

# physica **p** status **s** solidi **S**

[www.pss-journals.com](http://www.pss-journals.com)

**reprint**



# Photoreflectance study of the temperature dependence of excitonic transitions in dilute GaAsN alloys

Wataru Okubo<sup>1</sup>, Shuhei Yagi<sup>1</sup>, Yasuto Hijikata<sup>1</sup>, Kentaro Onabe<sup>2</sup>, and Hiroyuki Yaguchi<sup>\*1</sup>

<sup>1</sup> Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan

<sup>2</sup> Department of Advanced Materials Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8581, Japan

Received 22 August 2013, revised 12 February 2014, accepted 24 February 2014

Published online 21 March 2014

**Keywords** exciton, GaAsN, photoluminescence, photoreflectance

\* Corresponding author: e-mail [yaguchi@opt.ees.saitama-u.ac.jp](mailto:yaguchi@opt.ees.saitama-u.ac.jp), Phone/Fax: +81 48 858 3841

We have studied the temperature dependence of optical transitions in dilute GaAsN alloys using photoreflectance (PR). A delocalized-state transition is clearly observed in PR spectra while several localized-state emission lines due to isoelectronic centers appear in photoluminescence spectra. The energy of optical transitions observed in PR spectra is in agreement with the excitonic transition energy in photoluminescence excitation spectra, clearly showing

that the optical transitions in PR spectra are excitonic transitions. We analyzed the temperature dependence of the excitonic transition energies using the Bose–Einstein statistical expression, and found that even dilute alloys follow the same trend as GaAsN alloys with higher nitrogen concentrations. We discuss the coexistence of localized and delocalized states in dilute GaAsN alloys in terms of the random distribution of N atoms.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** As contrasted with conventional III–V ternary alloys, the incorporation of nitrogen into GaAs significantly reduces the band gap energy [1–4]. Thus, (In) GaAsN is expected to be a semiconductor material for optoelectronic device applications, such as long-wavelength semiconductor lasers with superior characteristics [5] and high efficiency solar cells [6]. In addition to the band gap reduction, sharp emission lines are obtained from isoelectronic traps due to nitrogen–nitrogen (NN) pairs [7] in dilute GaAsN alloys, which are promising candidates for generating single photons or entangled photon pairs [8–14].

We previously found from the temperature dependence of photoluminescence (PL) spectra of GaAsN alloys that the PL peak energy shift due to the temperature change decreases with increasing nitrogen concentration, which is attributed in part to the influence of the localized-state emission at lower temperatures [15]. Furthermore, we revealed that the small PL peak energy shift at higher temperatures is due to a decrease in the temperature dependence of the band gap energy. Contrary to the alloy regime where a broad PL peak is observed, a number of sharp emission lines related to NN pairs and photon replicas [16] appear prominently in dilute GaAsN alloys with lower nitrogen concentrations than the critical composition

for the localized-to-delocalized transition [17, 18]. In the present paper, we have studied the temperature dependence of photoreflectance (PR) spectra of dilute GaAsN alloys to accurately determine the delocalized exciton transition energy by eliminating the influence of localized states including isoelectronic centers.

**2 Experimental** The samples used in this study were GaAsN alloys grown on GaAs (001) by metalorganic vapor phase epitaxy [3]. The sources for Ga, As, and N were trimethylgallium, arsine, and 1,1-dimethylhydrazine, respectively. The nitrogen concentrations were ranged from 0% to 0.11%. The GaAsN layers were 300 nm thick, and coherently strained to the GaAs substrate. PR measurements were carried out at temperatures between 16 and 300 K. The PR experimental setup was a conventional one. A monochromatic probe beam was obtained from the white light of a halogen lamp using a 50-cm monochromator. The reflected light was detected with a photodiode detector. To modulate the surface electric field in the sample, a diode-pumped solid-state laser ( $\lambda = 532$  nm) was used as a pump beam chopped at 280 Hz. A modulated signal was measured with a lock-in amplifier. We also performed photoluminescence excitation (PLE) measurements using a Ti:sapphire

laser to examine the nature of optical transitions detected by PR. The typical excitation power densities used for PL, PR, and PLE measurements were 5, 0.1, and  $1 \text{ W cm}^{-2}$ , respectively.

