Photoluminescence quenching mechanisms in GaInNAs/GaAs quantum well grown by solid source molecular beam epitaxy

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The photoluminescence (PL) quenching characteristics of a thermal-annealed ~7 nm GaInNAs/GaAs quantum well (QW) with In=30% and N=1.5% were studied from 4 to 150 K. It is found that the integrated PL intensity versus temperature characteristic can be well fitted by a double activation energy model. One of the centers with low activation energy $E_B = 9$ meV is thought to originate from a localized state that traps carriers at temperatures below ~100 K. Therefore, E_B is the thermal energy required to activate the localized state carriers to the $e1$ state of the GaInNAs QW. Another center with larger activation energy $E_A = 38$ meV has a more significant PL quenching effect at temperatures above ~120 K. This center is possibly contributed by the EL6 defect level in the GaAs barrier layer, as a result of low V/III ratio of 15, and low growth temperature of 450 °C. [DOI: 10.1116/1.1617284]

I. INTRODUCTION

Current high-speed optical communication systems require optical devices operating at 1.3 or 1.55 μm wavelengths. InP-based lasers and detectors are currently used for these purposes. However, the lower cost and greater robustness of the GaAs substrate make GaAs-based long wavelength optical devices highly desirable. These factors greatly motivate current research and development efforts in high-speed optical devices fabricated on GaAs substrates. For example, the growth of GaInNAs and related quantum wells (QWs) on GaAs substrate to form vertical-cavity surface-emitting lasers,[1] and heterojunction bipolar transistors,[2] are currently receiving considerable attention by the research community.

Due to the large size difference between the N atom and other constituent atoms in the GaInNAs material, and the use of energetic N radicals from a plasma source, its photoluminescence (PL) efficiency is generally poor, as reported in existing literature.[2] It is equally well known that thermal annealing is one way of enhancing the GaInNAs photoluminescence intensity. However, thermal annealing of the GaInNAs material does not necessarily guarantee strong photoluminescence intensity at room temperature, which is one of the essential requirements of GaInNAs QW lasers grown on GaAs substrate. Hence, a detailed understanding of the PL quenching mechanisms in thermal-annealed GaInNAs QWs, which is lacking in existing literature, is essential for providing an insight into the mechanisms contributing to change in photoluminescence efficiency of the GaInNAs QW at different temperature.

II. EXPERIMENTAL PROCEDURE

The QW structures in this study were grown using solid source molecular beam epitaxy (SSMBE), which allows efficient incorporation of N and In at low growth temperature of 450 °C. The N radicals are generated using a radio-frequency (rf) plasma-assisted N source. Details of its operation will be described in the following. The low growth temperature also helps to minimize phase separation of the nitride materials as reported in existing literature.[3] In addition, the hydrogen-free growth environment in SSMBE[4] helps to eliminate hydrogen-related defects that are found in metalorganic chemical vapor deposition systems.[4]

The nitrogen admitted to the rf plasma source was fixed at 0.1 sccm and this contributed to the chamber background pressure of 3.5×10^{-6} Torr. This background pressure is optimum for nitride material growth. The above flow rate and background pressure minimize the interruption time required to pump away the nitrogen gas in the growth chamber after growing the GaInNAs QW layer. The smallest achievable flow rate of 0.1 sccm also ensures ease of nitrogen plasma ignition and high-brightness mode of nitrogen–plasma chamber operation. The rf source is operated at high-brightness mode, in contrast to low-brightness mode, to promote efficient generation of nitrogen radicals. This is observed during a GaNAs bulk layer growth, with less than 0.5% nitrogen is incorporated under low-brightness mode of operation, even though a high rf power of 300 W was applied to the plasma chamber. By operating the chamber in high-

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brightness mode, and by varying the rf power from 150 to 350 W while fixing the flow rate and maintaining the chamber background pressure, the nitrogen composition in GaNAs materials increases from 1.5% to 3.5%. As for GaInNAs QW, its nitrogen composition was found to decrease with increasing group-III beam-equivalent pressure (BEP)[5] or flux at the same rf power and chamber background pressure. The ratio of As flux to group-III (In and Ga) flux of 15 was measured using an ion gauge.

