Statistics of excitonic energy states based on phononic-excitonic-radiative model

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Received December 24, 2018; accepted February 5, 2019; published online May 23, 2019

Excitation and deexcitation dynamics of excitons in GaN are analyzed by theoretical simulation using a set of rate equations based on a phononic-excitonic-radiative (PXr) model, which is applied to the analysis of experimentally-observed photoluminescence (PL) properties using a short pulse excitation. In phononic processes, deformation and piezoelectric interactions of the LA phonon and Fröhlich interaction of the LO phonon are taken into account. This model is successfully applied to the analysis of experimentally-observed emission line intensity ratios for excitons. This analysis reveals that the strong population exchange between the state of the principal quantum number \( n = 2 \) and the continuum takes place due to the increase in temperature. Further, the long experimental radiative lifetime component in the temporal PL decay curve up to 100 ns at room temperature (RT) is attributed to the shift of the population distribution to higher \( n \) states, which work as population reservoirs of the \( n = 1 \) state. Theoretical calculation using this model suggests that the dominant phonon mode in the excitation transfers from the \( n = 1 \) and 2 states shifts from the LA phonon to the LO phonon due to the increase in temperature from 130 K to 240 K. The PXr simulation model is feasible for the analysis of exciton-carrier dynamics and radiation efficiency analyses. © 2019 The Japan Society of Applied Physics

1. Introduction

It is known that Wannier excitons in semiconductors have higher radiative recombination probability than free electron-hole pairs. The exciton binding energies \( E_B \) for wide bandgap materials are approximately equal to or higher than the thermal energy at room temperature (RT): approximately 27 meV for GaN,\(^1\) 57 meV for AlN,\(^2\) and 60 meV for ZnO.\(^3\) It is desired that this recombination process of excitons is exploited in light emission devices particularly for the ultra-violet region, where the acceptor activation efficiency at RT is limited to be low. Although excitonic photoluminescence (PL) from GaN has been observed at RT,\(^4\) the lasing mechanism in current-injection devices is complicated. It has been reported that the optical gain mechanism of inelastic exciton-exciton scattering in an optical pumping laser is observed to be below 150 K.\(^5\) In a higher temperature region, electron-hole plasma is reported to be the gain mechanism.\(^6\) A similar shift of emission mechanism from the excitonic to the electron-hole plasma below RT has been observed for a laser diode using InGaN quantum wells, which have an \( E_B \) of approximately 60 meV,\(^7\) while laser operation by optical pumping has been observed for ZnO with approximately the same \( E_B \) of the aforementioned quantum wells.\(^7\) On the other hand, lasing based on exciton polariton with a threshold excitation density (current density) of \( 4.5 \times 10^{16} \text{ cm}^{-3} \) (169 A cm\(^{-2}\)) has been observed, where the lasing threshold based on electron-hole plasma has been observed for ZnO with approximately the same \( E_B \) of the aforementioned quantum wells.\(^7\)

Now various mechanisms of exciton-related stimulated emission have been reported for exciton-exciton scattering,\(^8\) exciton-electron scattering,\(^9\) and polarion.\(^10\) Thermally nonequilibrium states of exciton kinetic energy have been reported for time-resolved PL (TRPL) measurements using pulse excitation of electron-hole pairs as well as for current-injection laser devices.\(^10\)–\(^13\)

The dynamics of high density carriers in the order of \( 10^{18} \text{ cm}^{-3} \) or greater have been theoretically discussed, where hot phonon effects and high carrier temperature of more than 300 K were observed within 2 ps after excitation.\(^10\)–\(^13\) On the other hand, for lower excitation density up to \( 10^{15} \text{ cm}^{-3} \) in GaAs, the 1 s state has been theoretically expected to be in a thermally nonequilibrium state even at 200 ps after the excitation, where the phonon-exciton, phonon-carrier, carrier-carrier scattering processes have been taken into account.\(^14\) Exciton kinetic energy or temperature \( T_x \) has been analyzed using LO phonon assisted emissions called LO phonon replicas (LORs).\(^15\) The exciton dynamics of GaN have been experimentally characterized by the analysis of \( T_x \). It has been found that thermally nonequilibrium \( T_x \) such as 50 K or higher just after the excitation lasts for tens of ps to 150 ps despite the lattice temperature of 20 K or lower, but this has been observed only for the 1 s (principal quantum number \( n = 1 \)) state.\(^16\) The population coupling of the \( n = 1 \) state and neutral donor bound state in nanocolumns has been reported.\(^17\) We have reported that the \( T_x \) just after a pulse excitation is higher for higher energy levels such as the 2 s (\( n = 2 \)) and continuum state, and that the \( n = 2 \) state shows peculiar properties.\(^18\) These articles report the long time duration of the thermally nonequilibrium state of excitons, even though the elementary processes of the LO or LA phonon emission by electrons show fast transition rates corresponding to a time of tens–thousands of fs.\(^19\) A discrepancy of lattice and exciton or electron temperatures has been also reported in other articles.\(^19\)–\(^23\)

