Localized and delocalized states in GaNAs studied by microphotoluminescence and photoreflectance

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(Received 1 October 2008; accepted 1 December 2008; published online 7 January 2009)

Optical transitions in GaNAs bulk layer containing 2.2% N have been studied with microphotoluminescence (μ-PL) and photoreflectance. At low temperatures and low excitation conditions, the μ-PL spectra showed sharp PL lines of 100–300 μeV widths about 10–20 meV below the energy gap. Those lines were attributed to the recombination of localized excitons trapped at local potential minima. When the excitation power was increased, an additional smooth PL band appeared at the higher-energy side. This band corresponds to the light-hole transition in photoreflectance spectrum, i.e., transition between the delocalized states. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3055605]

Incorporation of a few percentage of nitrogen into GaAs and other III-V alloys (so-called dilute nitrides) has a pronounced effect on the band structure leading to a large energy-gap reduction and a significant increase in the electron effective mass.[1–3] In addition, the existence of nitrogen atoms leads to a carrier localization effect at low temperatures and usually deteriorates photoluminescence (PL) in comparison to N-free system.[3] Currently, rapid thermal annealing is usually employed to improve the optical quality of dilute nitrides. However, even for the annealed materials, the low temperature PL spectra measured at low excitation conditions are dominated by the recombination of localized carriers (excitons) trapped at local potential minima,[4,5] where the exact nature of this recombination is still controversial. In general, it is expected that the broad PL band, which is attributed to the recombination of localized carriers (excitons), can be composed of sharp PL lines which are associated with individual excitons. An evidence for this scenario has been found in near-field PL spectroscopy.[6,7] The authors in Ref. 6 observed that the low temperature PL spectra are composed of sharp individual lines which are associated with localized carrier (exciton) recombination. They also noted that the recombination mechanism changes significantly between 10 and 300 K but they did not study the temperature dependence of the sharp PL lines. Such a study has been done in Ref. 7, but the energy-gap-related transition was not measured directly by an appropriate technique (i.e., an absorptionlike technique). Finally, there is no literature studying carefully with temperature the optical transitions between localized states (sharp exciton lines) and delocalized states (free exciton and/or band-to-band transitions) in dilute nitrides. This issue is especially interesting for GaNAs, since the so-called S-shape behavior for the temperature dependence of PL emission is typical and still unexplored deeply enough for this material. In this work, we apply microphotoluminescence (μ-PL) spectroscopy combined with photoreflectance (PR) to study the optical transitions in GaNAs bulklike layers focusing on the effect of localized and delocalized states.

A 300 nm thick $GaN_{0.022}As_{0.978}$ layer was grown by molecular beam epitaxy at 450 °C on semi-insulating (001) GaAs substrates, preceded by a 300 nm GaAs buffer grown at 580 °C. The sample was postgrowth annealed *ex situ* in nitrogen atmosphere at 750 °C for 60 s. Further relevant details of the growth are given in Ref. 8. μ-PL spectra were measured using a single grating 0.55 m focal length monochromator with a multichannel InGaAs detector. The 660 nm line of a semiconductor laser was focused on the sample by a long working distance objective. The diameter of the laser spot was estimated to be below 2 μm. A standard experimental setup was used for PR measurements.[9]

Figure 1 shows a comparison of PR spectrum and μ-PL spectra measured at various excitation conditions at low tem-

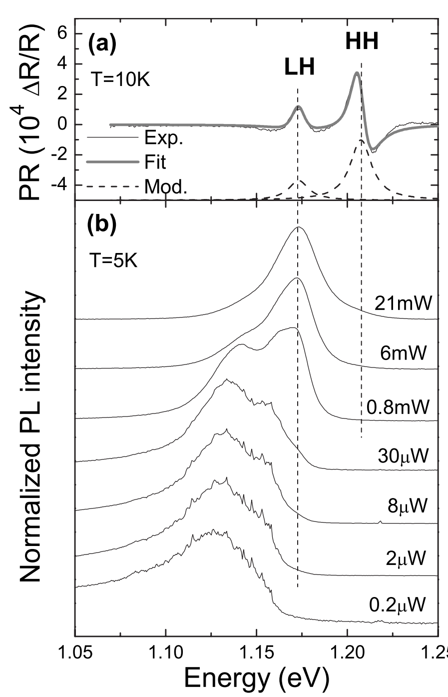

FIG. 1. (a) PR and (b) μ-PL spectra for GaNAs layer measured at low temperatures.

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peratures. In PR, two resonance lines are well distinguished. Due to the N-related tensile strain in GaNAs layer, the PR resonance at the lower energy corresponds to the optical transition occurring between the light-hole band and the conduction band (LH transition). The second line at higher energy is associated with the absorption between the heavy-hole band and the conduction band (HH transition). In general, both the transitions can be composed of two resonances: one related to excitonic and the other to band-to-band absorption.[10] However, in this study, we do not separate these two for simplicity. We have analyzed the PR spectrum using a Lorentzian shape model[11] similarly to our previous papers.[9] The dashed lines in Fig. 1(a) show the modulus of PR resonance, whose peak positions correspond to the LH and HH transitions.