The double quantum wells used in this study has GaInNAs QW and a reference GaInAs QW nominal thicknesses of ~7 nm. This study will mainly focus on the GaInNAs QW, while the reference GaInAs QW is used mainly for *in situ* monitoring purpose during growth. GaInAs QW has disjointed-streak reflection high-energy electron diffraction patterns while that of GaInNAs QW are almost streaky, indicating better two-dimensional (2D) growth in the latter due to the strain relieving effect of N in GaInNAs QW. The emergence of disjointed-streak patterns, or dashed-line patterns, during growth indicates an intermediate surface reconstruction stage between the 2D and 3D growth mode. During growth, the In and Ga BEP were maintained at 2.8×10^{-7} and 4.6×10^{-7} Torr, respectively, to obtain In composition of ~30%. The rf power applied to the N plasma source was fixed at 350 W using open-shutter configuration in which the nitrogen shutter is fully open during the growth of the nitride layer. The incorporated N composition was estimated to be 1.5% using the following inverse N composition versus growth rate empirical relationship obtained from a separate experiment:

$$\frac{1}{\mathrm{N}}=0.43+0.0015e^{R/0.16}, \qquad (1)$$

where N is the nitrogen composition in % and R is growth rate in μm/h. The growth rate for GaAs was fixed at 1 μm/h while the incorporation of In would slightly increase the growth rate[5] for the GaInNAs and GaInAs layers.

The GaAs barrier layers were grown at the same temperature as the well layers (450 °C), instead of the optimum growth temperature of ~590 °C. This is to prevent possible GaInNAs surface roughening by the annealing effect if the substrate temperature is increased from 450 to 590 °C, which can be done during the growth interruption period immediately after the GaInNAs layer growth. The barrier layer of 80 nm between the QWs is of sufficient thickness to eliminate interaction between the QWs' wave functions.

After growth, the sample was annealed at 840 °C for 10 min using a rapid thermal annealing (RTA) equipment to improve the GaInNAs crystalline quality. This annealing condition was established as optimum for giving enhanced PL intensity from separate experiments.[5] The equipment was calibrated by comparing the pyrometer temperature range between 350 and 950 °C with a standard thermocouple. The deviation of the temperature measured by the pyrometer was then adjusted automatically to that of the thermocouple by a built-in software. A long preheating time of 10 min at 380 °C provides a uniform starting temperature across a sample. A long annealing duration of 10 min was used to further ensure uniform heating during the annealing step in the RTA chamber.

