# Recombination dynamics of localized excitons in $In_{0.20}Ga_{0.80}N$-$In_{0.05}Ga_{0.95}N$ multiple quantum wells

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(Received 17 July 1996; revised manuscript received 27 September 1996)

Dynamical behavior of radiative recombination has been assessed in the $In_{0.20}Ga_{0.80}N$ (2.5 nm)/$In_{0.05}Ga_{0.95}N$ (6.0 nm) multiple-quantum-well structure by means of transmittance, electroreflectance (ER), photoluminescence excitation (PLE), and time-resolved photoluminescence (TRPL) spectroscopy. The PL at 20 K was mainly composed of two emission bands whose peaks are located at 2.920 eV and 3.155 eV. Although the peak at 3.155 eV was weak under low photoexcitation, it grew superlinearly with increasing excitation intensity. The ER and PLE revealed that the transition at 3.155 eV is due to the excitons at quantized levels between $n=1$ conduction and $n=1$ $A(\Gamma_{9v})$ valence bands, while the main PL peak at 2.920 eV is attributed to the excitons localized at the trap centers within the well. The TRPL features were well understood as the effect of localization where photogenerated excitons are transferred from the $n=1$ band to the localized centers, and then are localized further to the tail state. [S0163-1829(97)51004-6]

## I. INTRODUCTION

GaN-based semiconductors are attracting much interest because of both the realization of incandescent blue, green, and yellow light-emitting diodes[1] (LED's) and the first operation of purplish-blue laser diodes (LD's) at room temperature (RT) under the pulsed mode.[2,3] Although the achievement of the high quantum efficiency of these devices is owing to the use of $In_xGa_{1-x}N$ ternary alloys as the active layer, little has been known about the optical properties of $In_xGa_{1-x}N$ quantum wells (QW's).

An important feature of these materials is the role of excitons on the emission mechanism. Since the binding energy of excitons ($E_{ex}$) in hexagonal GaN ($h$-GaN) is 28 meV, which is larger than the thermal energy of RT, excitonic emissions have been observed up to RT in high-quality $h$-GaN epilayers.[4] Recently, it has been reported that biexciton (excitonic molecule) binding energy ($E_b$) in $h$-GaN is about 6 meV.[5,6] It is expected that values of both $E_{ex}$ and $E_b$ are enhanced in a quasi-two-dimensional QW system.

Preliminary PL measurements at low temperature of the $In_xGa_{1-x}N$ LD structure has shown that the linewidth of the emission is as large as about 80 meV, indicating that the energy levels formed in the QW's are broadened inhomogeneously by a disorder such as a fluctuation of well width and (or) alloy composition. This is interesting because Sugawara has predicted theoretically that excitons or biexcitons localized at deep potential minima (more than about 100 meV) contribute to the optical gain even at RT.[7] In fact, very recently, Chichibu *et al.* have proposed such a model for the lasing mechanism in the $In_xGa_{1-x}N$ multiple QW (MQW) structure,[8] and Sun *et al.* has reported the recombination lifetime of an $In_xGa_{1-x}N$ single quantum well (SQW) by means of time-resolved photoluminescence (TRPL) spectroscopy.[9] However, the detailed nature for the exciton localization has not been clearly understood. Therefore, the assessment is motivated on the dynamical behavior of localized excitons in $In_xGa_{1-x}N$ QW's.

In this paper, the mechanism of radiative recombination has been studied in the $In_{0.20}Ga_{0.80}N/In_{0.05}Ga_{0.95}N$ MQW structure by employing transmittance (TR), electroreflectance (ER), photoluminescence excitation (PLE), and TRPL spectroscopy.

## II. EXPERIMENTAL PROCEDURE

The sample used in this study was grown on a (0001)-oriented sapphire ($Al_2O_3$) substrate by a two-flow metal-organic chemical vapor deposition (TF-MOCVD) technique.[10] The layer consists of the separate confinement heterostructure where the undoped $In_{0.20}Ga_{0.80}N$ (2.5 nm)/$In_{0.05}Ga_{0.95}N$ (6.0 nm) MQW with six periods is sandwiched between GaN waveguiding layers (0.1 $\mu$m in each) and $Al_{0.15}Ga_{0.85}N$ cladding layers (0.4 $\mu$m in each). The top of the $Al_{0.15}Ga_{0.85}N$ clad and the GaN waveguide are Mg-doped $p$-type layers, while the bottom of the clad and the waveguide are Si-doped $n$-type layers. It is noted that the LD has been operated at 420 nm from this sample under pulsed mode at RT.

