Energy-relaxation dynamics of photogenerated excitons observed from time-resolved photoluminescence of exciton-exciton scattering in CuI thin films

H. Ichida and Y. Kanematsu
Venture Business Laboratory, Center for Advanced Sience and Innovation, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Japan

K. Mizoguchi, D. Kim, and M. Nakayama
Department of Applied Physics, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
(Received 3 April 2007; revised manuscript received 7 July 2007; published 16 August 2007)

We have investigated the excitation-photon-energy dependence of time-resolved photoluminescence spectra of the P emission due to exciton-exciton scattering at 10 K in CuI thin films from the viewpoint of energy-relaxation dynamics of photogenerated excitons. The ultrashort time resolution of 0.4 ps using an optical-Kerr-gating method enabled us to obtain precise information of the relaxation dynamics under various excitation-photon-energy conditions. It is found that the onset time of the P emission, which corresponds to the time required for the appearance of the P emission after the irradiation of an excitation pulse, increases with increasing excitation-photon energy, while the rise and decay times of the P emission are independent on the excitation-photon energy. These results indicate that the onset time is connected with an energy-relaxation time of the photogenerated excitons toward the bottleneck region of the exciton-polariton. On the basis of a Fröhlich-interaction model, we have quantitatively analyzed the energy-relaxation time, taking account of interactions between the excitons and longitudinal optical (LO) phonons, the so-called cascade process of LO-phonon scattering, in momentum space.

DOI: 10.1103/PhysRevB.76.085417 PACS number(s): 78.20.−e, 71.35.−y, 63.20.Ls, 78.47.+p

I. INTRODUCTION

Exciton dynamics in an ultrashort time range has been intensively investigated from theoretical and experimental aspects.[1] In particular, the energy-relaxation processes of photogenerated excitons toward the quasithermal equilibrium state in momentum space after the incidence of an excitation pulse is a much attractive subject in dynamics of excited states. In the initial process of the exciton dynamics, the exciton-phonon interactions play an important role in the exciton-formation process,[2] and the exciton-energy-relaxation process[3] results in the redistribution of excitons in momentum space. Under nonresonant-excitation conditions, it is known that hot excitons with large momentums (wave vectors) and kinetic energies are created. When the energy difference between the excitation-pulse energy and the exciton energy in the ground state is much larger than the energy of a longitudinal optical (LO) phonon, the excitons in momentum space are scattered by LO phonons toward the bottleneck region of the exciton-polariton branch with a scattering rate dominated by the Frölich interaction.[4,5] The scattering rate of excitons depends on the energy and wave vector of the excitons; namely, the scattering rate changes during the relaxation process. Therefore, it is expected that an energy-relaxation time of photogenerated excitons to reach the bottleneck region is dominated by the rate and event numbers of the exciton-LO-phonon scattering. The elementary step of the LO-phonon scattering is in a subpicosecond time range because the LO-phonon frequency is of the order of THz. Thus, it is difficult to precisely detect the exciton-relaxation dynamics using conventional methods of time-resolved photoluminescence (PL) spectroscopy owing to the requirement of an ultrashort time resolution. So, little has been known about the ultrafast energy-relaxation processes in PL dynamics.