Wide bandgap materials of III-V and II-VI families have strong electron–phonon interaction as shown in Fig. 1, where the term included in the electron–phonon interaction matrix element is taken as the ordinate. Here, \( E_{\text{LO}}, \varepsilon(\infty), \) and \( \varepsilon(0) \) are the LO phonon energy, the relative electric permittivities at the infinite frequency limit and the static limit, respectively. It is known that various physical properties of semiconductors such as the dependence of bandgap energy on temperature, broadening of the emission line, carrier diffusion length, etc. are determined by the interaction of phonon and electron or exciton.
Carrier and exciton dynamics analysis has been conducted using rate equations, where some rates or rate coefficients are dominated by electron (exciton)–phonon interaction. However, only a few articles report on exciton excitation and deexcitation dynamics by taking account of the interaction with the phonon. Recently, the ABC model has been proposed for the analysis of carrier dynamics, where exciton dynamics have been outside the target in this model. In theoretical analysis, we have proposed a model based on a set of rate equations for several n states and the continuum by taking into account the phononic, electron-collisional, and radiative processes for excitons. This phononic-excitonic-radiative (PXR) model is a carrier dynamics simulation in a field where all of the energy species of electron, exciton, and phonon are taken into account. Thus, thermally nonequilibrium states with excess phonon occupation, carrier kinetic energy, exciton kinetic energy, and quantum state energy are included in the simulation.

On the basis of our previous report on the PXR model and experimental results, we show characteristic properties of population distribution and population flows among several principal quantum number states depending on the $T_x$, the electron temperature $T_e$, and the lattice temperature $T_l$, which reveal the importance of the phonon processes particularly in terms of understanding the determination mechanism of the PL lifetime. Further, we show that the main phonon mode yielding excitation transfer of excitons at RT is the LO phonon mode, which replaces the LA mode due to the increase in temperature. The peculiar emission line intensity ratios for the $n=2$ excitons which have been previously reported are analyzed using the exciton population distribution and flow properties obtained by the PXR model.

### 2. Analysis method

#### 2.1 Experimental

Experimental analysis was conducted using a 6.0 μm-thick GaN film grown on a substrate of selective-area-growth GaN with a thickness of 9.7 μm on a sapphire wafer by a metal-organic vapor phase epitaxy method. The respective values of full width at half maximum (FWHM) values of (0004) and (10–11) X-ray rocking curves were 290 and 383 (arcsec). The electron density measured by infrared reflectance analysis at RT was less than $5 \times 10^{16}$ cm$^{-3}$. The sample was excited by the 267 nm line of the third harmonic wave of a Ti: Al$_2$O$_3$ laser with a pulse width of 150 fs, the 266 nm line of the forth harmonic wave of a YAG laser with a pulse width of 500 ps, or the 337 nm line of a nitrogen laser with a pulse width of 300 ps. An excitation laser power of 1 mW for the 267 nm line was estimated to generate electron-hole pairs of $1.4 \times 10^{15}$ cm$^{-3}$ per pulse. The penetration depth of the laser light was referred to in previous literature. The 266 nm line based on the YAG laser and the 337 nm line were utilized to obtain higher excitation exciton density. Two sets of PL measurement systems were utilized. A system consisting of a monochromator ($F=25$ cm) and a streak camera was utilized for the excitation using the Ti: Al$_2$O$_3$ laser, and a system consisting of a monochromator ($F=50$ cm), photomultiplier, and a digital oscilloscope with a 75 ps rise time was used for the excitation of the 266 nm or 337 nm line. The measurement temperature was 23 K.