In order to make assignment of emissions under low excitation, the cw PL was measured by the excitation of a He-Cd laser (325 nm) and it was compared with TR, ER, and PLE spectra. PL detections were carried out using a cooled-charge-coupled device (CCD) and a 50 cm monochromator with a 150 lines/mm grating. The light source used for TR, ER, and PLE was obtained by passing the Xe-lamp through a 25 cm monochromator. The TR and ER signals were detected by a Si photodiode and amplified by a lockin amplifier.

The TRPL measurement was performed with a fast scan streak camera in conjunction with a 25 cm monochromator using a 100 lines/mm grating. Pulsed excitation was provided by the frequency doubled beam of a mode-locked $Al_2O_3$:Ti laser which was pumped by an $Ar^+$ laser. In order to avoid the multiexcitation, repetition rate of the source (80.0 MHz) was selected to 4.0 MHz by the acoustic optic

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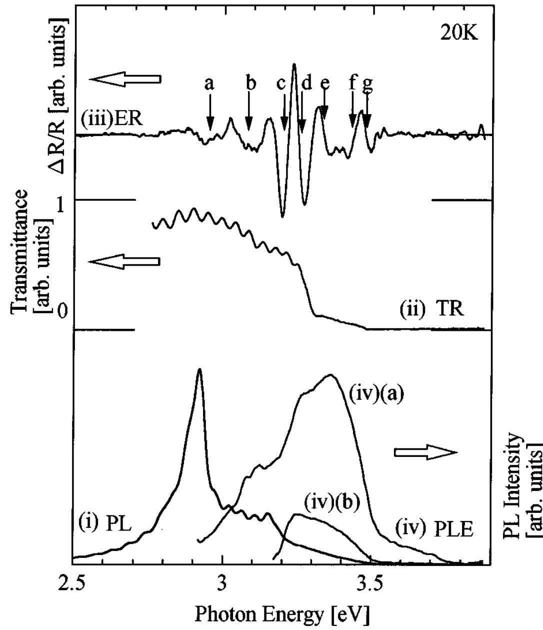


FIG. 1. (i) Photoluminescence taken under a He-Cd laser excitation (4 W/cm$^2$). (ii) Transmittance spectrum. Oscillations below about 3.25 eV are due to the interference effect. (iii) Electroreflectance spectrum. Energy positions labeled $a-g$ are theoretical ones fitted by Eq. (1). (iv) Photoluminescence excitation spectra monitored at (a) 2.920 eV and (b) 3.155 eV.

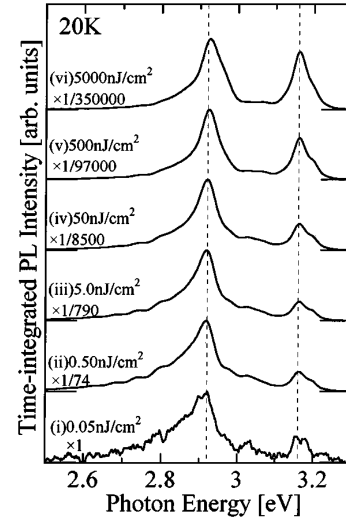


FIG. 2. Time-integrated PL spectra taken under pulsed excitation. Excitation energy densities ranged from (i) 0.05 nJ/cm$^2$ to (vi) 5000 nJ/cm$^2$.

(AO) modulator. The wavelength and the pulse width were 357 nm and 1.5 ps, respectively. The spectral resolution of all measurements was about 1 nm, which is well below the linewidth of the PL. Whole measurement has been done at 20 K.