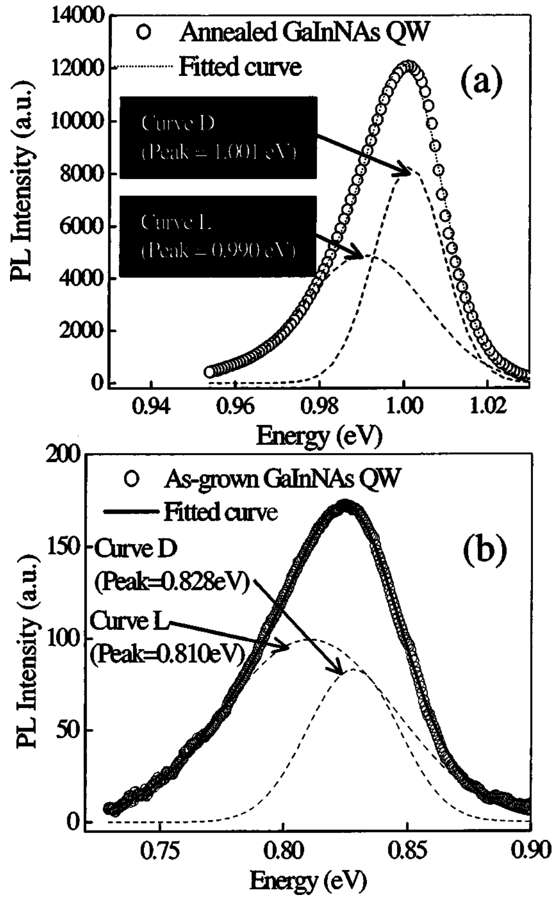

FIG. 1. 4 K PL characteristics of: (a) thermal-annealed GaInNAs/GaAs QW and (b) as-grown GaInNAs/GaAs QW. Both are fitted with two Gaussian functions.

III. RESULTS AND DISCUSSION

Figure 1(a) shows PL spectrum of the annealed GaInNAs QW. As expected, the thermal anneal results in significant improvement of the as-grown GaInNAs QW's optical quality in Fig. 1(b). The PL (4 K) intensity increases by almost 6× after anneal, and the full width at half maximum (FWHM) decreases from 66 to 26.4 meV. The PL peak energy of the GaInNAs QW before and after anneal is 0.825 and 1 eV, respectively. The blueshift in the PL peak energy could be the result of either N–As or In–Ga outdiffusion.[5] The annealed GaInNAs QW PL spectrum can be conveniently decomposed into two Gaussian functions as represented by curve L and curve D as in Fig. 1(a). During the autofitting process, the peak energy and FWHM of the two Gaussian functions were allowed to vary. Similarly, the as-grown GaInNAs QW PL spectrum can be decomposed in a same manner. It will be shown in this article that curve D is attributed to the $e1-$hh1 transition, which is the desired transition; while curve L is attributed to the impurity related transition called the localized state. By comparing the

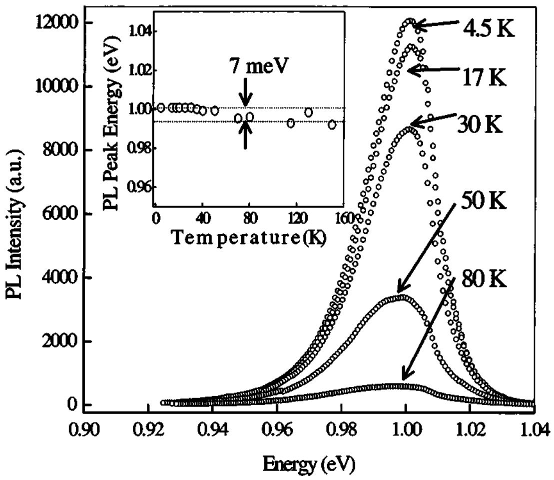

FIG. 2. Change of PL intensity in the annealed GaInNAs QW with temperature. The inset shows the change in the PL peak energy of the annealed GaInNAs QW with temperature.

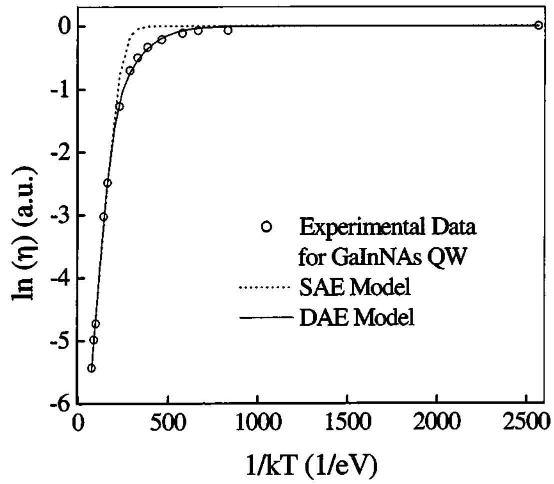

FIG. 3. Plot of PL efficiency vs inverse of temperature. The SAE model (dotted line) and DAE model (solid line) are used to fit the experimental data.

decomposed PL spectrum of Figs. 1(a) and 1(b), it is found that the relative peak intensity of curve D to curve L increases from ~0.8 to 2 after annealing, suggesting the improvement in the PL efficiency of the GaInNAs QW is related to the suppression of localized state and enhancement of the $e1-\mathrm{hh}1$ state. The following paragraphs will describe the analysis of temperature dependent PL properties including this localized state.