**3 Results and discussion** Figure 1a–c shows PR, PLE, and PL spectra of GaAsN with a nitrogen concentration of 0.05%, respectively. As can be found from the PL spectrum shown in Fig. 1c, sharp lines labeled as  $\text{NN}_B$ ,  $\text{NN}_C$ ,  $\text{NN}_D$ , and  $\text{NN}_E$  [7] due to NN pairs are observed, which is typical of dilute GaAsN alloys.

Unlike the PL spectrum showing the localized state-related emission lines, only optical transitions due to delocalized states are seen for a PR spectrum in Fig. 1a. In order to analyze PR spectra, the first derivative of a Lorentzian lineshape [19, 20] was used because the observed transitions are excitonic in nature as described below. For GaAsN with higher nitrogen concentrations, the energy splitting of heavy-hole and light-hole excitons was reported [21]. A higher-energy shoulder of the PL peak from GaAsN shown in Fig. 1c may come from heavy-hole excitons split from light-hole excitons due to the biaxial tensile strain in the GaAsN layer. Similarly, a lower-energy shoulder of the PLE peak due to GaAsN shown in Fig. 1b is

probably attributed to light-hole excitons. The identification concerning heavy- and light-hole transitions is also supported by the fact that the intensity of the higher-energy peak is larger than that of the lower-energy shoulder because the oscillator strength of the heavy-hole component is larger than that of the light-hole component for the  $(x,y)$ -polarized light [22] when the  $z$ -axis is perpendicular to the sample surface.

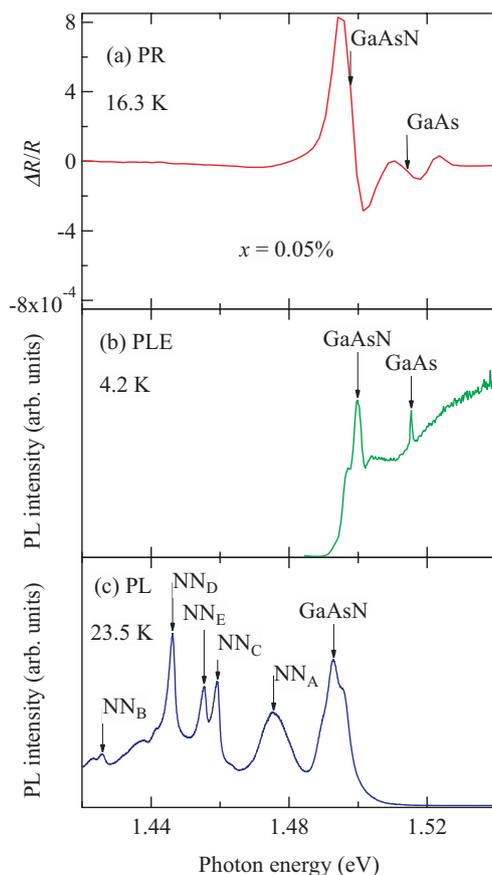
Since the nitrogen concentration of GaAsN layers used in this study was much lower than that in Ref. [21], the splitting was so small that PR measurements could not observe it unlike PLE measurements. Thus, we assumed one optical transition for GaAsN because obtained results are not much different. The lower- and higher-energy optical transitions indicated by two arrows are due to GaAsN and GaAs, respectively.

Two sharp excitonic transition peaks due to GaAsN and GaAs are also seen in the PLE spectrum shown in Fig. 1b, indicating that delocalized states are evidently formed even if the nitrogen concentration is as low as 0.05% and even if several emission lines due to isoelectronic centers are simultaneously observed in the PL spectrum. The energy of optical transitions obtained from the PR spectrum is in good agreement with the energy of excitonic transition peaks seen in the PLE spectrum. It is much the same for other GaAsN alloys. These results clearly show that PR measurements can detect delocalized exciton transitions in dilute GaAsN alloys.