#### 2.2 PXR model

Numerical simulation of the exciton dynamics was conducted using the following rate equations, where rate or rate coefficients of the respective elementary processes were calculated using theoretical formulae. The schematic of exciton energy levels and transition processes are exhibited in Fig. 2. The processes taken into account were the Fröhlich interaction of the LO phonons, deformation and piezoelectric interactions of the LA phonon, electron-collisional processes, and radiative recombination processes. Experimentally, the transition lines of A, B, and C exciton states and $n=1$ and 2 states of the A exciton have been observed for GaN. In this paper, these energy states were modeled by a simple energy structure of five states of $n=1$ to 5 for the exciton

![Fig. 2. (Color online) Schematic of energy level diagram and the transition processes in the PXR model.](image-url)
with the $E_R$ of 27 meV, while only free A excitons were taken into account as a simple case, which means no donor bound state or polariton state was taken into account.

The rate or rate coefficients of the electron-collisional processes are referred to in the formulae for hydrodynamic plasma.\textsuperscript{43–45} The dispersion relations of the LO phonon and LA phonon were taken into account. Population densities of each exciton state $N_e(n)$ and the continuum (free electron) $N_C$ were numerically obtained by solving the following set of rate equations under a quasi-steady-state approximation, where the density of holes was assumed to be the same as $N_e$.

$$\frac{d}{dt}N_e(n) = \sum_{n'=n} [A(n', n) + C(n', n)N_e + W_{cx}(n', n)N_e - \{\beta(n) + \alpha(n)N_e + W_{cx}(n)N_e\}^2 - \{A(n, n') + C(n, n')N_e + W_{cx}(n, n') + S(n)N_e + W_{cx}(n)\}N_e(n),$$

$$\frac{d}{dt}N_C(n) = \sum_{n'=[n]} [S(n)N_e + W_{cx}(n)N_e(n) + R_{ve} - \sum_{n} [\alpha(n)N_e + \beta(n) + W_{cx}(n)]N_e^2 (1)$$

$A(n, n')$, $C(n, n')$ and $W_{cx}(n, n')$ are the rates or rate coefficients of transitions from the $n$ state to the $n'$ state by radiative, electron-collisional, and phononic processes, respectively. $P_{\text{re}}(n, n')$ is the radiative recombination rate of the state $n$. $\beta(n)$, $\alpha(n)$, and $W_{cx}(n)$ are the exciton formation rate coefficients of radiative, electron-collisional (three-body), and phononic processes, respectively. $S(n)$ is the exciton dissociation rate coefficient by electron-collisional processes. $W_{cx}(n)$ is the rate of exciton dissociation by phononic processes. The radiative recombination of free electrons and holes was neglected as a simple model. The $T_e$, $T_x$, $T_b$, and the rate of electron excitation from the valence band to conduction band $R_{ve}$ were taken as parameters. Here, the formation rate of the $n$ state of exciton $R_{ve}(n)$ from the vacuum level was assumed to be zero. The kinetic-energy distributions of electrons and excitons were obtained by the Maxwell–Boltzmann distribution function. The phonon occupation factor $n_q$ was obtained by the Bose–Einstein distribution function.

The rate or rate coefficients in these rate equations were calculated by averaging them for the energies of phonon modes and kinetic energies of electrons and excitons under the condition of energy and momentum conservation. The thermally nonequilibrium condition was investigated by varying the respective temperatures. The utilized physical parameters of GaN and the details of the calculation are referred to in our previous article.\textsuperscript{35}

3. Results and discussion

3.1 Effects of LO phonon and LA phonon on excitation transfer rate coefficients

The LO phonon energy at the $\Gamma$ point is approximately 91 meV, which means that the occupation factor of the LO phonon is far lower than that of the LA phonon even at RT. However, the Fröhlich interaction of the LO phonon is stronger than the deformation potential and piezoelectric interactions of the LA phonon. Figure 3 shows the plots of the strength factor $s_j$ of Fröhlich ($j=fr$), the deformation potential ($j=dp$), and piezoelectric ($j=pz$) interactions, which are described as $e^{2\pi n_{LO}/h} \left( \frac{1}{\gamma^n(\infty)} - \frac{1}{\gamma^n(0)} \right)$, $hD^2a^4/4\rho_{LO}c_a$, and $e^{2\pi n_{LA}/h} q^2 \left( \frac{1}{\gamma^n(0)} - \frac{1}{\gamma^n(\infty)} \right)$, respectively. Here, $\omega_{LO}$, $D$, $\rho_{LO}$, $q$, $\gamma^n(\infty)$, and $\gamma^n(0)$ are the LO phonon frequency, deformation potential, mass density, piezoelectric constant, and phonon wave number, respectively. The $s_j$ is included in the following expression of the phononic transition rate of $W_{cx}(n, n')$.

