantum dots.^{32,33} However, no detailed spectroscopic investigation has been reported there, especially with respect to the observation of the electronic states of QDs. For GaInNAs quaternary alloy, Asomoza, Elyukhin, and Pena-Sierra have pointed out that $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ epitaxially grown alloys with the composition $x=0.28\text{--}0.38$, $y=0.009\text{--}0.02$ should be deeply inside the spinodal decomposition range at their growth temperature.³⁴ The increase of compositions of In and N, especially the latter, will surely increase the decomposition range. It is expected that phase separation should bring about In-rich and Ga-rich areas in consideration of the high In concentration. Actually, the 31 meV phonon energy in the lower energy range suggests that the optical process in this energy range is related to In-rich QDs, because this energy is very close to the InAs LO-phonon energy.³⁵ With respect to the distribution of N, N atoms would more likely exist in In-rich dots for the relief of local strain energy.^{36–38} Therefore possibly there are roughly two composition phases: one with high In and N contents, which corresponds to zone I the other one with lower In and N contents which corresponds to zone II. The simultaneous decomposition of In-Ga and As-N enlarges the difference of the band gap energies in the two phases, which enables the observation of several excited states in the low-energy QD ensemble. Selectively excited PL spectroscopy may further manifest the existence of the second phase.

In Fig. 4, we compare the PL features of the two samples as the excitation energy changes. The excitation energies are marked on the respective PLE curves. While the PL characteristics do not change with excitation energy in the 1.3 μm sample [Fig. 4(a)], it is worthwhile to note the change of PL spectra as a function of the excitation energy in the 1.5 μm sample [Fig. 4(b)]. As has been pointed out, we associate the electronic states in zone I with the low-energy QD ensemble. At low-energy excitation [labeled (1) and (2) in Fig. 4(b)], the first excited states of particular QDs are selectively created, and we can observe only one peak ground state emission. It is possible that the ground states of some QDs may be excited and resonant ground state emission may be generated, but this emission is not resolvable from the scattered excitation light. Note that different excitation energies in (1) and (2) correspond to different QDs selected, therefore different ground state emissions were observed. With the increase of the excitation energy, the excitation photons may

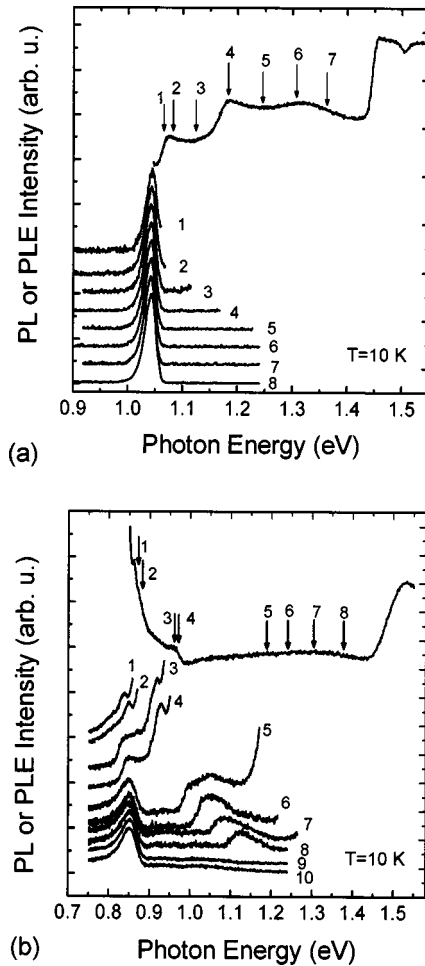


FIG. 4. PL spectra with different excitation energies at 10 K for two different GaInNAs/GaAs QWs: (a) 1.3 μm structure and (b) 1.5 μm structure. The excitation energies for each PL spectrum are marked in the respective PLE curves.