## III. RESULTS AND DISCUSSION

Figure 1 (i) shows cw PL spectrum obtained under a He-Cd laser excitation. The PL was composed of a few (or several) emission bands. Among them, two bands are clearly observed as peaks where the main peak was located at 2.920 eV, while another peak at 3.155 eV was weak in intensity. If the alloy composition of $In_xGa_{1-x}N$ well layers is randomly distributed, alloy broadening of excitons is calculated to be about 10 meV.[11] The PL linewidth of the main peak was about 80 meV which is much larger than the value estimated above. Consequently, it follows that the energy levels within the well are distributed by the disorder such as the fluctuation of well width and (or) the separation of In composition.

The TR spectrum is depicted in Fig. 1(ii). The dips were observed at about 3.32 eV and about 3.49 eV which can be ascribed to the absorption edge of $In_{0.05}Ga_{0.95}N$ barrier and GaN waveguiding layers, respectively. Although the energy levels within the well are distributed in the range between 3.0 eV to 3.3 eV, no clear structure could be observed due to the periodic oscillations that arise from the interference multireflection.

In order to avoid such effects, the ER spectrum [Fig. 1(iii)] was measured by applying the reverse bias to the *pn* junction. The ER signal is expressed as $\Delta R/R$, where $R$ is the reflection intensity and $\Delta R$ represents modulated reflection intensity. If the ER signal is composed of a number of excitonic energy levels labeled $E_{\mathrm{ex},j}$, it can be expressed by the following equation

$$\Delta R/R(E) = \mathrm{Re}[\Sigma_j C_j (\exp i\theta_j)(E - E_{\mathrm{ex},j} + i\Gamma_j)^{-2}], \quad (1)$$

where $C_j$ is the constant that is proportional to the density of state, $\theta_j$ is the phase term and $\Gamma_j$ shows the broadening factor. Because of a lot of parameters, it is difficult to obtain a unique fitting of the experimental data using Eq. (1). Nevertheless, the optimum fitting was made assuming the seven energy levels labeled $a-g$. According to the x-ray-diffraction measurement, it was found that GaN layers are under compressive stress by about 0.3% due to the difference of thermal expansion coefficient between epilayers and the substrate. Lattice mismatch between the GaN and $In_{0.20}Ga_{0.80}N$ well is 2.2%. Since the whole layer was almost coherently grown, the well layers are compressively strained by about 2.5%. Valence bands of $h$-GaN based semiconductors consist of three bands labeled $A(\Gamma_{9v})$, $B(\Gamma_{7uv})$, and $C(\Gamma_{7lv})$.[12] The transition $g$ located at 3.488 eV is attributed to the $A$ exciton in the GaN layers. This energy position is blueshifted by about 10 meV compared to that in bulk GaN due to strain.[13] The $B$ exciton, which should be observed at about 3.496 eV, could not be observed. This may be due to the limitation of spectral resolution. The transition $f$, whose oscillator strength is small, is located at 3.430 eV. It is difficult to make an assignment of this transition at the moment. The transition $e$ at 3.326 eV is ascribed to the $A$ exciton in the $In_{0.05}Ga_{0.95}N$ barrier layers.

The transitions $a-d$ are energy levels within the quantum wells. The transitions of $c$ and $d$ are strong in intensity, while those of $a$ and $b$ are much weaker and broader. If the deformation potential of $In_xGa_{1-x}N$ is assumed to be the same as that of GaN,[13] blueshift energy of band gaps in $In_{0.05}Ga_{0.95}N$ barriers and $In_{0.20}Ga_{0.80}N$ wells are calculated to be approximately 30 meV and 80 meV, respectively. Thus, the band-gap energies of $In_{0.05}Ga_{0.95}N$ barriers and $In_{0.20}Ga_{0.80}N$ wells are estimated to be about 3.40 eV and 3.09 eV, respectively. The energy difference of band gaps between barriers and wells are about 310 meV. Even if this energy is equal to the conduction-band offset, only the $n=1$ quantized level is formed in the conduction band in the case of the thin well layer thickness of 2.5 nm. For this estimation, the electron effective mass in the $In_{0.20}Ga_{0.80}N$