$$W_{cx}(n, n') = \frac{2}{g(n)} \sum_{l,m,p} \int \int \left( n_q + \frac{1}{2} \pm \frac{1}{2} \right) \frac{2\pi s_j}{h} \times |S_{\nu,\nu'}(\beta q') - \sigma S_{\nu,\nu'}(-\alpha q')|^2 \times \delta(E_l' - E_{l'} + E_q)f_{\text{eff}}(M, K, T),$$

$$d^3K \left[ \frac{2\pi}{(2\pi)^3} \right] \int d^3\Phi_{\nu}(\vec{r})$$

where $g(n) = 2n^2$ is the statistical weight, $l$ is the azimuthal quantum number, $m$ is the magnetic quantum number, $n_q$ is the phonon occupation factor, $V_{\nu}$ is the phonon coherence volume, $M$ is $m_e + m_h$ ($m_e$ and $m_h$ are the electron and hole effective mass), $\beta$ is $m_h/M$, $\alpha$ is $m_e/M$, $\sigma_l$ is $-1$ for the deformation potential interaction or $+1$ for the Fröhlich and piezoelectric interactions, $E_{l'}$ is the exciton energy, $E_q$ is the phonon energy, $f_{\text{eff}}(M, K, T)$ is the Maxwell–Boltzmann distribution function, $K$ is the exciton wave vector, $V_{\text{int}}$ is the interaction volume of an exciton and a phonon, $\nu$ indicates a set of $(n, l, m)$, $\vec{r}$ is the real-space coordinate, and $\Phi_{\nu}(\vec{r})$ is the hydrogenic wave function.\textsuperscript{20,35} $s_{fr}$ is greater than $s_{dp}$ and $s_{pz}$ for the LA phonon. The share of the LO phonon or LA phonon absorption in the excitation transfer from the $n = 1$ or $n = 2$ state is plotted in Fig. 4. This result shows that the excitation rate coefficient in the low temperature region is dominated by the LA phonon, which is replaced by the LO phonon in the range of 130–240 (K). The excitation and deexcitation processes are a mixture of the LA and LO phonon processes in the vicinity of these temperatures, and the dominant process...
depends on the energy state of $n = 1$ or 2, while the LO phonon process is the crucial factor for exciton dissociation at RT despite the lower thermal energy at RT (26 meV) than the LO phonon energy of 91 meV (at the $\Gamma$ point), which means the low LO phonon occupation factor at RT.

3.2 Thermally nonequilibrium state by phonon generation in TRPL

Figure 5(a) shows time-integrated PL spectra for two excitation wavelengths of 266 nm and 337 nm. The spectrum by the 337 nm excitation has zero phonon lines (ZPLs) of free A excitons with $n = 1$ (FA(1)) and $n = 2$ (FA(2)), free B exciton with $n = 1$ (FB(1)), neutral donor bound A exciton with $n = 1$ (D$^0$X), two electron transition (TET), and their one-LOR lines (1LORs). The recombination processes of these peaks were identified by a reflectance spectra, the energy differences between the peaks, and previous literature.\textsuperscript{3,21) As the pulse width values of these lasers are 300 ps (337 nm line) and 500 ps (266 nm line), the excited electron density is decreasing during the excitation. This condition is thought to be the reason why the excitonic emission lines are clearly observed even for the high excited carrier number per pulse ($9 \times 10^{17}$ cm$^{-3}$/pulse).