resonate with the first excited states of smaller QDs and/or the second excited states of relatively larger QDs and the PL spectra will gradually demonstrate broadened complex structures. Especially when the excitation energy further increases to (3) and (4), the photon energy is resonant with the third excited states of some QDs. In this case we can observe the emission of excited states besides the ground state emission. In order to further support the assignment of the QD states, we show comparatively in Fig. 5 the PL spectrum excited at (4) in Fig. 4(b) and the PLE spectrum detected at the corresponding ground state emission peak. It is clearly seen that transition energies of various states in these two spectra map well. It is observed that the emission from the first excited states is relatively weak. The reason is not clear at the moment, but may be related to the energy relaxation processes in the QDs. When the excitation energy is located in zone II, a new PL peak appears at the higher energy side of this low energy peak. The appearance of this new peak seems to confirm the existence of the second phase due to the phase segregation. As the excitation in this zone is no longer selective with respect to QD states in zone I, the resulting PL spectra in this zone show broadened structures which are determined by the distribution of the QD sizes and/or composition and

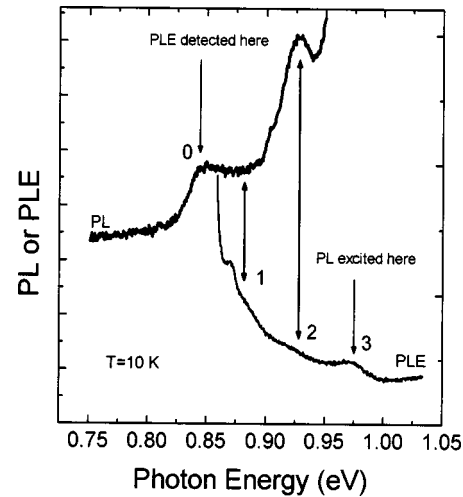


FIG. 5. A typical PLE spectrum and a PL spectrum excited at the third excited state in the 1.5 μm sample.

do not change with the excitation energy. One can see that in zone II, the luminescence photon energy also changes sensitively with the excitation photon energy. Similar to the feature in zone I, the PLE spectra change with the detection energy as well (not shown here). This indicates that the electronic states in this zone are highly inhomogeneous just as in zone I. Returning to the PLE spectrum shown in Fig. 1, it is now understandable that the PLE signals in zone II are relatively small. The reason is that some of the carriers excited in zone II cannot have recombined radiatively rather than relaxed to the lower energy states in zone I. With further increase of the excitation energy to zone III [(9) and (10) with excitation energies of 1.653 and 1.851 eV, respectively], the excitation photons are resonant with the quantum states in neither zone I nor zone II, and the spectra at the lower energy region have the same line shape as those excited in zone II. It is noted that emission band in zone II is negligibly small in this situation. This is because the carriers excited in the barriers are highly energetic and hardly captured by the intermediate states in zone II, but are captured efficiently by the low energy QDs in zone I, which is also responsible for the efficient long wavelength optical emission at room temperature.

IV. SUMMARY

In conclusion, we have reported different electronic structures in 1.3 and 1.5 μm InGaNAs/GaAs QWs grown by MBE. Whereas standard 2D electronic structure has been observed in the 1.3 μm sample, the 1.5 μm sample demonstrates QD-like electronic states as a result of strong phase segregation. We attribute the 1.5 μm PL to the recombination of ground states in phase-separated QDs with higher In and N contents. Spectroscopy of PLE with variable detection wavelength and PL with selective excitation energies has enabled us to observe the ground and several excited states of the QDs and the existence of the second phase. Selectively excited PL spectra have verified the existence of two phases. It should be noted that the presented results may not be universal in the GaInNAs/GaAs system because the microstruc-

ture is very sensitive to the growth conditions. Nevertheless, our findings indicate that efficient emission at 1.5 μm or beyond can be realized in nanostructured QDs. Due to the inevitable damaging effect of N plasma during the growth of GaInNAs epilayers, the optimized growth for nanostructured GaInNAs/GaAs may provide a viable alternative approach to “perfect” quantum well structures for 1.5 μm optoelectronic devices.

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