OPTO-ELECTRONICS REVIEW **17**(3), 260–264

DOI: 10.2478/s11772-009-0008-9

Evaluation of optical quality and properties of $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$ lattice matched to GaAs by using photoluminescence spectroscopy

M. GHOLAMI[1*], M. ESMAEILI[1], H. HARATIZADEH[2,3], P.O. HOLTZ[3], and M. HAMMAR[4]

[1]Department of Science, Islamic Azad University, Damghan Branch, Damghan, Iran
[2]Physics Department, Shahrood University of Technology, 3619995161, P.O. Box 316, Shahrood, Iran
[3]Department of Physics, Chemistry and Biology, Linkoping University, SE-581 581 83 Linkoping, Sweden
[4]Department of Microelectronics and Applied Physics, School of Information and Communication Technology, Royal Institute of Technology (KTH), Electrum 229, 16440 Kista-Stocholm, Sweden

We have investigated optical properties of $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$*/GaAs single quantum-well structures using photoluminescence technique. We have found that nitrogen creates potential fluctuations in the InGaNAs structures, so it is the cause of trap centres in these structures and leads to localized excitons recombination dynamics. The near-band edge PL at 2 K exhibited a blueshift with an increase in excitation intensity of a sample but there is not such a shift in the PL peak position energy of same sample at 150 K. It has been found that PL spectra have a large full width at half maximum (FWHM) value at 2 K. These results are discussed in terms of carrier localization. Additionally, our results suggest decreasing PL integrated intensity in this structure, possibly due to non-radiative recombination. It has been shown that thermal annealing reduces the local strain created by nitrogen. By annealing process, a blue shifted emission can be observed.*

Keywords: optical efficiency, photoluminescence (PL), InGaNAs/GaAs single quantum well (SQW) nanostructures, localized excitons, full width at half maximum (FWHM), PL integrated intensity, thermal annealing.

1. Introduction

In recent years, GaInNAs/GaAs has been suggested as a novel compound semiconductor material system for the realization of high-performance laser diodes emitting at the 1.3-μm optical fiber window [1], and high efficiency multijunction solar cell [1–3].

It has been demonstrated that an addition of nitrogen to GaAs or GaInAs changes essentially the conduction band (CB) structure leading to several unexpected effects:

- reduction of the band gap energy as large as 60 meV for 0.25% of N in InGaNAs,
- nitrogen induced splitting of the CB (to the E^- and the E_+ bands),
- drastic increase in the CB electron effective mass and a giant nonparabolicity of the CB [4–7].

It has been shown that GaN and GaAs have many different lattice constants, which mean that GaAsN layers grown on a GaAs substrate should be highly strained. By adding indium we can grow InGaAsN layer completely lattice matched to GaAs substrate [8–11]. These observations could be explained according to the band anticrossing model by assuming that N gives rise to the level E_N localized in real space and degenerate with the states of the $In_xGa_{1-x}As$ conduction band (CB) as expected for substitution of As with N atoms [4,12].

The interaction between the CB states and E_N leads to a band repulsion, which is responsible for the observed band-gap shrinkage, and to an increase in the electron effective mass because of the mixed free/localized character of the electron wave function. As a result, the recombination energy of carriers confined in InGaAsN quantum well (QW) can be written as [4]

$$h\nu = 1/2\{E_N + E_M - [(E_N - E_M)^2 + 4V_{MN}^2]^{1/2}\}. \quad (1)$$

Where E_M is the energy of the InGaAsN unperturbed conduction sub-band. An estimate of VMN has been obtained by pressure-dependent photo reflectance measurements and by optical absorption spectroscopy [5,13]. Two major growth techniques, molecular beam epitaxy (MBE) and metal-organic vapour-phase epitaxy (MOVPE) are used for the growth of these material systems. From a view point of mass-production and interaction with different devices by selective growth and HBT-based power-amplifiers for wireless applications MOVPE is more attractive. In this paper we have investigated the effect of temperature and excitation intensity and also rapid thermal annealing on the MOVPE grown InGaNAs SQW nanostructures sample.