In μ-PL, sharp PL lines can be resolved at low excitation conditions. We have examined that the sharp spectra are reproducible at the exact measurement position by moving out and then bringing back the beam spot at that position. Consequently, the whole fine structure within the main PL band certainly stemmed from the particular position dependence and cannot be system related. These lines showed no shift of spectral peak position with increasing excitation power; however, the sharp features smeared out. This is mainly due to the increased number of the emission lines (more excitons will contribute), causing the number (density) of the individual lines to become too large to resolve. Eventually, the envelope of the whole emission band blueshifts with the increase in the excitation power and an additional broad emission band appears at the high-energy side. At specific excitation conditions, e.g., the spectra measured at 8 μW, 30 μW, and 0.8 mW, two emission bands become observable in the spectra. The lower-energy band is composed of sharp PL lines whereas the higher-energy band is smooth. The peak energy of the smooth band corresponds to the LH-transition energy observed in the PR spectrum of Fig. 1(a). At high excitation, LH-related emission dominates the μ-PL spectra. Moreover, a contribution of HH-related emission becomes observable at the highest excitation power of 21 mW. The unambiguous identification of LH and HH transitions in μ-PL spectra is possible because of their detection in PR spectra which are insensitive to localized states. In the case of PL the peak shifts to blue because of the saturation of the localized states at the beginning. Above some excitation conditions this peak can shift to blue because of the contribution of free carrier recombination with $\boldsymbol{k} \neq 0$. Such a situation was also observed for the GaNAs layer at the excitation power higher than 50 mW. It means that measuring just PL without support from absorptionlike technique is insufficient to study the optical transitions between localized and delocalized states.

Based on the above-described comparison and discussion of the μ-PL and PR (emissionlike and absorptionlike experiments), we conclude that the smooth PL band at the higher-energy side is associated with delocalized states in GaNAs layer, namely, free exciton and/or band-to-band recombination. The sharp PL lines are separated from the LH transition by an energy of ~10–20 meV. Hence, they are attributed to some localized states in this material. So far, such sharp PL lines below the energy gap of dilute nitride, i.e., in the spectral range of localized recombination, have been observed solely in the near-field PL measurements for GaNAs (Ref. 6) and GaInNAs (Ref. 7) alloys where the size

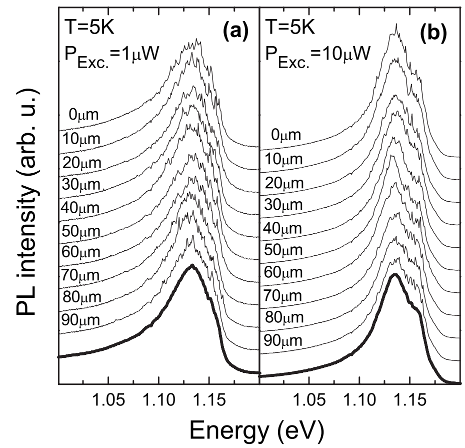

FIG. 2. Low temperature μ-PL spectra measured along a line at the excitation powers of (a) 1 μW and (b) 10 μW.

of the laser spot was by about one magnitude smaller than in our measurements. Common μ-PL results shown in this work provide an experimental evidence that the emission band attributed to the localized recombination in GaNAs (Ref. 4) is composed of individual sharp PL lines each of which is associated with a single exciton which is localized at a characteristic potential minimum. These local minima are expected to have different properties and hence they should change with the position on the sample and show different thermal sensitivities. Therefore, we perform position and temperature dependences of μ-PL measurements.

Figures 2(a) and 2(b) show two series of μ-PL spectra measured at the excitation powers of 1 and 10 μW, respectively. The spectra were recorded at different spots on the sample along a line with a step of 10 μm. The energy positions of the sharp lines vary by changing the excitation space. It is an evidence of the coexistence of very many localized excitons with various localization energies. Because of the spectral variation with the size of tens of micrometers, they cannot be resolved in standard macro-PL spectra whose beam spot is typically several hundreds of micrometers and the spectrum is integrated over the area. In order to visualize this effect, we present an imitated macro-PL spectrum in Fig. 2 (bold line) obtained from a simple summation of all the μ-PL spectra plotted above.

Figures 3(a) and 3(b) show the temperature dependence of the μ-PL spectra measured at the excitation powers of 1 and 10 μW, respectively. At the lower excitation power, the sharp lines are more pronounced. They are observable at temperatures below 50 K. Above the temperature, most of photogenerated carriers recombine nonradiatively. For the higher excitation power of 10 μW, sharp PL lines are less resolved but the spectra can be observed up to higher temperatures than in the former. This result suggests the coexistence of radiative and nonradiative centers in this alloy. At the low temperatures these radiative centers can be the origin of localized emission. However, at higher temperatures the nonradiative centers become comparatively more active and lead to a dominant nonradiative recombination in the system. At low excitation conditions, most of the photogenerated carriers can be captured by those centers and therefore only localized emission is observed below 50 K. We believe that the sharp PL lines are associated with the recombination of localized excitons, which are confined on these radiative centers. It is expected that deep acceptor- and donorlike states