In our previous work, we investigated the PL dynamics of exciton-exciton scattering in CuI thin films by using an optical-Kerr-gating (OKG) method.[6] Exciton-exciton scattering is a typical phenomenon under intense excitation conditions.[7] In the inelastic scattering of two ground-state ($n=1$) excitons, one exciton is scattered into a higher excited state with $n \geqslant 2$, while the other is scattered into a photonlike state, the energy of which is lower than that of the $n=1$ exciton state by the energy difference between the $n=1$ and $n \geqslant 2$ states. This scattering process leads to the so-called P_n emission, where the subscript n denotes the quantum number of the higher excited exciton state. From the time-resolved PL spectra of the P emission, we revealed the following characteristics: (i) The decay time of the P emission is governed by the radiative lifetime of the photonlike polariton leading to emission; (ii) the inverse of the PL rise time reflects the collision rate of excitons in the $n=1$ state; (iii) the temporal change of the peak energy of the P emission reflects the effective temperature of the excitonic system; and (iv) an onset time for the emergence of the P emission exists after the irradiation of an excitation pulse. It is noted that the onset time of the P emission is a good probe for the energy-relaxation dynamics. Recently, Takeda *et al.* investigated the dynamics of exciton-exciton scattering in ZnO thin films at room temperature under a nonresonant excitation condition.[8] They suggested that the onset time of the P emission reflects the intraband-energy-relaxation time of excitons characterized by the exciton-LO-phonon scattering time. In Ref. 8, however, the systematic excitation-photon-energy dependence, which is important to reveal the mechanism of the relaxation dynamics, was not reported. In addition, the scattering process is considered to be blurred thermally at room temperature. Since the LO-phonon energy of CuI (18.7 meV) is lower than that of ZnO (72 meV), the number

of events of the exciton-LO-phonon scattering until the exciton reaches the bottleneck region in CuI is larger than that in ZnO under the situation of the same excess energy for the photogenerated exciton. Thus, it is expected that the energy-relaxation process of the photogenerated exciton in CuI is markedly affected by the LO-phonon scattering in comparison with that in ZnO.

In the present work, we have focused on the onset time of the P emission in CuI thin films in order to reveal the energy-relaxation dynamics in momentum space at a low temperature. We measured the excitation-photon-energy dependence of time-resolved PL spectra of CuI thin films using the OKG method with a typical time resolution of 0.4 ps. It is found that the onset time of the P emission clearly increases with an increase in excitation-photon energy. We quantitatively discuss the relation between the onset time of the P-PL band and the energy-relaxation time of the photogenerated excitons taking account of the Fröhlich interaction resulting in the exciton-LO-phonon scattering.

II. EXPERIMENTS

The samples of CuI thin film were grown on a (001) NaCl substrate at 170 °C by vacuum deposition in high vacuum of $\sim 1 \times 10^{-6}$ Pa. We confirmed by x-ray diffraction that the thin films are preferentially oriented along the ⟨111⟩ crystal axis.[9] The film thickness was fixed at 100 nm. The sample temperature was maintained at 10 K using a constant He-flow cryostat. Time-resolved-PL spectra were measured using the following OKG method. The excitation pulse was provided by the fourth harmonic pulse from an optical-parametric amplifier operated by a Ti:sapphire regenerative amplifier laser system with a repetition rate of 1 kHz and a pulse width of about 200 fs. The energy of the excitation pulse was tuned from 3.10 to 3.26 eV, which is higher than the fundamental exciton energy, 3.053 eV, of the CuI thin film at 10 K. The gating pulse with an energy of 1.60 eV was delayed by a variable optical delay line in a time range up to 30 ps. We used an SFS1 glass as the Kerr-gating material. The time resolution was approximately 0.4 ps. The time-resolved PL spectra were measured using an intensified charge-coupled-device detector attached to a single monochromator with a spectral resolution of 0.8 nm.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the time-integrated PL spectra of the CuI thin film excited at the photon energies of 3.10 and 3.26 eV, respectively, with an excitation-power density of 18 μJ/cm^2. The arrow labeled X denotes the lowest free-exciton energy of the CuI thin film at 10 K obtained from the absorption spectra (not shown here). At both the excitation-photon energies, we clearly observe the PL band labeled P on the low-energy side of the free-exciton energy. The energy spacing between the P-PL band and free exciton is about 45 meV. This energy is almost equal to the energy difference between $n=1$ and $n=2$ exciton states in CuI.[10] In our previous work,[11] we clearly observed the P_2 emission in CuI thin films with the use of a nanosecond-pulsed nitrogen laser as an excitation source. The energy of the previously observed P-PL band agrees with the present result. We note that the excitation-power-density (P_{exc}) dependence of the P-band intensity (I_P) exhibits an almost quadratic dependence on the previous work: $I_P \propto P_{exc}^{1.7}$.[11] Thus, the P-PL band is assigned to be the P_2-emission due to the inelastic scattering of excitons from the $n=1$ state to the $n=2$ state.