---

[*] e-mail: mgholamim@gmail.com

2. Experiment

We have performed cw- photoluminescence experiment on the $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs single quantum well (SQW) which have been grown on the undoped (001) oriented GaAs substrates by metal-organic vapour-phase epitaxy (MOVPE) technique using triethylgallium (TEGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs), and dimethyhydrazine (DMHy). The growth temperature and the growth rate were 495°C and 0.0035 nm/s. The reactor pressure during growth was 100 mbar. In epitaxial growth V/III ratio was 2300.

This sample has been grown on a 300-nm thick undoped GaAs buffer layer which followed by a 6.75-nm InGaNAs quantum well (QW) structure and then a 100-nm-thick GaAs-capping layer. Low temperature PL measurement was carried out by mounting the samples in a liquid helium cryostat with a variable temperature and using the 514.5-nm line of an Ar^+ laser as the excitation source. A thermoelectrically cooled Ge photodiode was used to detect the signal at the existence of a 50-cm monochromator through an amplifier. Rapid thermal annealing (RTA) was performed on this SQW sample at different annealing times (between 5 up to 30 s) under N_2 flow at 2 K.

3. Results and discussion

The excitation intensity dependence of PL spectra for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW at different temperatures (2 K and 150 K) has been illustrated in Fig. 1. At the first glance we see a strong blueshift in PL peak energy due to the screening of the localization potential by the photo-generated carriers at low temperature. Figure 1(a) shows blueshifting about 15 meV in the PL peak position of the $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW sample with increasing the excitation intensity from 5 to 27 mW. As it has been mentioned earlier, this behaviour could be explained in term of screening the localization potential by carriers, i.e., by increasing the excitation intensity, the photogenerated carrier density will increase and partly screen the localization potentials caused by nitrogen uniformity distribution in the QW region. These results are comparable with the results of R.A. Mair *et al.* taken from Refs. 14, 15, and 16. Nevertheless, such behaviour does not be observed at higher temperature (150 K) due to the detrapping of localized carriers with thermal energy.

Composition fluctuation (In-rich and N-rich cluster regions) mentioned by Xin *et al.* in Ref. 16, or even the existence of highly localized nitrogen-related deep levels in the band gap, has some small role in the generation of such trap centres. However, nitrogen is most probably responsible for the localization of carriers, according to the study by Shirakata *et al.* in Ref. 17, the localization effect is not observed in nitrogen-free reference samples.

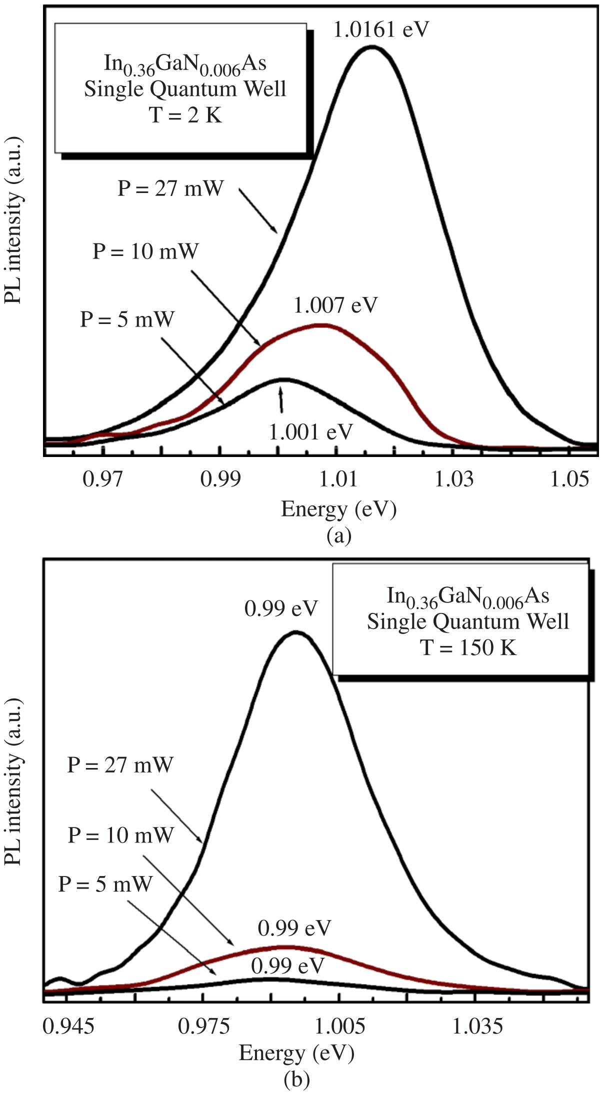


Fig. 1. Excitation intensity dependence of PL spectra for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW at: (a) 2 K and (b) 150 K.