In the PL spectrum from the 266 nm excitation with the same excitation density as the 337 nm excitation, no clear peaks of free excitons are observed. The spectrum slope at the higher energy side of the 1LOR of the FA(1) line from the 337 nm excitation is steeper than that from the 266 nm excitation. This result reveals that the 266 nm excitation yields higher exciton kinetic energy. The difference between these two excitation conditions is the difference in the carrier relaxation energy: 1.17 eV (4.66 eV–3.49 eV) for 266 nm and 0.19 eV (3.68 eV–3.49 eV) for 337 nm, which corresponds to the difference in the generated LO phonon number per excitation photon between the 266 nm line (twelve) and the 337 nm line (one). Thus, a thermally nonequilibrium state in the exciton kinetic energy is established by the 266 nm excitation. When the excitation carrier density by the 266 nm line is decreased by one order, the PL spectrum becomes similar to that which results from the 337 nm line excitation. This result is explained by the difference in the released energy difference or emitted phonon number between the two excitations from the 266 nm and 337 nm laser beams. As the released energy by one excitation photon is 1.17 eV for the 266 nm light and 0.19 eV for the 337 nm light, when the excitation photon number of the 266 nm light is decreased to 10% of that of the 337 nm light, the totally released energy from the 266 nm light is approximately the same as that of the 337 nm light. Thus, the spectrum shape is thought to be dominated by the totally released energy by the carrier energy relaxation after the photo-excitation or the interaction of excitons and phonons generated in the energy relaxation processes. Figure 5(b) shows the temporal development of the PL spectrum, which shows the long relaxation lifetime of FA(2). This spectrum shape lasts more than 500 ps at least. This long lifetime of the population of FA(2) is against our expectation based on the fast rate of
approximately $2 \times 10^{10} \text{s}^{-1}$ of the transition from FA(2) to FA(1) by emitting an LA phonon ($W_{xx}(2, 1)$). Thus, it is thought that this long PL lifetime of FA(2) at this low temperature means the existence of excitation population flows from FA(2) which substantially affect the population distribution among exciton states.

The intensities of the constituent spectrum lines were obtained by spectrum fitting, from which intensity ratios of the peaks were obtained. The utilized functions are exhibited in Ref. 23. The observed FA(1) spectrum line width of 2.6 meV is greater than the critical width 1.5 meV of exciton–photon coupling. The exciton scattering lifetime estimated from the line width is approximately 1.2 ps or shorter, which indicates that the polaritons are scattered at a high rate in the order of $10^{11} \text{s}^{-1}$. Thus, the exciton ZPLs were fitted by a quasi-Voigt function with a peak energy of $E_n$ and a FWHM of $\gamma_n$. This function was defined as the superposition of a Gaussian and Lorentzian with the same FWHM. The spectra of TET and its LORs were also fitted using this function. The function of $(E - E_n + mE_{LO})^{3/2} \exp[-(E - E_n + mE_{LO})/k_BT]$ was used for 1LOR ($m = 1$) and 2LORs ($m = 2$) of free excitons. Here $E_n$ is the energy of the $n$ state of free exciton. The ZPL spectrum of the continuum was fitted by a function proportional to $(E - E_0)^{1/2} \exp[-(E - E_0 + mE_{LO})/k_BT]$. $(E - E_n + mE_{LO})^{3/2} \exp[-(E - E_n + mE_{LO})/k_BT]$ was adopted for its LOR spectra ($m = 1$ for 1LOR, and $m = 2$ for 2LOR). The spectrum functions obtained by this process satisfactorily fitted the experimental data. As we have constraints for the energy regions and spectrum shapes of the constituent lines, uniqueness of the fitting was obtained. The temperatures of excitons and free electrons were determined by the 1LOR or 2LOR spectrum fitting. Although the obtained temperatures are effective values determined using the functions based on the thermal equilibrium condition, it is known that the best-fit parameters allow discussion on the exciton dynamics.

Figure 6 shows the obtained effective temperatures, indicating the kinetic energies, for the excitation power of 1 and 10 (mW) of the 267 nm line. The power of 1 mW corresponds to the totally excited carrier density of $1.4 \times 10^{17} \text{cm}^{-3}$/pulse.

Figure 7 shows the obtained population distribution at 10 K (a) and 300 K (b) and population lifetime of the $n = 1$ state (c). The $n = 1$ population lifetime is plotted by closed circles in (c). The line denoted by $T^{3/2}$ shows the radiative lifetime of $n = 1$ excitons under the thermal distribution of kinetic energy to the non-zero region where radiative recombination is forbidden. The dependence of the radiative component of the experimental PL lifetime on the temperature in Ref. 50 is plotted by open circles.