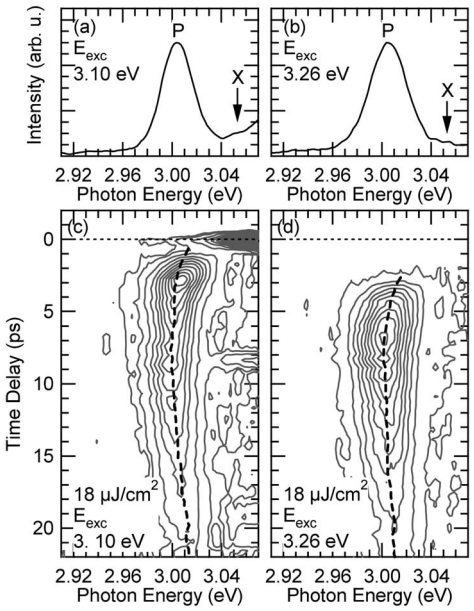

FIG. 1. Time-integrated PL spectra of CuI thin film with a thickness of 100 nm at 10 K for the excitation-photon energies of (a) 3.10 eV and (b) 3.26 eV. The excitation-power density is fixed at 18 μJ/cm^2. Contour plots of the time-resolved PL spectra for excitation-photon energies of (c) 3.10 eV and (d) 3.26 eV observed using the OKG method. The dashed line indicates the peak energy of the PL band labeled P.

The contour plots of the time-resolved PL spectra obtained at the excitation-photon energies of 3.10 and 3.26 eV are shown in Figs. 1(c) and 1(d), respectively. The intense signal around 3.06 eV in Fig. 1(c) is due to the scattered light of the excitation-laser pulse. The contour plots clearly indicate the time evolution of the P-PL band. The dashed curves in Figs. 1(c) and 1(d) indicate the peak energy of the P-PL band as a function of time delay. It is found that the peak energy of the P-PL band exhibits a temporal change with time delay; namely, the peak energy at first shifts to the lower energy side and, subsequently, to the higher energy side. The peak energy of the P-PL band due to the inelastic scattering of two excitons is given by[12]

$$\hbar\omega_p = E_{n=1,k_1} - (E_{n\geqq 2,k_1+k_2} - E_{n=1,k_2}) - 3\sigma k_B T_{eff}, \qquad (1)$$

where $E_{n=i,k_j}$ is an exciton energy in the $n=i$ exciton state with the wave vector of k_j, σ is a positive constant smaller than 1, and T_{eff} is an effective temperature of the excitonic system. The temporal changes of the peak energy of the P-PL band in Figs. 1(c) and 1(d) indicate that the effective temperature of the excitonic system changes with time delay. From Eq. (1), the initial low-energy shift reflects an increase

of the effective temperature of the excitonic system, and the subsequent high-energy shift corresponds to a decrease of the effective temperature. The temporal change of the peak energy of the P-PL band causes the broad widths of the time-integrated PL spectra shown in Figs. 1(a) and 1(b). We note that the initial energy of the P-PL band and the temporal change of the peak energy hardly depend on the excitation-photon energy. In the exciton-relaxation process in momentum space, it is usually considered that the photogenerated excitons are heated, owing to a large excess energy of the excitons with an increase in excitation energy. However, the results described above with Figs. 1(c) and 1(d) indicate that the effective temperature of the excitonic system hardly changes in spite of an increase of the excitation-photon energy, providing an excess energy in the relaxation process. One of possible reasons is that the excess energy released to the lattice system during the relaxation process is not turned back to the excitonic system. This means that the quasithermal equilibrium condition between the excitonic and lattice systems is not formed in the ultrashort time range because acoustic phonons with low frequencies corresponding to much longer scattering time than the present time range play an important role for the achievement of the thermal equilibrium. In Figs. 1(c) and 1(d), the P-PL band is hardly observed just at the time of irradiation of the excitation pulse, which indicates that an onset time is required for the appearance of the P-PL band. Moreover, the onset time at the excitation-photon energy of 3.26 eV is larger than that at 3.10 eV, while the rise time and decay time do not change with the excitation-photon energy. In order to clarify the excitation-photon-energy dependence of the characteristic times such as the onset, rise, and decay times of the P-PL band, the time profiles of the spectrally integrated intensity of the P-PL band at various excitation-photon energies are shown in Fig. 2, where the excitation-power densities were changed: (a) 18 μJ/cm^2 and (b) 35 μJ/cm^2. The time profile of the excitation pulse is also shown at the top of Fig. 2 for reference. It is evident that the onset time of the P-PL band increases with increasing excitation-photon energy. For the evaluation of the onset time of the P-PL band, the time profiles were fitted with the following equation, phenomenologically,[6]

