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Photoluminescence dynamics of exciton-exciton scattering processes 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

T. Shimomura, K. Mizoguchi, D. Kim, and M. Nakayama
Department of Applied Physics, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

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We have investigated the dynamical process of exciton-exciton scattering in CuI thin films grown on a (100) NaCl substrate under intense-excitation conditions. The time-integrated photoluminescence spectra clearly exhibit two photoluminescence bands which originate from the excitonic molecule and the inelastic scattering of excitons, so-called P emission. The time-resolved PL spectra obtained by using an optical Kerr gating method show that the peak energy of the P-emission band temporally changes in a picosecond region, which reflects the thermal distribution of excitons. In the time profile of the P-emission band, the rise time that is around 1 ps becomes remarkably fast with increasing excitation power, while the decay time hardly depends on the excitation power. Moreover, we have found that the inverse of the rise time of the P emission exhibits an almost quadratic dependence for the excitation power. This finding suggests that the inverse of the rise time corresponds to the rate of the exciton-exciton scattering.

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I. INTRODUCTION

Exciton-exciton scattering, which is one of typical phenomena in semiconductors under intense excitation conditions, has been intensively investigated from the viewpoint of stimulated emission.[1] In the inelastic scattering process 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.[1] This scattering process leads to stimulated emission, the so-called P_n emission, where the subscript n means the quantum number of the higher excited exciton state. From an aspect of ultrafast phenomena, there are two interesting subjects in the dynamical processes of the P emission: One is the initial process of the exciton-exciton scattering, and the other is the temporal change of the effective temperature of excitons under nonequilibrium conditions. It is expected that the investigation of the photoluminescence (PL) dynamics of the P emission provides us the information about the dynamical processes described above; however, the previous works of time-resolved PL spectra of the P emission in II–VI semiconductors[2–4] were insufficient in the time resolution. Thus, the details of the dynamical process of the P emission have not yet been revealed.

In order to reveal the dynamical process of the P emission in femtosecond and picosecond regions, it is important that excitons possess large exciton binding energies, which leads to the high stability of excitons under intense-excitation conditions. Thus, we employ cuprous halide crystals that have been model materials for the investigation of the excitonic properties because of the large exciton binding energies of 210, 108, and 62 meV for CuCl, CuBr, and CuI, respectively.[5] Actually, we reported the P emission leading to stimulated emission in CuBr and CuI thin films under intense-excitation conditions[6,7] and discussed the excitation power dependence of the effective temperature of excitons in steady states. The investigation of the time-resolved PL spectra of cuprous halides in an ultrafast time region will give information of the dynamics of the P emission.

In the present work, we have investigated the time-resolved PL spectra in CuI thin films under intense-excitation conditions by using an optical Kerr gating (OKG) method with the highest time resolution of ∼0.4 ps in order to reveal the dynamical process of the P emission. In the time-resolved PL spectra, we have observed two PL bands: One is due to an excitonic molecule, and the other originates from the P emission. It is found that the peak energy of the P-emission band, which depends on the excitation power, temporally changes. As the excitation power is increased, the decay time of the P-PL band hardly changes, while the rise time for reaching a maximum intensity depends on the excitation power. We discuss the excitation-power dependence of the time-resolved PL spectra observed in the CuI thin film from the viewpoint of the inelastic scattering of excitons.

II. EXPERIMENTS

The samples of CuI thin films were grown on a (001) NaCl substrate at 170 °C by vacuum deposition in high vacuum of $\sim 1 \times 10^{-4}$ Pa. The film thickness was fixed at 100 nm. We confirmed by x-ray diffraction that the thin films are preferentially oriented along the $\langle 111 \rangle$ crystal axis. The details of the x-ray diffraction patters were already reported in our previous work:[8] The very sharp line of the (111) face was observed without other face-related lines, which indicates the high crystal quality of the deposited CuI thin film. From an aspect of the optical characterization, the excitonic absorption spectrum of a CuI thin film grown on a NaCl substrate provides us important information, which was also reported in our previous work.[7] The absorption spectrum and

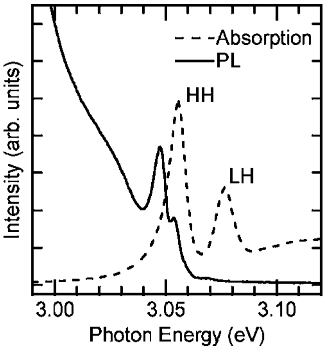

FIG. 1. Absorption spectrum (dashed curve) and PL spectrum (solid curve) of the 100-nm-thick CuI thin film at 10 K. The excitation source for the PL spectrum under a weak excitation condition was a 325 nm line of a He—Cd laser with the power density of ~1 mW/cm^2.