In order to ascertain the origin of curves L and D in Fig. 1, which could provide the physical insight for the PL quenching in the annealed GaInNAs QW, the change of PL characteristics with temperature is investigated. Only five of the PL spectra are shown in Fig. 2 for the purpose of clarity. As temperature increases from 4.5 to 80 K, the PL intensity reduces by 20 times. Also, the PL peak energy of the GaInNAs QW shifted slightly by 7 meV as temperature was increased from 4.5 to 150 K (see inset in Fig. 2) due to temperature dependent energy shrinkage (Varshni relationship). As compared to the larger PL peak energy change of 23 meV for the GaInAs QW within the 4.5–150 K temperature range (not shown here), the GaInNAs QW showed better thermal stability. The PL efficiency, η, with respect to measurement temperature was then calculated from the above experiment. η is defined as ratio between the PL intensity at temperature T, $I(T)$, and PL intensity at 4 K, I_0. At 4 K, the thermal energy contribution to carrier excitation, and nonradiative recombination is assumed to be minimal. Hence,

$$\eta=\frac{I(T)}{I_0}. \tag{2}$$

Also, it will be shown later that the η versus T data are better fitted using a dual-activation energy (DAE) model, compared to a single-activation energy (SAE) model. Exponential relationships between PL efficiency and temperature are used, and the overall PL efficiency is formulated as[6]

$$\frac{1}{\eta}=\frac{I_0}{I(T)}=1+Ae^{-E_A/kT}+Be^{-E_B/kT}, \tag{3}$$

where A and B are constants, k is Boltzmann's constant, and T the absolute temperature. By plotting $\ln(\eta)$ versus $1/kT$, the unknown parameters in Eq. (3) can be obtained.

As evident in Fig. 3, a SAE model (dotted line) fits relatively poorly to the experimental data over the temperature range from 4 to 150 K. Setting $B=0$ and $E_B=0$ in Eq. (3) satisfies the SAE model, yielding activation energy of E_A. On the other hand, a DAE model (solid line) as described by Eq. (3) fits the experimental data very well. This result suggests the existence of intermediate energy levels (in addition to $e1$) that facilitate carrier loss by thermal and optical excitation. These intermediate energy levels can be quantified by fitting the experimental data in Fig. 3 with the DAE model, yielding $E_A\sim 38$ meV and $E_B\sim 9$ meV.

The value of $E_B(\sim 9$ meV) is close to the energy separation between curves D and L of 11 meV in Fig. 1(a). In order to investigate the origin of E_B, the original temperature dependent PL spectrums were fitted with two Gaussian functions as in Fig. 1. The same notations of curves D and L are used in Fig. 4(a) to indicate the trend of the PL intensity of the high-energy and low-energy Gaussian functions. Hence E_B is related to the activation of carriers from the low energy impurity state to a higher energy $e1$ state as describe in the above. It is believed that the impurity state is related to the localization effect as a result of N incorporation.[7] This is evident in the change in peak PL intensity with temperature as shown in Fig. 4(a) where the $e1$ state (curve D) tends to increase linearly with increasing laser excitation power, while the localized state (curve L) tends to saturate with the same treatment above ~100 mW. In the low excitation power region of below ~100 mW in Fig. 4(a), although the peak intensities of curves L and D may look close to each other, their intensity difference are actually large. For example, the relative intensities of curves D to L are about 3.4 and 4 times at excitation powers of ~12 and 20 mW, respectively. Obvious intensity saturation of curve L only occurs above ~200 mW. The above observation is consistent with the experimental observation of Luo *et al.* in nitride