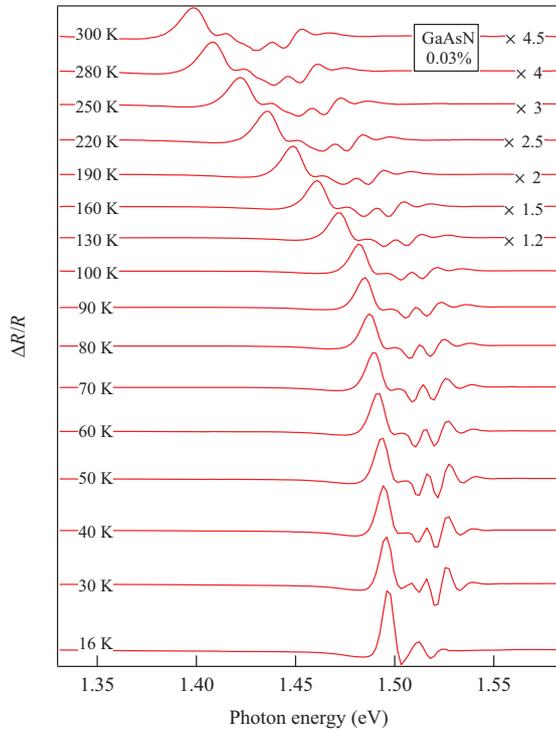
Although sharp emission lines due to NN pairs and localized-state emission at 1.475 eV which originates from  $\text{NN}_A$  are predominant in PL spectra of dilute GaAsN alloys at 4.2 K, we have successfully observed a PL peak (labeled as GaAsN) due to the same origin observed in PR and PLE spectra by increasing the temperature and excitation power density, as shown in Fig. 1c. This PL peak is located at 1.493 eV, which is lower than the transition energy observed in PR and PLE spectra. The Stokes shift is believed to be attributed to excitons weakly localized by alloy fluctuations or bound to donor or acceptor impurities.

As mentioned above, PR is one of the most appropriate methods to investigate the temperature dependence of the delocalized exciton transition energy because it can avoid the effect of exciton localization, and can be used even at room temperature. The temperature dependence of PR spectra of  $\text{GaAs}_{1-x}\text{N}_x$  ( $x=0.03\%$ ) is shown in Fig. 2. Indeed, the excitonic transition due to GaAsN smoothly shifts to lower energies with increasing temperature as can be found from the spectra, indicating that the transition observed in the PR spectrum remains excitonic up to room temperature. Incidentally, the PR concerning GaAs becomes complicated with increasing temperature because of the Franz–Keldysh effect.

Figure 3 shows the delocalized exciton transition energies of GaAsN alloys obtained by fitting the first derivative of a Lorentzian function to PR spectra. We have analyzed the temperature dependence of the excitonic transition energies using the following Bose–Einstein



**Figure 1** (a) PR, (b) PLE, and (c) PL spectra of  $\text{GaAs}_{1-x}\text{N}_x$  ( $x=0.05\%$ ).

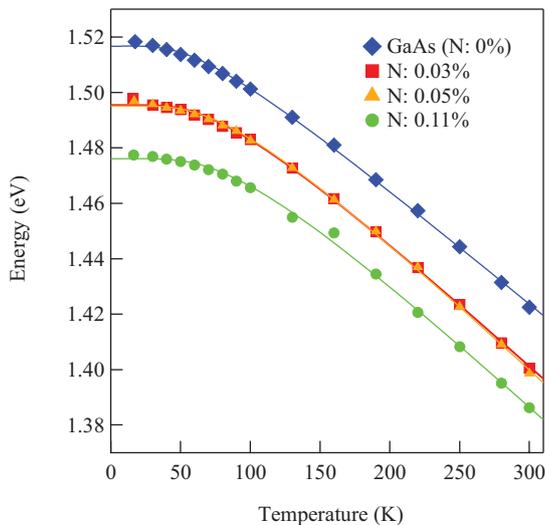


**Figure 2** Temperature dependence of PR spectra of GaAs<sub>1-x</sub>N<sub>x</sub> ( $x = 0.03\%$ ).

statistical expression [23],

$$E_{\text{ex}}(T) = E_{\text{ex}}(0) - a_B \left[ \frac{2}{\exp(\Theta_B/T) - 1} \right], \quad (1)$$

where  $E_{\text{ex}}(0)$  corresponds to the excitonic transition energy at 0 K,  $a_B$  represents the electron–phonon interaction



**Figure 3** Excitonic transition energies of GaAsN alloys. The solid lines were obtained by fitting the Bose–Einstein expression to the experimental data.