$$I(t) \propto -\exp[-(t-t_{onset})/\tau_{rise}] + \exp[-(t-t_{onset})/\tau_{decay}], \tag{2}$$

where τ_{rise} (τ_{decay}) is the mean rise (decay) time and t_{onset} is the onset time of the P-PL band. The results of the temporal PL-intensity changes fitted with Eq. (2), which are shown by the dashed curves in Fig. 2, are in agreement with the experimental results. The rise, onset, and decay times obtained from the fitting procedure are listed in Table I. From Table I, it is found that the onset time increases from 0.3 to 2.3 ps with increasing excitation-photon energy from 3.10 to 3.26 eV at 18 μJ/cm^2. On the other hand, the mean rise and decay times for all the excitation-photon energies are almost constant values of 2.2 and 8.2 ps, respectively. It should be noted that the values of the mean decay time of the P-PL band at the several excitation-photon energies at the

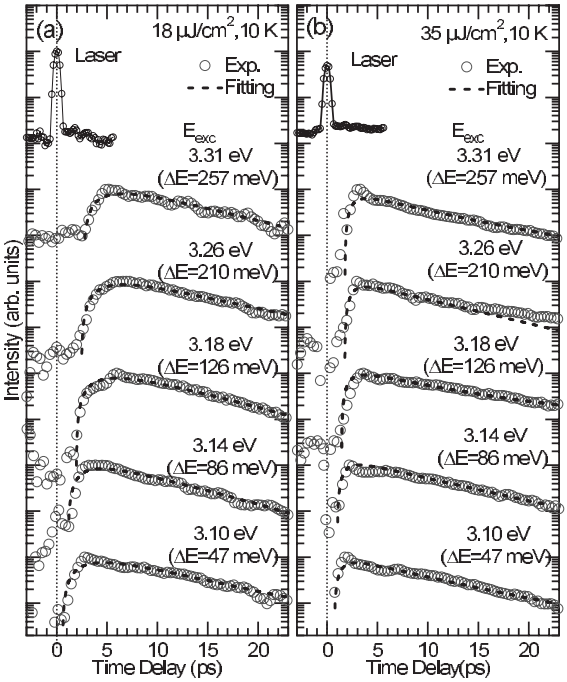

FIG. 2. Integrated PL intensity of the P-PL band as a function of time delay of various excitation-photon energies at the excitation-power densities of (a) 18 μJ/cm^2 and (b) 35 μJ/cm^2. The time profile of the excitation pulse is depicted at the top as a reference. The dashed curves indicate the fitted results of the time profiles of the P-PL band with Eq. (2).