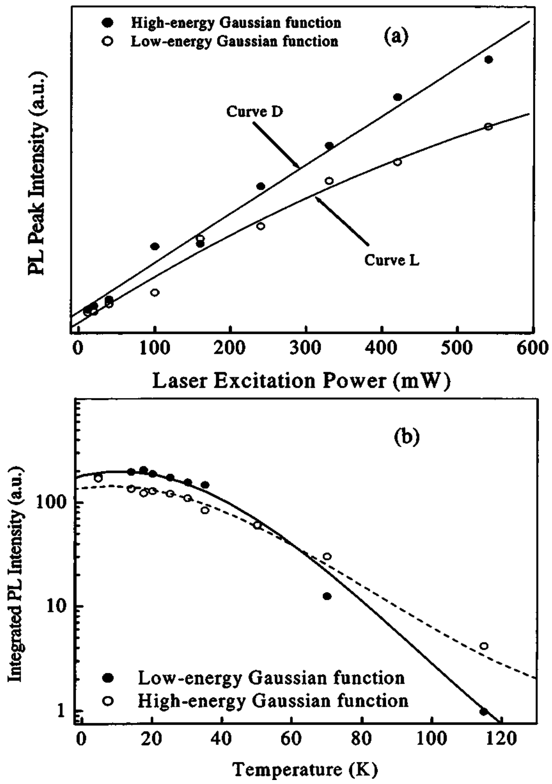

FIG. 4. Plot of (a) PL peak intensity vs laser excitation power and (b) integrated PL intensity vs temperature.

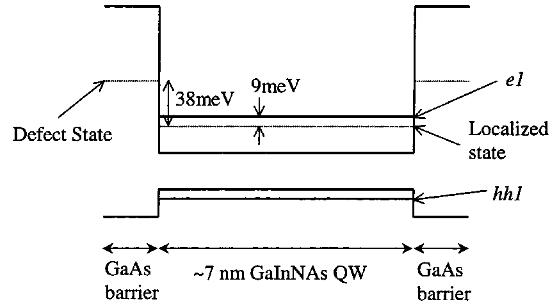

FIG. 5. Energy band diagram of PL quenching model for GaInNAs/GaAs QW.

materials[7] and hence, confirms the assignment of E_B as localized-state-related activation energy. The results can be further explained based on the band filling effect. At low temperature, carriers tend to stay at low energy state, and therefore the carriers are trapped by localized states (low-energy Gaussian function). This is evident in Fig. 4(b) where the integrated intensity of the localized state (low energy Gaussian function) is higher than that of the $e1$ state (high energy Gaussian function) at low temperature. Following increase in temperature, the carriers in the localized states acquire more energy to populate the $e1$ state, leading to higher integrated PL intensity for the high-energy Gaussian function. Hence, the integrated PL intensity of the localized states, which has limited carrier density, quenches faster as temperature increases.

A separate study on the localized states in GaInNAs/GaAs QW by time-resolved PL measurements has further confirmed the findings of this article, and will be published in a separate article. In that study, stronger emission-energy-dependent carrier lifetime has been observed in GaInNAs/GaAs QW, as compared to the reference GaInAs/GaAs QW. In this article, we will only concentrate on using PL studies to address two types of transitions that could affect the desired $e1-\mathrm{hh}1$ transition, namely the localized state presented in the above, and a GaAs-barrier-defect-related transition in the following. The assignment of this defect will be presented first, followed by the explanation for the creation of such a carrier loss center at increasing PL measurement temperature.