3.3 Population distribution depending on excitation density and temperature: thermal equilibrium case

Figure 7(a) shows the population distribution of exciton states under the condition of thermal equilibrium at 10 K as a function of the total electron density $N_{tot}$, the sum of the densities of free electrons and excitons, which is obtained by the PXR model. The continuum is dominantly populated in the low excitation density region, while the $n = 1$ state is the most populated state in the high excitation density region.
This variation in the distribution is attributed to the difference in the dependence of exciton formation and dissociation rates on the exciton or electron density: a bimolecular process of exciton formation despite the monomolecular process for exciton dissociation. The excitation electron density by using a continuous wave light is generally in the range equal or lower than $10^{15} \text{cm}^{-3}$, while the initial electron density by a pulse excitation in the TRPL measurement is higher. Figure 7(b) shows the calculated population distribution at a thermal equilibrium temperature of 300 K. The population densities are plotted up to $4 \times 10^{17} \text{cm}^{-3}$, because the $n = 5$ state is estimated to disappear above $3.6 \times 10^{17} \text{cm}^{-3}$ because of Coulomb screening. Although the population share of the $n = 1$ state in $N_{\text{tot}}$ is the lowest, it increases to nearly 10% by the increase in $N_{\text{tot}}$ accompanied by the drastic decrease in $N_{n}/N_{\text{tot}}$. Reference 49 reported a high exciton generation efficiency by high carrier density excitation of $10^{13} \text{cm}^{-2}$ at RT. This experimental observation is possibly related to the high exciton formation rate at a high excitation density. Figure 7(c) shows the dependence of the population decay time of the $n = 1$ state on the temperature, which is calculated by the PXR model for $N_{\text{tot}}$ of $5 \times 10^{16} \text{cm}^{-3}$. This lifetime corresponds to the radiative component in the experimental PL lifetime. Here, it is assumed that the radiative recombination lifetime of $n = 1$ excitons subject to thermal kinetic-energy distribution is proportional to $T^{3/2}$ on the basis of the reduction of the probability for an exciton to have zero or nearly zero kinetic energy enabling the radiative recombination in three-dimensional space when the temperature increases. In the temperature range lower than 50 K, a constant lifetime due to exciton polaron is also assumed. The population lifetime of the $n = 1$ state increases to approximately 100 ns at 300 K. This result exactly agrees with the open circles representing the experimental radiative lifetime reported by Ref. 50, where the radiative lifetime has been obtained by decomposing a PL decay rate to radiative and nonradiative components using the dependence of the PL decay rate and intensity on the temperature. This result indicates that the populations in higher $n$ states work as reservoirs of the $n = 1$ population. In the following section, it is theoretically manifested that the population flows to upper $n$ states are dominated by phononic processes.

### 3.4 Population distribution and flow under thermally nonequilibrium state

Figure 8 shows the experimental results on the temporal development of the PL intensity ratio of the ZPL of $D^0X$ ($I_{Z_D}$) and the 2LOR or ZPL of FA(1) ($I_{2LO A1}$ or $I_{2LO A1}$) for 1 and 10 (mW) excitations of the 267 nm line. As the intensities of the ZPL and its 2LOR show the population density in the vicinity of zero momentum ($k = 0$) and total population density, respectively, this figure reveals that the FA(1) population in the vicinity of zero kinetic energy is decreasing against the population of the $D^0X$ state, while the total populations of the $D^0X$ and FA(1) have been balanced at an incipient time earlier than 60 ps. Figure 8(c) shows the intensity ratio of $I_{2LO A1}/I_{ZLO A1}$, which means the population share in the vicinity of zero kinetic energy for FA(1). When we assume kinetic-energy relaxation of FA(1) by the time evolution, this intensity ratio is expected to increase with time, whereas the experimental result goes against the expectation. It appears that the thermally nonequilibrium condition of the exciton kinetic energy affects the kinetic-energy distribution. This phenomenon is pronounced in the result of FA(2) as described as follows.

Figure 9(a) shows the PL intensity ratio of the 2LOs of FA(2) ($I_{2LO A2}$ and $I_{ZLO A1}$) and FA(1) ($I_{2LO A1}$ and $I_{ZLO A1}$), which indicates the total population ratio of FA(2) and FA(1). This ratio is decaying in the time region earlier than 130 ps, and looks to be approximately constant in the later time region, whereas the ratio varies depending on the excitation density. This difference between the excitation powers indicates that the population distribution between FA(1) and FA(2) is in a nonequilibrium state. Figure 10 shows the theoretical 2LO intensity ratio of FA(1) and FA(2) as a function of thermal equilibrium temperature, which is calculated by the PXR model for $N_{\text{tot}} = 1 \times 10^{16} \text{cm}^{-3}$. Here, two conditions are assumed: that the radiative recombination rate of FA(2) is 2$^{-3}$ times the rate of FA(1), and the intensity ratio of the ZPL and 2LOR for FA(2) is the same as that for FA(1). This figure exhibits that the $I_{ZLO A2}/I_{ZLO A1}$ varies between 0.008 and 0.3 in the temperature range below 300 K, and that the value at 140 K is 0.1. The order of the experimental highest value 0.4 shown in Fig. 9(a) agrees with the theoretical value in the temperature range higher than 140 K. The experimental ratio is higher than the theoretical value for the obtained $T_x$ by several factors. The higher $T_x$ of FA(2) than that of FA(1) is a reason for the high experimental $I_{ZLO A2}/I_{ZLO A1}$ values. Another reason is the nonthermal distribution of exciton...
kinetic energy, which limits the feasibility of the Boltzmann function using an effective temperature, and induces the underestimation of the exciton temperature. The experimental exciton kinetic energy is possibly distributed to a higher region determined by $T_x$ in the present analysis. As $D^0X$ with a lower density of state than that of FA(1) tightly couples with FA(1), the effect of $D^0X$ is thought to be minor. Further, it is thought that the $T_x$ in the time range later than 120 ps probably remains higher than the thermal temperature measured at the surface of the sample by a thermocouple.