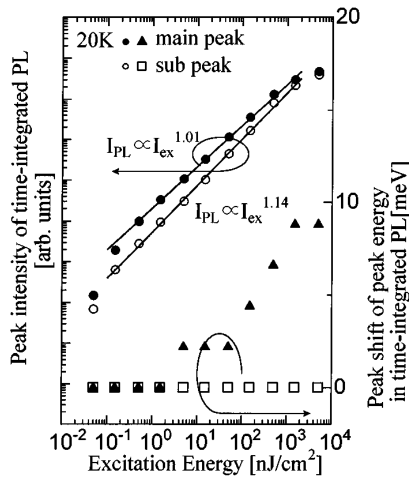


FIG. 3. Peak intensity and blue shift of peak energy in time-integrated PL as a function of excitation energy density. PL peaks are monitored at two major emission bands that are located in the vicinity of 2.920 eV and 3.155 eV.

wells is approximated to be $0.18m_0$, which is obtained by linear extrapolation of effective masses between GaN $(0.20m_0)$ and InN $(0.11m_0)$. Therefore, the allowed transitions in the well are between $n=1$ conduction to $n=1$ $A$, $B$, and $C$ valence bands. Among them, the excitonic transitions between $n=1$ conduction to $n=1$ $A$ valence band $(E_{\mathrm{ex}1A})$, and $n=1$ conduction to $n=1$ $B$ valence band $(E_{\mathrm{ex}1B})$ would be major transitions considering their oscillator strength. Consequently, the transitions of $c$ at 3.203 eV and $d$ at 3.255 eV are most probably attributed to the $E_{\mathrm{ex}1A}$ and $E_{\mathrm{ex}1B}$, respectively. The propriety of these assignments will be proved if unknown parameters such as deformation potentials, band offsets, effective masses of holes are clarified. It is concluded that the PL peak at 3.155 eV arises from the lowest quantized energy level $(E_{\mathrm{ex}1A})$ whose absorption band corresponds to the transition $c$. The transitions $a$ and $b$ are attributed to the localized trap centers whose density of states are lower than the quantized energy levels $c$ and $d$ because they are located at lower-energy side compared to the estimated band gap of $In_{0.20}Ga_{0.80}N$ wells (3.09 eV). The transition $b$ at 3.071 eV may be related to the weak emission component, which is located between two PL peaks. The transition $a$ at 2.953 eV is located at higher photon energy by 33 meV compared with the main PL peak. This energy difference corresponds to the Stokes shift of the PL.

Figure 1(iv) shows PLE spectra monitored at 2.920 eV (a) and 3.155 eV (b). PLE spectrum shown in Fig. 1(iv) $a$ is composed of a number of broad bands whose shoulder almost corresponds to the transition energies $a$–$g$ described in Fig. 1(iii). The main PL peak is located at the tail of the absorption edge.

The effects of high excitation on the PL has been investigated by the pulsed photo excitation. Figure 2 shows the time-integrated PL taken under various excitation energy densities $(I_{\mathrm{ex}})$ which varied from 0.05 nJ/cm$^2$ to 5000 nJ/cm$^2$. Spectral features are almost unchanged if the $I_{\mathrm{ex}}$ value is below about 5 nJ/cm$^2$. However, the ratio of peak intensities between the main peak at 2.920 eV and another peak at 3.155 eV decreases with $I_{\mathrm{ex}}$ above about a few tens of nJ/cm$^2$. Accordingly, blueshifts of peak energies are

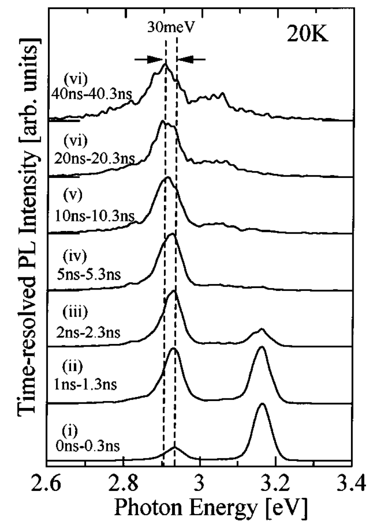


FIG. 4. Time-resolved PL spectra monitored at various time-interval after pulsed excitation. Excitation energy density is 210 nJ/cm$^2$. Each spectrum is normalized in intensity.

observed for the main emission band due to the band-filling effect, while another peak at 3.155 eV remained constant as shown in Fig. 3. These phenomena can be understood as the band filling of the localized tail states occurs more easily than that of the quantized energy levels. It is noted that the stimulated emissions originating from these localized excitons have been observed in the photopumped experiment.[14]