As in the case of the GaNAs alloy, the near-band edge PL emission in the GaInNAs has a very asymmetric PL lineshape at low temperature [Fig. 1(a)] which is attributed to localized excitons emission [8,18–20]. Also similarly to GaNAs, the large localization potential in GaInNAs is at least partly attributed to the composition and strain non-uniformity of the alloy which originates the N existence. In particular, the N- enhanced undulation of the GaInNAs QWs due to lateral variations in strain is clearly seen from bright field cross-sectional transmission electron microscopy (TEM) image as shown in Fig. 2.

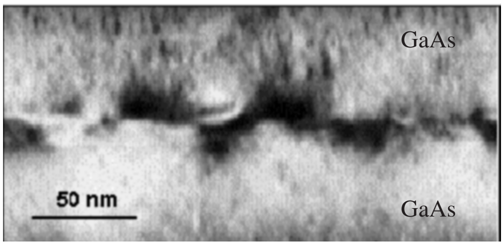


Fig. 2. Bright field cross-sectional transmission electron microscopy (TEM) of as-grown GaInNAs/GaAs SQW.

These behaviours could be evaluated by alternation of full width at half maximum (FWHM) of PL spectra. We have calculated FWHM of $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW at different temperatures. At low temperature (2 K), the FWHM value tends to be a large value of 37 meV, as it can be seen in Fig. 3. Actually, with increasing temperature from 2 K to 50 K, the FWHM of PL spectra decrease from 37 meV to 33 meV which is due to the decreasing fluctuation potentials caused by N and also making the flat interfaces and good homogeneity by increasing temperature. But at higher temperatures (T > 50 K) there is a surging in FWHM and it is explained by converting the localized excitons to free excitons and then increase in their kinetic energy at high temperatures. At T > 75 K there are not localization centre and excitons correlation, so due to increase in the temperature, all excitons convert to the free electrons and holes and follow a high enlargement at FWHM of these PL spectra. Therefore we realize that with increase in temperature, the optical efficiency of this nanostructure could be more improved. Similarly to the results obtained by Shirakata *et al.* [17] these results show that the recombination mechanism at low temperature is different from that at higher temperature. Such a tendency was not observed for the GaInAs SQW.

On the other side, increasing temperature creates phonons in the structure and increases non-radiative recombination and reduces optical emission intensity of the InGaNAs. To evaluate this effect we have considered the variation of PL integrated intensity by temperature. Figure 4(a) shows the PL integrated intensity related to the $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW sample at different temperatures. Besides, although N introduces non-radiative recombination centres, the larger carrier confinement achieved in our QWs with nitrogen makes the luminescence signal more thermally stable, enough to compensate the effect of these non-radiative centres. This leads to increase in optical efficiency at higher temperatures. Therefore saturation in PL integrated intensity for this sample at higher temperatures could be seen. All of these results are similar to the results by A. Polimeni *et al.* [19] which could be seen in Fig. 4(b). According to this figure, such saturation is not seen in the without N sample. So that, PL integrated intensity of "nitrogenated" samples is greater than that of the corresponding N-free blanks at room temperature (RT) and is lower, instead, at $T = 10$ K due to the thermal stability of luminescence signal and then balance of the effect of these non-radiative centres at higher temperatures.