excitation-power density of 35 μJ/cm^2 are almost identical to those at 18 μJ/cm^2. On the other hand, the value of the mean rise time of ~0.82 ps at 35 μJ/cm^2 is much faster than that of ~2.2 ps at 18 μJ/cm^2. For the onset time, the values at 35 μJ/cm^2 are slightly different from those at 18 μJ/cm^2; however, the tendency of the excitation-photon-energy dependence at 35 μJ/cm^2 is similar to that at 18 μJ/cm^2. The difference of the onset times at 18 and 35 μJ/cm^2 will be discussed later with the model calculation. The overall results are summarized to the following three points: (i) The onset time depends on the excitation-photon energy; (ii) the mean decay time and the mean rise time are almost independent of the excitation-photon energy; and (iii) the mean rise time depends only on the excitation power. The fact that the mean decay time is almost independent of the excitation-photon energy is reasonable because the mean decay time is considered to originate from the radiative lifetime of the photonlike polariton, which is the final state leading to emission, at a given energy, as discussed in our previous report.[6] The inverse of the mean rise time reflects the collision rate of $n=1$ excitons around the bottleneck region, which depends on the exciton density. The excitation-power dependence of the mean rise time obtained in this work is consistent with that reported in our previous work.[6] Moreover, the fact that the mean rise time hardly changes with the excitation-photon energy indicates that the exciton density around the bottleneck region related to exciton-exciton scattering does not change with the excitation-photon energy. This implies that the density of the photogenerated excitons is maintained until the arrival at the bottleneck region.

TABLE I. Onset, rise, and decay times of the P-PL band obtained from the data fitting with Eq. (2) in the various excitation-photon energies at the excitation-power densities of 18 and 35 $\mu J/cm^2$.

	18 $\mu J/cm^2$			35 $\mu J/cm^2$		
Excitation energy (eV)	t_{onset} (ps)	τ_{rise} (ps)	τ_{decay} (ps)	t_{onset} (ps)	τ_{rise} (ps)	τ_{decay} (ps)
3.31	2.3	2.2	8.2	1.7	0.83	8.2
3.26	2.2	2.4	8.1	1.7	0.82	8.4
3.18	1.4	2.2	8.4	1.6	0.84	8.8
3.14	0.77	2.1	8.4	0.83	0.83	8.8
3.10	0.30	2.2	8.3	0.72	0.82	8.6

Hereafter, we focus on the excitation-photon-energy dependence of the onset time in the *P*-emission process. Figure 3 shows the onset time of the P-PL band as a function of excitation-photon energy. The open and closed circles indicate the onset time of the P-PL band obtained at the excitation-power densities of 18 and 35 $\mu J/cm^2$, respectively. It is obvious that the onset time of the P-PL band exhibits an almost monotonic increase with the excitation-photon energy though the data at 35 $\mu J/cm^2$, exhibit a scattered profile. This fact indicates that the onset time of the P-PL band is dominated by the excitation-photon energy. When the excess energy of the photogenerated exciton is much larger than the LO-phonon energy, the photogenerated exciton with a significant momentum and kinetic energy immediately relaxes toward the bottleneck region of the $n=1$ exciton state along the lower-polariton dispersion accompanying the cascade emission of LO phonons. On the relaxation process of the exciton, a finite time is needed until the photogenerated exciton reaches the bottleneck region in which the exciton-exciton scattering occurs. In order to evaluate this finite time, we introduce a relaxation time t_{relax} expressed by the summation of the cascade LO-phonon scattering time during the energy relaxation. In order to clarify the relation between the exciton-scattering rate by the LO phonon and the exciton-energy-relaxation time, we calculated the scattering rate $1/\tau_{LO}$ on the basis of the Frölich interaction. According to Refs. 4 and 5, $1/\tau_{LO}(E_{ex,k_{ex}})$ is represented by

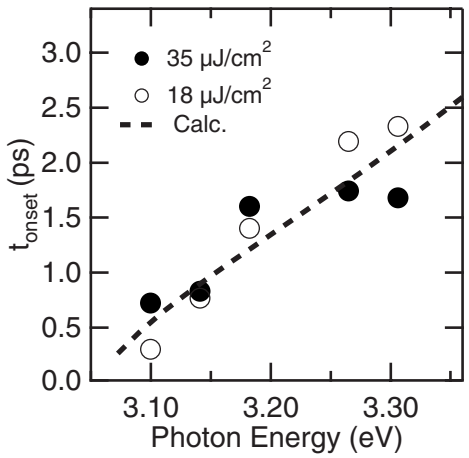

FIG. 3. Onset time of the P-PL band as a function of excitation-photon energy at excitation-power densities of 18 (solid circles) and 35 (open circles) $\mu J/cm^2$. We depict the theoretical results on the basis of Eqs. (3)–(5) as the dashed curve connected continuously between the calculated relaxation times by the LO-phonon scattering at different energies of $E_{ex,0}+n'\Omega_{LO}$.