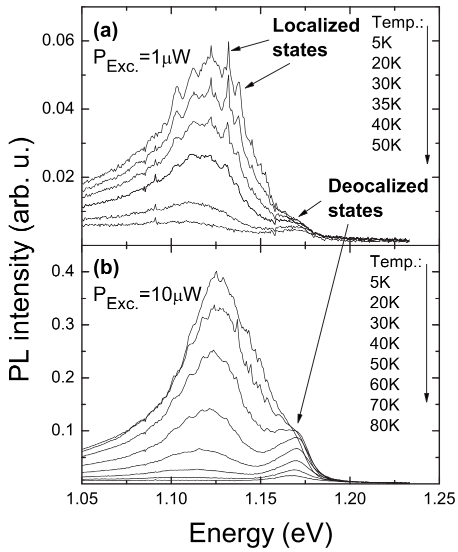

FIG. 3. Temperature dependence of μ-PL spectra measured at the excitation powers of (a) 1 μW and (b) 10 μW.

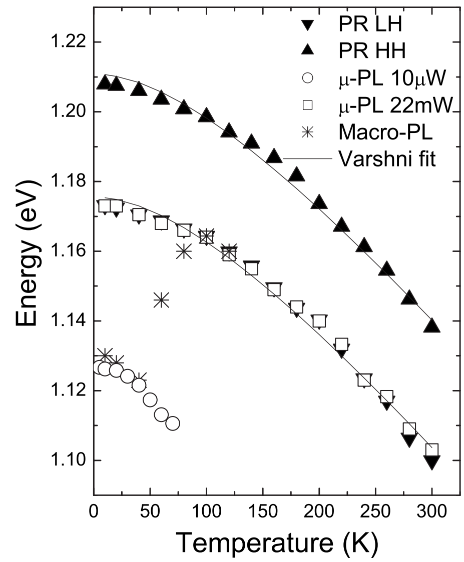

FIG. 5. Temperature dependence of LH (▼) and HH (▲) transitions in GaNAs layer extracted from PR spectra and the energy of PL peak (i.e., the envelope of PL band). Varshni parameters: $\alpha^{LH}=\alpha^{HH}=0.42$ meV/K and $\beta^{LH}=\beta^{HH}=230$ K.

can play the role of both the radiative and nonradiative centers. Since the energy gap in GaNAs significantly varies with the local alloy content, it is expected that the binding energy for the same deep acceptorlike (donorlike) centers (the same from the structural viewpoint) can largely change from place to place due to various nearest-neighbor environments of these centers. As a result, almost continuous distribution of the sharp PL lines is observed in our μ-PL spectra as seen in Fig. 2. In addition to the sharp exciton lines associated with the deep acceptor- and donorlike centers, alloy fluctuations can also lead to localized emission from GaNAs. Such a scenario is often proposed for GaInNAs alloys due to the large miscibility gap in this alloy.[7] The results presented there show that the source of localized emission can also be deep acceptor- and donorlike centers.

Figure 4 shows the temperature dependence of PR spectra. The energies of LH and HH transitions extracted from those spectra[11] are plotted in Fig. 5, comparing the PL peak energy for the two excitation densities. At low temperatures, the well known S-shape behavior of the PL peak position related to the localized emission is observed. Note that the peak of the envelope of the PL band depends strongly on the excitation power as seen in Fig. 1(b). Therefore, various Stokes shifts can be observed for GaNAs layers and quantum wells depending on the excitation conditions.

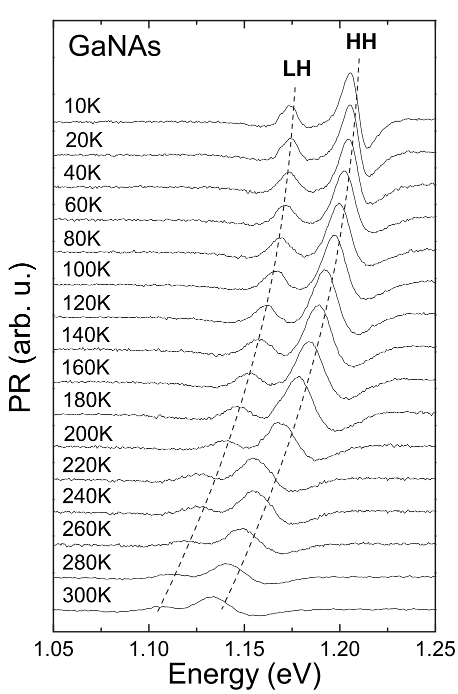

FIG. 4. Temperature dependence of PR spectra for GaNAs layer.

In conclusion, emission bands associated with the recombination of photogenerated carriers through the localized and delocalized states in GaNAs have been resolved in μ-PL spectra. The PL band attributed to the recombination of localized excitons was composed of individual sharp PL lines. The temperature dependence of these lines suggested that the deep acceptor and/or donorlike complexes can be the origin of the exciton localization at low temperatures and the nonradiative recombination at temperatures higher than 50 K.

R.K. acknowledges the financial support from the Foundation for Polish Science and the MNiSW Grant No. N N202 285634.

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