As measurement temperature increases beyond ~120 K, the center with activation energy $E_A = 38\,\mathrm{meV}$ further quenches the PL intensity of the QW. This center is attributed to the presence of defects in the GaAs barrier, and it is determined based on QW calculation.[8] From room temperature GaInNAs/GaAs QW calculations, the confined energy states of $e1 = 44\,\mathrm{meV}$ and hh1=15 meV, with respect to the conduction band and valence band, respectively, are obtained. Together with the calculated conduction band offset and valence band offset of 414 and 177 meV, respectively, the defect state, as labeled in Fig. 5, is found to be located at 0.34 eV from the conduction band. This value is close to the 0.35 eV defect state of EL6, which was reported to be a Ga vacancy–As vacancy (V_{Ga}–V_{As}) complex.[9] This defect in GaAs could dissociate at high temperature and then reform after thermal annealing and hence, is likely to occur in the GaInNAs/GaAs QW used in this study due to the choice of growth conditions.

Although carriers are mostly trapped in the QW layer, and one would logically deduce that PL transition would only occur in the well layer, and not in the thin GaAs barrier layer (80 nm in this study) in ideal situation. However, Vening *et al.* has deduced in his study that barrier layer defects created during growth can contribute to the thermal quenching of their GaInAs/GaAlAs QW's PL efficiency,[10] through the detrapping process of carriers into the barrier layer. Hence their finding supports the argument in this article that the above GaAs-barrier defect could contribute to the PL efficiency reduction in the GaInNAs/GaAs QW. In this study, the creation of the V_{Ga}–V_{As} defect in the GaAs barrier during growth could be promoted primarily by a low V/III ratio of 15, and secondarily by a low growth temperature of 450 °C. All the above results are consolidated into a PL quenching model as depicted in Fig. 5.

IV. CONCLUSIONS

In conclusion, this article reports a study of the PL quenching mechanisms in GaInNAs/GaAs QW. The physical mechanism of carrier localization in the annealed GaInNAs QW was analyzed from the change in PL spectra with temperature and laser excitation power. By fitting the individual PL spectrum with two Gaussian functions, the signature of the localized and $e1$ energy states can be identified. The existence of two PL quenching states (E_A and E_B) results in significant PL intensity reduction following increase in temperature. The activation energy E_B is confirmed to be a localized state, and an EL6 defect level was identified, both of which could degrade PL efficiency in GaInNAs/GaAs QW. Our results indicate that improving the barrier material quality and reducing the localized states in the GaInNAs QW could lead to enhanced PL efficiency in such a material system.

[1] M. C. Larson, M. Kondow, T. Kitatani, K. Nakahara, K. Tamura, H. Inoue, and K. Uomi, IEEE Photonics Technol. Lett. **10**, 188 (1998).
[2] R. Szweda, III-Vs Review **16**, 36 (2003).
[3] Z. Pan, L. H. Li, W. Zhang, Y. W. Lin, and R. H. Wu, Appl. Phys. Lett. **77**, 214 (2000).
[4] T. Kitatani, M. Kondow, and T. Tanaka, J. Cryst. Growth **227–228**, 521 (2001).
[5] T. K. Ng, S. F. Yoon, S. Z. Wang, W. K. Loke, and W. J. Fan, J. Vac. Sci. Technol. B **20**, 964 (2002).
[6] J. D. Lambkin, L. Considine, S. Walsh, G. M. O'Connor, C. J. McDonagh, and T. J. Glynn, Appl. Phys. Lett. **65**, 73 (1994).
[7] X. D. Luo, Z. Y. Xu, W. K. Ge, Z. Pan, L. H. Li, and Y. W. Lin, Appl. Phys. Lett. **79**, 958 (2001).
[8] W. J. Fan and S. F. Yoon, J. Appl. Phys. **90**, 843 (2001).
[9] Z. Q. Fang, T. E. Schlesinger, and A. G. Milnes, J. Appl. Phys. **61**, 5047 (1987).
[10] M. Vening, D. J. Dunstan, and K. P. Homewood, Phys. Rev. B **48**, 2412 (1993).