Dynamics of radiative recombinations are studied by the TRPL spectroscopy. Figure 4 shows TRPL spectra monitored at various time after pulsed excitation. The whole spectra [(i) to (vii)] are integrated during the same time interval (300 ps), and are normalized in intensity. Just after the excitation [(i) 0 ns–0.3 ns], the spectrum is dominated by the emission band at 3.16 eV. The rise time of this emission band was about 100 ps, while the main PL band reaches maximum at about 300 ps. Moreover, emission bands at 3.16 eV quench more rapidly than the main emission bands. These features indicate that photogenerated excitons are transferred from the $n=1$ quantized level $(E_{\mathrm{ex}1A})$ to the localized centers. The main PL peak shifts towards lower photon energy with increasing time. The energy difference of the peak between (i) (0 ns–0.3 ns) and (vii) (40 ns–40.3 ns) is about 30 meV. This behavior suggests that density of states of localized centers are distributed to some extent, and that localized excitons are transferred further to the lower-lying energy levels. If time is increased above about 10 ns, the emission band located at about 3.05 eV becomes apparent. This band corresponds to the transition $b$ assigned in the ER spectrum. The PL transient monitored at around 3.05 eV was well expressed by the double exponential curve whose decay times were 1 ns and 70 ns. Fast decay component is contributed from the overlapping of neighboring emission bands, while long decay time represents the intrinsic lifetime of this emission band. The reason why the oscillator strength of this emission is suppressed is now under consideration.

Figure 5 shows PL decay times as a function of monitored emission energies whose range is selected to two major emission bands. Time-integrated PL is also inserted in the figure. Decay times monitored in the vicinity of 3.16 eV are almost constant at about 600 ps. Decay times in the main PL

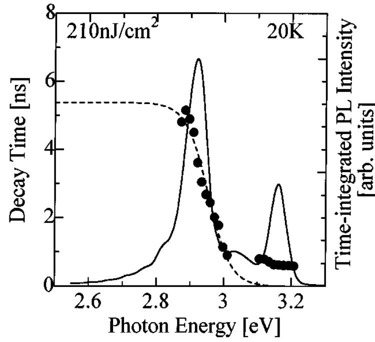


FIG. 5. Time-integrated PL taken under 210 nJ/cm$^2$ as well as PL decay times monitored at various emission energies. The dotted curve is the theoretical one fitted by Eq. (2).

band decreases with increasing monitored photon energy. This is because the decay of localized exciton is not only due to radiative recombination but also due to the transfer process to the tail state. If the density of tail state is approximated as $\exp(-E/E_0)$, and if the radiative recombination lifetime $[\tau_r]$ does not change with emission energy, observed lifetime $[\tau(E)]$ can be expressed by the following equation,[15,16]

$$\tau(E)=\frac{\tau_r}{1+\exp(E-E_{me})/E_0}, \quad (2)$$

where $E_0$ represents the degree of the depth in the tail state and $E_{me}$ is the characteristic energy which is analogous to the mobility edge. The best fit could be obtained using $\tau_r=5.34$ ns, $E_0=33.3$ meV and $E_{me}=2.953$ eV. The energy position of $E_{me}$ is same as the transition $a$ in the ER spectrum.

ER and TRPL spectroscopy have revealed that the main PL peak is located below the lowest $n=1$ quantized level by about 250 meV. This energy is relatively close to the ionization energy of acceptor such as Zn or Mg substituted to Zn site. If the PL is related to such impurities or defect centers,[17] there is a possibility that the emission mechanism is not due to localized excitons but due to electron-acceptor or donor-acceptor pair recombinations. However, it is generally known that the bound-to-bound or bound-to-free carrier transitions do not play an important role for the emission in low-dimensional confined system. Moreover, the large increase in recombination time as the energy decreases across the PL band is in favor of the localized exciton model, whose trap centers originate from the disorder such as the fluctuation of the well width and/or the fluctuation of In composition within the wells.