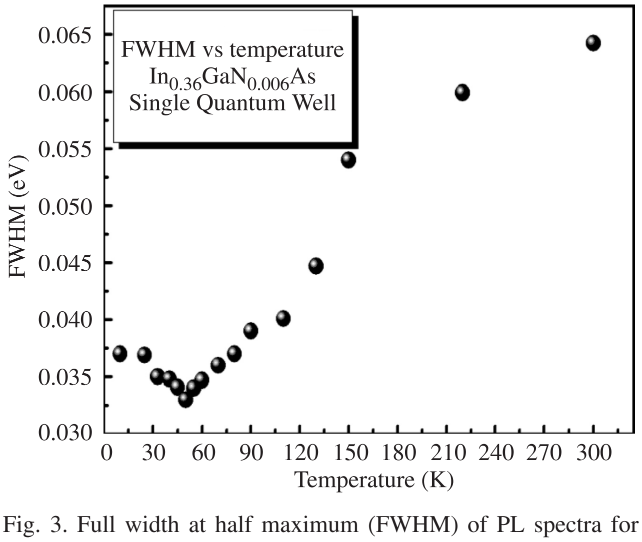
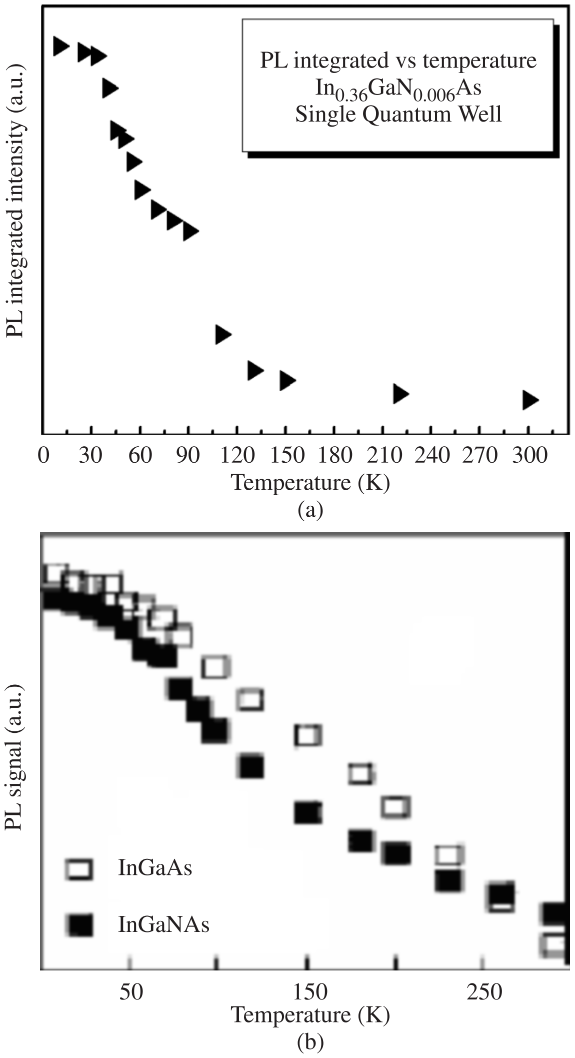


Fig. 3. Full width at half maximum (FWHM) of PL spectra for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW at different temperatures.



(a)

(b)

Fig. 4. PL integrated intensity related to the $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW sample at different temperatures (a) and PL integrated intensity of a "nitrogenated" and also N- free SQW nanostructures (after Ref. 19) (b).

Furthermore, rapid thermal annealing (RTA) treatments influence the PL efficiency. The normalized PL spectra for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW sample at different annealing time, from 0 up to 30 s, are illustrated in Fig. 5. We have shown clearly in this figure how the spectra vary with annealing time.

By annealing, a blue shifted emission can be observed. The main reason for observation of such behaviour is due to interdiffusion of In and Ga between well and barrier layers

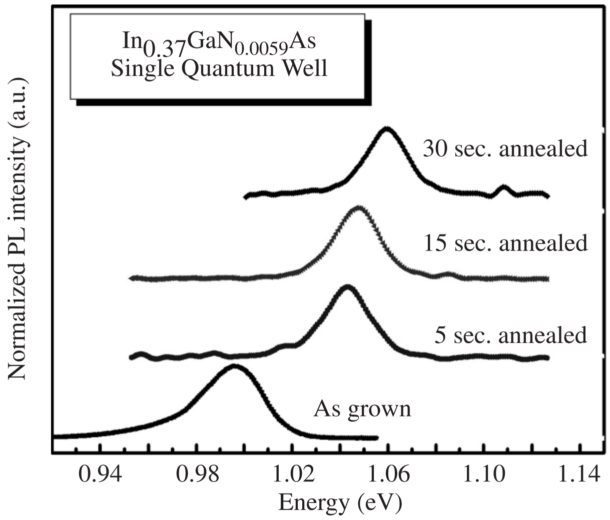


Fig. 5. Normalized PL spectra for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW sample at different annealing time, from 0 up to 30 s.