$$1/\tau_{LO}(E_{ex,k_{ex}}) = \frac{e^2\Omega_{LO}\mu_{ex}}{\hbar^2}\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\frac{N_{LO}(T)+1}{\hbar k_{ex}} \times \int_{k_{ex}-k_{ex}[1-(2\mu_{ex}/\hbar^2 k_{ex}^2)(\Delta E_{ex}-\Omega_{LO})]^{1/2}}^{k_{ex}+k_{ex}[1+(2\mu_{ex}/\hbar^2 k_{ex}^2)(\Delta E_{ex}-\Omega_{LO})]^{1/2}} \times \frac{(q_e-q_h)^2}{q}dq, \quad (3)$$

where $E_{ex,k_{ex}}$ is the exciton energy with the wave vector of k_{ex}, Ω_{LO} is the LO-phonon energy, μ_{ex} is the reduced mass of the exciton, ϵ_∞ (ϵ_0) is the optical (static) dielectric constant, $N_{LO}(T)$ is the occupation number of the LO phonon at the temperature T, ΔE_{ex} is the excess energy of the exciton, $\Delta E_{ex}=E_{ex,k_{ex}}-E_{ex,0}$, and q_e (q_h) is the Fourier transform of the electron (hole) charge distribution functions. The formulations of q_e and q_h are given by[5]

$$q_e = \left[1+\left(\frac{m_h}{m_e+m_h}\frac{qa_B}{2}\right)^2\right]^{-2},$$

$$q_h = \left[1+\left(\frac{m_e}{m_e+m_h}\frac{qa_B}{2}\right)^2\right]^{-2}. \quad (4)$$

Here, m_e (m_h) is the effective mass of an electron (hole) and a_B is the Bohr radius of the exciton. From Eq. (3), we can obtain the scattering time of the exciton with the LO phonon at the wave vector of k_{ex}. Thus, t_{relax} is expressed by

$$t_{relax} = \sum_{n'=1}^{N} \tau_{LO}(E_{n'}),$$

$$E_{n'} = \hbar\omega_{exc} - n'\Omega_{LO}, \quad (5)$$

where $\hbar\omega_{exc}$ is the excitation-photon energy and n' ($\geqslant 1$) is the number of the exciton-LO-phonon scattering events until the exciton reaches the bottleneck region. The physical parameters in the calculation are $E_{ex,0}=3.053$ eV,

Ω_{LO}=18.7 meV, m_e (m_h)=0.33 m_0 (1.4 m_0), ϵ_∞ (ϵ_0)=4.84 (6.5), and a_B=1.6 nm.[13] We note that there is no fitting parameter. In a precise sense, the excitation-energy dependence of the relaxation time calculated using Eqs. (3)–(5) shows a discrete step at the excess energy equal to $n'\Omega_{LO}$; namely, it is expected that an oscillatory behavior occurs. The discrete value of the relaxation time by the once LO-phonon scattering is calculated to be about 0.25 ps. However, the experimental results do not exhibit such a oscillatory behavior at the energy of $E_{ex,0}+n'\Omega_{LO}$. The reason for the disappearance of the oscillatory behavior is as follows. The time resolution of the OKG method is about 0.4 ps, which is considerably longer than the LO-phonon-scattering time of 0.25 ps. So, we could not experimentally resolve the oscillatory behavior of the onset time of the P emission. We depict the theoretical results on the basis of the curve connected continuously between the calculated relaxation times by the LO-phonon scattering at different energies of $E_{ex,0}+n'\Omega_{LO}$ in Fig. 3. It is obvious from Fig. 3 that the theoretical curve explains well the excitation-energy dependence of the onset time. Thus, we can conclude that the onset time reflects the overall relaxation process. It is found that the experimental results of the onset time at the excitation-power density of 35 μJ/cm^2 deviate from the calculated results compared with the results at 18 μJ/cm^2. Strictly speaking, the onset profile of the *P*-emission process should be treated with the consideration of the entire process including the population buildup in the bottleneck region, which initiates the exciton-exciton scattering, after the energy-relaxation process of photogenerated excitons. Therefore, the deviation of the experimental results at 35 μJ/cm^2 from the model calculation may be due to the fact that the effect of the population buildup becomes significant in the higher excitation-power density generating a larger number of excitons. Anyway, the good agreement of the experimental results at the excitation-power density of 18 μJ/cm^2 with the model calculation without any fitting parameter demonstrates that the onset time of the P-PL band is dominated by the cascade emission of LO phonons via the Fröhlich interaction during the energy-relaxation process toward the bottleneck region of the exciton-polariton.