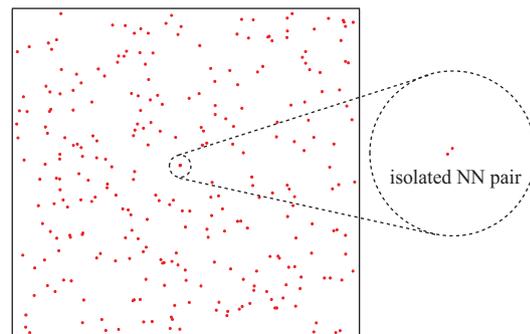
strength, and  $\Theta_B$  is the average phonon energy. The solid lines shown in Fig. 3 were obtained by fitting the Bose–Einstein expression to the experimental data. Although the solid line for 0.03% is slightly higher than that for 0.05%, the two lines are considerably close to each other, which is partly due to the experimental error in determining the nitrogen concentration.

Table 1 lists the nitrogen concentration dependence of  $E_{\text{ex}}(0)$ ,  $a_B$ , and  $\Theta_B$  of dilute GaAsN alloys obtained from the analysis using Eq. (1). The delocalized exciton transition energy at 0 K naturally decreases with increasing nitrogen concentration, and both  $a_B$  and  $\Theta_B$  increase with  $x$  and continuously lead to the alloy regime studied previously [15]. It is, therefore, found that even dilute alloys follow the same trend as GaAsN alloys with higher nitrogen concentrations of 1–3% [15], suggesting that electrons distributed around N atoms interact preferentially with the localized Ga–N vibration mode with higher phonon energy.

For dilute GaAsN alloys, as mentioned above, a delocalized-state optical transition is unequivocally observed in PR and PLE spectra while localized-state emission lines appear in PL spectra. In other words, localized and delocalized states exist together in dilute GaAsN alloys. We therefore would like to discuss the coexistence of localized and delocalized states. Figure 4 shows schematically the distribution of N atoms in dilute GaAsN alloy. The random distribution of N atoms stochastically generates spatially isolated NN pairs which lead to localized states in some regions, as illustrated by a dashed circle. This can explain the fact that the emission energy of NN pairs is almost

**Table 1** Excitonic transition energy at 0 K, electron–phonon interaction strength, and average phonon energy obtained from the analysis using the Bose–Einstein expression.

$x$ (%)	$E_{\text{ex}}(0)$ (eV)	$a_B$ (eV)	$\Theta_B$ (K)
0.03	$1.4954 \pm 0.0004$	$0.052 \pm 0.003$	$223 \pm 9$
0.05	$1.4951 \pm 0.0004$	$0.057 \pm 0.003$	$236 \pm 9$
0.11	$1.4761 \pm 0.0006$	$0.061 \pm 0.005$	$259 \pm 15$



**Figure 4** Schematic view of the random distribution of N atoms in dilute GaAsN alloy.

unchanged even if the average N concentration of GaAsN alloys is changed. On the other hand, delocalized states are formed in other regions where N atoms are relatively uniformly distributed. Consequently, it is essential to consider the impact of the random distribution of N atoms on the electronic structure of GaAsN alloys.

**4 Conclusions** We investigated the temperature dependence of PR spectra of dilute GaAsN alloys. We revealed that a delocalized-state transition is clearly observed in PR spectra while a number of localized-state emission lines appear in PL spectra, and accurately determined the delocalized exciton transition energy. The temperature dependence of the excitonic transition energies was analyzed using the Bose–Einstein statistical expression, and it is found that even dilute alloys follow the same trend as GaAsN alloys with higher nitrogen concentrations of 1–3%. We discussed the coexistence of localized and delocalized states in dilute GaAsN alloys based on the random distribution of N atoms.

**Acknowledgements** This study was partially supported by Grant-in-Aid for Scientific Research (No. 24360004) from the Japan Society for the Promotion of Science. PLE measurements were performed using facilities of the Institute for Solid State Physics, the University of Tokyo.