and reducing fluctuation potential and also due to elimination of some grown-in competing non-radiative channels. Sara Kurtz *et al.* reported Fourier transform infrared (FTIR) absorption spectrum of InGaNAs after various annealing. So that, according to this report, GaInAsN samples, grown at 550°C, show IR absorption spectra which imply that the domination local environment for nitrogen atoms is NGa_4. After annealing, more of the nitrogen atoms are found in NGa_3In clusters. The formation of this In-N cluster reduces the strain in the alloy [21]. Therefore this could be a reason for the blue shift of PL peak position after annealing. For example, after 5-s annealing of $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQW, the PL peak energy is blushifted about 47 meV. Variation of a full width at half maximum (FWHM) is second important change that occurs during annealing. Also RTA reduces the local strain created by nitrogen, therefore the FWHM of the annealed samples decreases due to reduced interface roughness and improved composition uniformity of fluctuation potential that acts as non-radiative centres. These results have been summarized in Table 1. The conditions of doing annealing effect on the structure are given. For example, higher temperature and also increase in annealing time cause penetration of N atoms from quantum a well layer to a barrier. This behaviour also makes structural defects in the sample that affect optical emission. Thus, for preventing the loss of the N content, annealing has been done under N_2 atmosphere.

Table 1. PL peak energy and FWHM for $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs SQWs at $T = 2$ K.

Sample	As grown	5 s annealed	15 s annealed	30 s annealed
Peak position (eV)	0.995	1.043	1.047	1.059
FWHM (meV)	37	28	27	21

4. Conclusions

In summary, we have shown experimental data for nitrogen containing III-V quaternary alloy, $Ga_{0.64}In_{0.36}N_{0.006}As_{0.994}$/GaAs, grown by MOVPE on the undoped (001) oriented GaAs substrates, relevant for high-performance LD. Although nitrogen creates some fluctuations at the surface of these nanostructures and increases the non-radiative recombination especially at low temperatures, but with exceeding temperature, the quality of alloys and efficiency will improve. Temperature dependence of the PL spectra indicates localized carriers and free carriers dominating the radiative recombination processes at low and high temperature, respectively. We have shown that annealing decreases the density of non-radiative recombination centres, thus improving the PL efficiency. Furthermore, it improves the material homogeneity, thus reducing carrier localization.

Acknowledgements

The authors would like to thank Dr. Carl Asplund from the Royal Institute of Technology (KTH), Sweden, for helpful assistance in providing our samples.