Figure 9(b) shows the PL intensity ratio of the ZPL of FA(2) ($I_{ZA2}$) and its 2LOR ($I_{Z2LO A2}$), indicating the kinetic-energy distribution of FA(2). As in the case of FA(1), this feature of kinetic-energy distribution is an unexpected form when we assume simple temporal kinetic-energy relaxation, and is further enhanced compared to the case of FA(1). The following mechanism possibly explains this phenomenon.

In the experimental dynamics, exciton diffusion possibly reduces its density in addition to the radiative and nonradiative recombination. Exciton diffusion length has been discussed in the literature, and is estimated to be approximately 200 nm at a temperature of 40 K. Figure 7(a) infers that the decrease in the total electron density by the time evolution induces a shift of the population distribution to the continuum. On the other hand, free electrons are relaxing to excitonic states, and generated excitons are relaxing from higher $n$ states to lower $n$ states, and finally, FA(1)s and $D^0X$s are annihilated radiatively or nonradiatively, which works as a drain of population. Simultaneously, a diffusion of phonon energy is taking place in this time region. These processes reduce the electron and exciton kinetic energy, which is reflected in the temperatures shown in Fig. 6. Further, it is calculated that excitons with a higher kinetic energy have higher rate coefficients of excitation and deexcitation transfer, and that the excitation rate from the $n = 2$ state to the continuum is in the order of $10^{11}$ s$^{-1}$ at 50 K, which is higher than the excitation rate from the $n = 1$ state, approximately $10^9$ s$^{-1}$, by two orders. The exciton formation rate coefficient of the $n = 1$ state is calculated to be approximately one order lower than that of the $n = 2$ state in the temperature range lower than 100 K. These experimental and theoretical results reveal that the injection of high kinetic energy of the continuum to the FA(2) state modifies the population distribution despite the overall cooling. This mechanism means the stronger population exchange is between FA(2) and the continuum rather than that between FA(2) and FA(1), which is illustrated in Fig. 9(c). Figure 11 shows the population flows for thermal equilibrium states of 10 K and 300 K, and thermally nonequilibrium states of $(T_e, T_x, T_i) = (10 \text{ K}, 50 \text{ K}, 10 \text{ K})$ and $(50 \text{ K}, 10 \text{ K}, 10 \text{ K})$. The red, orange, and blue colored arrows indicate radiative, electron-collisional, and phononic transition processes, respectively. Figure 11(c) shows the high population exchange rate between the $n = 2$ state and the continuum by the direct excitation and deexcitation via upper states under a thermally nonequilibrium condition of $T_x = 50 \text{ K}$. Thus, the high kinetic energy of free electrons or the continuum is partly transferred to FA(2) excitons, which leads to the unexpected kinetic-energy distribution in the FA(2) state exhibited in Fig. 9(b). Further, as some of the kinetic energy is transferred to FA(1), a similar property is observed for FA(1), which is illustrated in Fig. 9(c).