IV. SUMMARY

We have investigated the excitation-photon-energy dependence of time-resolved PL spectra of the P emission due to exciton-exciton scattering in CuI thin films using the OKG method from the viewpoint of energy-relaxation dynamics of photogenerated excitons. It is found that the onset time of the P emission, which corresponds to the time required for the appearance of the P emission after the irradiation of an excitation pulse, increases with increasing excitation-photon energy, while the rise and decay times of the P emission are independent of the excitation-photon energy. These results indicate that the onset time is connected with the energy-relaxation time of the photogenerated excitons toward the bottleneck region of the exciton-polariton. From the calculation of the energy-relaxation time of the excitons on the basis of the Fröhlich-interaction model taking account of interactions between the excitons and LO phonons in momentum space, we found that the excitation-photon-energy dependence of the onset time of the P emission is in good agreement with the calculation results without any fitting parameter. This demonstrates that the onset time of the P-PL band is dominated by the cascade emission of LO phonons via the Fröhlich interaction during the energy-relaxation process toward the bottleneck region of the exciton-polariton.

ACKNOWLEDGMENTS

This research was partially supported by the Ministry of Education, Science, Sports and Culture, Japan, Grant-in-Aid for Creative Scientific Research (No. 17GS1204).

[1] For a review, see J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer-Verlag, Berlin, 1996), p. 225.
[2] P. W. M. Blom, P. J. vanHall, C. Smit, J. P. Cuypers, and J. H. Wolter, Phys. Rev. Lett. **71**, 3878 (1993).
[3] M. Umlauff, J. Hoffmann, H. Kalt, W. Langbein, J. M. Hvam, M. Scholl, J. Söllner, M. Heuken, B. Jobst, and D. Hommel, Phys. Rev. B **57**, 1390 (1998).
[4] E. M. Conwell, in *Solid State Physics*, edited by F. Seitz, D. Turnbull and H. Ehrenreich (Academic, New York, 1967), Suppl. 9, p. 105.
[5] C. Weisbuch and R. G. Ulbrich, in *Light Scattering in Solid III*, edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin, 1982), p. 207.
[6] H. Ichida, Y. Kanematsu, T. Shimomura, K. Mizoguchi, D. Kim, and M. Nakayama, Phys. Rev. B **72**, 045210 (2005).
[7] C. Klingshirn and H. Haug, Phys. Rep. **70**, 315 (1981).
[8] J. Takeda, N. Arai, Y. Toshine, H. J. Ko, and T. Yao, Jpn. J. Appl. Phys., Part 1 **45**, 6961 (2006).
[9] D. Kim, M. Nakayama, O. Kojima, I. Tanaka, H. Ichida, T. Nakanishi, and H. Nishimura, Phys. Rev. B **60**, 13879 (1999).
[10] M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Process in Solids* (Springer-Verlag, Berlin, 1986), p. 119.
[11] I. Tanaka and M. Nakayama, J. Appl. Phys. **92**, 3511 (2002).
[12] C. Klingshirn, Phys. Status Solidi B **71**, 547 (1975).
[13] *Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. B, edited by O. Madelung (Springer, Berlin, 1982), pp. 270 and 272.