In order to assess the origin of the localization, cross sectional transmission electron microscopy (TEM) has been performed. The interface between $In_{0.20}Ga_{0.80}N$ wells and $In_{0.05}Ga_{0.95}N$ barriers were flat and the fluctuation of well width was as small as $\pm 0.25$ nm. However, the isotropic dotlike structures, whose diameter is about a few nm, were observed in the wells. It has been found by energy-dispersive x-ray microanalysis (EDX) that In compositions monitored at quantum dotlike regions are always larger than those at neighboring well regions.[14] Therefore, the origin of localization is likely attributed to the region of In-rich composition which act as quantum dot centers. Such mechanism may result from the intrinsic nature of $In_xGa_{1-x}N$ alloys[18] because it is reported that randomly mixing of alloy composition is hardly achieved in this system.[19,20]

## IV. CONCLUSIONS

It has been found by means of PL, TR, ER, PLE, and TRPL spectroscopy that PL main peak observed in the $In_{0.20}Ga_{0.80}N/In_{0.05}Ga_{0.95}N$ MQW structure is ascribed to excitons localized at trap centers which are located below the lowest $n=1$ quantized level by about 250 meV. The origin of the localization center is possibly ascribed to a self-formed In-rich region that may act as a quantum dot. It is interesting to note that the depth of localization was so large that localized excitons have been observed even at RT.

## ACKNOWLEDGMENTS

The authors are grateful to M. Funato for his contribution to the TEM observation. A part of this measurement was done using the facility at the Venture Business Laboratory in Kyoto University.

[1] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Jpn. J. Appl. Phys. **34**, L797 (1995).
[2] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys. **35**, L74 (1996).
[3] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys. **35**, L217 (1996).
[4] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, J. Appl. Phys. **79**, 2784 (1996).
[5] K. Okada, Y. Yamada, T. Taguchi, F. Sakaki, S. Kobayashi, T. Tani, S. Nakamura, and G. Shinomiya, Jpn. J. Appl. Phys. **35**, L787 (1996).
[6] Y. Kawakami, Z. G. Peng, Y. Narukawa, Sz. Fujita, Sg. Fujita, and S. Nakamura, Appl. Phys. Lett. **69**, 1414 (1996).
[7] M. Sugawara, Jpn. J. Appl. Phys. **35**, 124 (1996).
[8] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. (to be published).
[9] C.-K. Sun, S. Keller, G. Wang, M. S. Minsky, J. E. Bowers, and S. P. DenBaars, Appl. Phys. Lett. **69**, 1936 (1996).
[10] S. Nakamura, Jpn. J. Appl. Phys. **30**, L1705 (1991).
[11] The value of alloy broadening can be estimated by taking into account the standard deviation of alloy composition within the volume of excitons. See, for example, R. Zimmerman, J. Cryst. Growth **101**, 346 (1990).
[12] R. Dingle, D. D. Sell, S. E. Stokowski, and M. Ilegems, Phys. Rev. B **4**, 1211 (1971).
[13] B. Gil, O. Briot, and R. Aulombard, Phys. Rev. B **52**, R17 028 (1995).
[14] Y. Narukawa, Y. Kawakami, M. Funato, Sz. Fujita, Sg. Fujita, and S. Nakamura, Appl. Phys. Lett. (to be published).
[15] C. Gourdon and P. Lavallard, Phys. Status Solidi B **153**, 641 (1989).
[16] S. Yamaguchi, Y. Kawakami, Sz. Fujita, Sg. Fujita, Y. Yamada, T. Mishina, and Y. Masumoto, Phys. Rev. B **54**, 2629 (1996).
[17] C. Wetzel, S. Fisher, J. Krüger, E. E. Haller, R. J. Molnar, T. D. Moustakas, E. N. Mokhov, and P. G. Baranov, Appl. Phys. Lett. **68**, 2556 (1996).
[18] Large localization of excitons is also reported in the $In_xGa_{1-x}N$ single epilayer. T. Taguchi, T. Maeda, Y. Yamada, S. Nakamura, and G. Shinomiya, in *Proceedings of the International Symposium on Blue Laser and Light Emitting Diodes, Chiba University, Japan, 1996* (unpublished).
[19] A. Koukitsu, N. Takahashi, T. Taki, and H. Seki, Jpn. J. Appl. Phys. **35**, L673 (1996).
[20] I-hisu Ho and G. B. Stringfellow, Appl. Phys. Lett. **69**, 2701 (1996).