## References

- [1] M. Weyers, M. Sato, and H. Ando, *Jpn. J. Appl. Phys.* **31**, L853 (1992).
- [2] W. G. Bi and C. W. Tu, *Appl. Phys. Lett.* **70**, 1608 (1997).
- [3] K. Onabe, D. Aoki, J. Wu, H. Yaguchi, and Y. Shiraki, *Phys. Status Solidi A* **176**, 231 (1999).
- [4] H. Yaguchi, S. Matsumoto, Y. Hijikata, S. Yoshida, T. Maeda, M. Ogura, D. Aoki, and K. Onabe, *Phys. Status Solidi B* **228**, 269 (2001).
- [5] M. Kondow, T. Kitatani, K. Nakahara, and T. Tanaka, *Jpn. J. Appl. Phys.* **38**, L1355 (1999).
- [6] S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, *Appl. Phys. Lett.* **74**, 729 (1999).
- [7] T. Makimoto, H. Saito, and N. Kobayashi, *Jpn. J. Appl. Phys.* **36**, 1694 (1997).
- [8] Y. Endo, K. Tanioka, Y. Hijikata, H. Yaguchi, S. Yoshida, M. Yoshita, H. Akiyama, W. Ono, F. Nakajima, R. Katayama, and K. Onabe, *J. Cryst. Growth* **298**, 73 (2007).
- [9] Y. Endo, Y. Hijikata, H. Yaguchi, S. Yoshida, M. Yoshita, H. Akiyama, F. Nakajima, R. Katayama, and K. Onabe, *Physica E* **40**, 2110 (2008).
- [10] T. Fukushima, Y. Hijikata, H. Yaguchi, S. Yoshida, M. Okano, M. Yoshita, H. Akiyama, S. Kuboya, R. Katayama, and K. Onabe, *Physica E* **42**, 2529 (2010).
- [11] H. Yaguchi, *Proc. SPIE* **7945**, 79452F (2011).
- [12] K. Takamiya, Y. Endo, T. Fukushima, S. Yagi, Y. Hijikata, T. Mochizuki, M. Yoshita, H. Akiyama, S. Kuboya, K. Onabe, R. Katayama, and H. Yaguchi, *Mater. Sci. Forum* **706–709**, 2916, (2012).
- [13] M. Ikezawa, Y. Sakuma, L. Zhang, Y. Sone, T. Mori, T. Hamano, M. Watanabe, K. Sakoda, and Y. Masumoto, *Appl. Phys. Lett.* **100**, 042106 (2012).
- [14] K. Takamiya, T. Fukushima, S. Yagi, Y. Hijikata, T. Mochizuki, M. Yoshita, H. Akiyama, S. Kuboya, K. Onabe, R. Katayama, and H. Yaguchi, *Appl. Phys. Express* **5**, 11201 (2012).
- [15] H. Yaguchi, S. Kikuchi, Y. Hijikata, S. Yoshida, D. Aoki, and K. Onabe, *Phys. Status Solidi B* **228**, 273 (2001).
- [16] H. Yaguchi, T. Aoki, T. Morioke, Y. Hijikata, S. Yoshida, M. Yoshita, H. Akiyama, D. Aoki, and K. Onabe, *Phys. Status Solidi C* **4**, 2760 (2007).
- [17] P. R. C. Kent and A. Zunger, *Phys. Rev. Lett.* **86**, 2613 (2001).
- [18] A. V. Mialitisin and A. Mascarenhas, *Appl. Phys. Express* **6**, 052401 (2013).
- [19] D. E. Aspnes, *Surf. Sci.* **37**, 418 (1973).
- [20] B. V. Shanabrook, O. J. Glembocki, and W. T. Beard, *Phys. Rev. B* **35**, 2549 (1987).
- [21] J. Hashimoto and M. Nakayama, *Phys. Status Solidi C* **6**, 358 (2009).
- [22] Y. C. Chang and J. N. Schulman, *Phys. Rev. B* **31**, (2069). (1985).
- [23] L. Vina, S. Logothetidis, and M. Cardona, *Phys. Rev. B* **30**, (1979). (1984).