Figure 9(b) shows that $Z_{A2} 2LO A2$ for 10 mW excitation/2 state and the continuum by the direct excitation and deexcitation via upper states under a thermally nonequilibrium condition of $T_x = 50 \text{ K}$. Thus, the high kinetic energy of free electrons or the continuum is partly transferred to FA(2) excitons, which leads to the unexpected kinetic-energy distribution in the FA(2) state exhibited in Fig. 9(b). Further, as some of the kinetic energy is transferred to FA(1), a similar property is observed for FA(1). Figure 9(b) shows that $I_{ZA2}/I_{Z2LO A2}$ for 10 mW excitation decreases to a lower value than that for 1 mW excitation. It is estimated that the interaction rate of carriers or excitons and LA phonons is greater for a greater excitation power because of the higher phonon occupation factor, which enhances the interaction between FA(2) and the continuum. This is thought to be the reason for the decrease in $I_{ZA2}/I_{Z2LO A2}$ to a lower value by the higher power excitation. The possibility of this
mechanism is numerically evidenced using rate equations in the previous article, \(^{23}\) and further in this paper, this mechanism is supported by the theoretical discussion on population flows based on the PXR model. The detail properties of population flows are described in the following.

Figure 11(a) shows that at a low temperature of 10 K, transitions of one level up or one level down (\(\Delta n = \pm 1\)) are approximately balanced between the \(n\) and \(n + 1\) state for states equal to or higher than \(n = 3\), while for the lower states of \(n = 1\) and \(2\), a down flow is the dominant process. On the other hand at 300 K [Fig. 11(b)], the main population flows of each \(n\) state are processes of the population exchange with the continuum, which are dominated by phononic processes. The diagram in Fig. 11(c) shows that the phononic processes are enhanced when the \(T_e\) is increased despite the low lattice temperature, and that the increase in \(T_e\) to 50 K is effectual in terms of changing the population flow characteristics. The interaction with the continuum is strong for FA(2), while it is weaker for FA(1), which is consistent with the experimental result. This theoretical result indicates that the high kinetic energy of the continuum is injected to FA(2), and some of the energy is further injected to FA(1) via FA(2). Further, Fig. 11(c) reveals that the main flow process of the excitation from each \(n\) state to the continuum is a phononic one. The increase in \(T_e\) shown in Fig. 11(d) enhances the flow rates of electron-collisional processes of \(\Delta n = \pm 1\), and makes phononic processes minor. This electron-collisional process may dominate the exciton dynamics in the incipient time region when the electron density is high.

The lower limit of the \(n\) state where the down-flow and upward flow processes are competing between \(n\) and \(n + 1\) states is 3 under a thermal equilibrium condition of 10 K, as shown in Fig. 11(a), while it is \(n = 2\) under the thermally nonequilibrium conditions of \((T_e, T_x, T_l) = (10 K, 50 K, 10 K)\) (c) and \((50 K, 10 K, 10 K)\) (d). Further, this boundary is disappeared under a thermal equilibrium state of 300 K. Down-flow processes dominate the population transition below this boundary, which is called Byron’s boundary in the collisional radiative model of atomic plasma spectroscopy, \(^{43-45}\) where the dynamics of excitation and deexcitation population flows of atomic states are classified into several phases. The dynamics of exciton are possibly classified into characteristic phases, whereas it is necessary to characterize the interaction between excitons and phonons which is not included in atomic plasma. This classification of the electron-hole-exciton plasma is a future issue.

4. Conclusion

Excitation and deexcitation dynamics of excitonic states of GaN were investigated by TRPL analysis and a theoretical
PXR model. This PXR model gives the properties of population distribution and population flows among the exciton states, and is feasible for the analysis of exciton radiation properties in thermal equilibrium and also thermally nonequilibrium states. For example, the mechanism of the experimentally-obtained unexpected emission intensity ratio of the ZPL and 2LOR of FA(2) was solved by this model. This model reveals that the increase in $T_x$ enhances the direct transition from each $n$ state to the continuum and the population flow from the upper states to the $n = 2$ state, which agrees with the experimental result. This interaction between each $n$ state and the continuum is a characteristic property of phononic processes. The dominant phonon mode in the excitation transfer of $n = 1$ and $n = 2$ states shifts from the LA phonon to the LO phonon in the temperature region of $130$–$240$ K. Further, the PXR model shows the mechanism of the long population lifetime of FA(1) up to 100 ns at RT, which agrees with the radiative component of the experimental PL lifetime reported in the literature. When we take into account nonradiative recombination processes, it is thought that it is possible to apply this scheme to the analysis of internal quantum efficiency in PL measurements.

Acknowledgments

This work was partly supported by JSPS Grants-in-Aid for Science Research (B) (No. JP17H02772) and for Science Research on Innovative Areas (No. JP16H06415 and No. JP16H06425), and also the Fujikura Foundation.

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