References

1. M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, “GaInNAs: A novel material for long-wavelength-range laser diodes with excellent high-temperature performance”, *Jpn. J. Appl. Phys.*, *Part* 2 **35**, 1273 (1996).
2. S.R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J. Banas, and B.E. Hammons, “InGaAsN solar cells with 1.0-eV band gap, lattice matched to GaAs”, *J. Appl. Phys. Lett.* **74**, 729 (1999).
3. N.Y. Li, P.C. Chang, A.G. Baca, X.M. Xie, P.R. Sharps, and H.Q. Hou, “DC characteristics of MOVPE- grown Npn InGaP/InGaAsN DHBTs”, *Electron. Lett.* **36**, 81–83 (2000).
4. W. Shan, W. Walukiewicz, J.W. Ager III, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson, and S.R. Kurz, “Band anticrossing in GaInNAs alloys”, *Phys. Rev. Lett.* **82**, 1221–1224 (1999).
5. P. Perlin, P. Wisniewski, C. Skierbiszewski, T. Suski, E. Kamińska, S.G. Subramanya, E.R. Weber, D.E. Mars, and W. Walukiewicz, “Interband optical absorption in free standing layer of $Ga_{0.96}In_{0.04}As_{0.99}N_{0.01}$”, *J. Appl. Phys. Lett.* **76**, 1279 (2000).
6. C. Skierbiszewski, P. Perlin, P. Wisniewski, T. Suski, J.F. Geisz, K. Hingerl, W. Jantsch, E.D. Mars, and W. Walukiewicz, “Band structure and optical properties of $In_yGa_{1-y}As_{1-x}N_x$ alloys”, *Phys. Rev.* **B65**, 035207 (2001).
7. C. Skierbiszewski, P. Perlin, P. Wisniewski, W. Knap, T. Suski, W. Walukiewicz, W. Shan, J.W. Ager, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson, and S.R. Kurtz, “Large, nitrogen-induced increase of the electron effective mass in $In_yGa_{1-y}N_xAs_{1-x}$”, *J. Appl. Phys. Lett.* **76**, 2409 (2000).
8. M. Weyers, M. Sato, and H. Ando, “Red shift of photoluminescence and absorption in dilute GaAsN alloy layers”, *Jpn. J. Appl. Phys.* **31**, L853–L855 (1992).

9. S.H. Wei and A. Zunger, "Giant and composition-dependent optical bowing coefficient in GaAsN alloys", *Phys. Rev. Lett*. 76, 664–667 (1996).
10. A. Rubio and M.L. Cohen, "Quasiparticle excitations in $GaAs_{1-x}N_x$ and $AlAs_{1-x}N_x$ ordered alloys", *Phys. Rev.* **B51**, 4343–4346 (1995).
11. J. Neugebauer and C.C. Van de Walle, "Electronic structure and phase stability of $GaAs_{1-x}N_x$ alloys", *Phys. Rev.* **B51**, 10568–10571 (1995).
12. H.P. Hjalmarson, P. Vogl, D.J. Wolford, and D. Dow, "Theory of substitutional deep traps in covalent semiconductors", *Phys. Rev. Lett*. **44**, 810–813 (1980).
13. P.J. Klar, H. Gruning, W. Heimbrodt, J. Koch, F. Hohnsdorf, W. Stolz, P.M.A. Vicente, and J. Camassel, "From N isoelectronic impurities to N-induced bands in the GaN_xAs_{1-x} alloy", *J. Appl. Phys. Lett.* **76**, 3439 (2000).
14. R.A. Mair, J.Y. Lin, H.X. Jiang, E.D. Jones, A.A. Allerman, and S.R. Kurtz, "Time-resolved photoluminescence studies of $In_xGa_{1-x}As_{1-y}N_y$", *J. Appl. Phys. Lett*. **76**, 188 (2000).
15. L. Grenouillet, L. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, S. Vannuffel, A. Millon, and A. Chenevas-Paule, "Evidence of strong carrier localization below 100 K in a GaInNAs/GaAs single quantum well", *J. Appl. Phys. Lett*. **76**, 2241 (2000).
16. H.P. Xin, K.L. Kavanagh, Z.Q. Zhu, and C.W. Tu, "Observation of quantum dot-like behaviour of GaInNAs in GaInNAs/GaAs quantum wells", *J. Appl. Phys. Lett.* **74**, 2337 (1999).
17. S. Shirakata, M. Kondow, and T. Kitatani, "Photoluminescence and photoreflectance of GaInNAs single quantum wells", *J. Appl. Phys. Lett.* **79**, 54–56 (2001).
18. S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, "Luminescence of as-grown and thermally annealed GaAsN/GaAs", *Appl. Phys. Lett*. **72**, 1857 (1998).
19. A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhadt, and A. Forchel, "Effect of temperature on the optical properties of (InGa)(AsN)/GaAs single quantum wells", *Appl. Phys. Lett*. **77**, 2870 (2000).
20. B. Halperin and M. Lax, "Impurity-band tails in the high-density limit. I. Minimum counting methods", *Phys. Rev. Let*. **148**, 722–740 (1996).
21. S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, and N. Karam, "Structural changes during annealing of GaInAsN", *Appl. Phys. Lett*. **78**, 748 (2001).