the PL spectrum under a weak excitation condition in the CuI thin film with the thickness of 100 nm at 10 K are shown in Fig. 1. In the absorption spectrum, we clearly observe two absorption peaks. The low-energy and high-energy peaks are attributed to the heavy-hole (HH) and light-hole (LH) excitons, respectively.[8] The HH and LH excitons that are degenerate in a bulk crystal are split by a thermal strain effect caused by a difference in the thermal expansion coefficients of CuI and the substrate material of NaCl.[8] The full width at half maximum of the excitonic absorption band is 6 meV that is comparable to the splitting energy between the longitudinal and transverse excitons (6.1 meV):[9] the so-called *L-T* splitting energy. Thus, the width of the exciton absorption indicates the high crystallinity of the CuI thin film. In the measurements of the PL spectrum under a weak excitation condition, we used a 325 nm line of a He—Cd laser for the excitation source, where the excitation-power density was ~1 mW/cm^2. In the PL spectra, the free-exciton PL band whose peak energy agrees with that of the HH-exciton absorption is clearly observed. The PL bands observed in the lower energy region than the HH-exciton energy are attributed to a bound exciton leading to the sharp PL band and donor-acceptor-pair recombination leading to the broad PL band.[5] The observation of the PL band of the free exciton also indicates the high crystallinity of the CuI thin film. We note that the exciton treated hereafter corresponds to the HH exciton because that is the lowest in energy.

The sample was attached to the cold fin of a constant He-flow cryostat and its temperature was kept at 10 K. Time-resolved PL spectra were measured by using the following OKG method. The excitation (gating) pulse was provided by the second harmonic (fundamental) pulse from a Ti:sapphire regenerative amplifier laser system with a repetition of 1 kHz and a pulse time width of about 200 fs. The energy of the excitation pulse was 3.20 eV that is higher than the fundamental exciton energy, 3.053 eV, of the CuI thin film at 10 K. The spot size of the excitation pulse was about 200 μm in diameter. The incident angle of the excitation pulse on the sample surface was about 30°, and the PL was collected perpendicularly from the sample surface using an off-axis parabolic mirror. In this optical configuration, there is no waveguide effect on emitted light, so that cavity-modelike stimulated emission will not be expected in principle. The gating pulse with the energy of 1.60 eV was delayed by a variable optical delay line in a time range over 40 ps. Toluene was mainly used as a Kerr-gate material which was located between two polarizers orthogonal to each other. The time resolution by the use of toluene was approximately 1 ps. When we measured the initial stage of the time-resolved PL spectra in detail, we used an SFS1 glass as a Kerr-gate material because the time resolution was achieved to be about 0.4 ps. The time-resolved PL spectra were measured by using a lens-coupled intensified charge coupled device (CCD) camera system attached to a single monochromator with a spectral resolution of 0.8 nm.

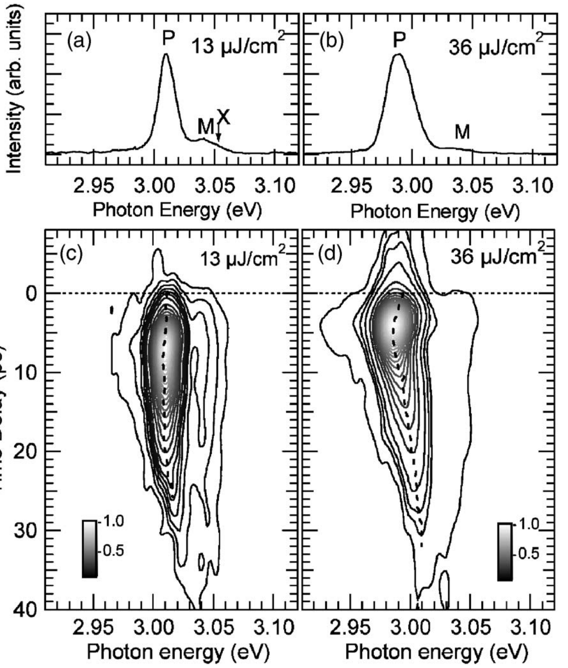

FIG. 2. Time-integrated PL spectra of the CuI thin film with the thickness of 100 nm at 10 K under the excitation powers of (a) 13 and (b) 36 μJ/cm^2. Image plots of time-resolved PL spectra under the excitation powers of (c) 13 and (d) 36 μJ/cm^2 observed by using the OKG method. The dashed line is the eye guide for the peak energy of the PL band labeled *P*.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the time-integrated PL spectra of the CuI thin film under the excitation powers of 13 and 36 μJ/cm^2, respectively. In the PL spectrum obtained under the excitation power of 13 μJ/cm^2, two PL bands labeled *P* and *M* are predominantly observed, and the additional PL band labeled *X* in the high-energy shoulder of the *M*-PL band is slightly found. The peak energies of the *X*-PL, *M*-PL, and *P*-PL bands are 3.053, 3.044, and 3.008 eV, respectively. The energy spacing between the *X*-PL and *M*-PL bands is about 9 meV, and that between *P*-PL and *X*-PL bands is about 45 meV. Since the peak energy of the *X*-PL band agrees with the energy of the heavy-hole exciton observed in the absorption spectrum of the CuI thin film (not shown here), the *X*-PL band is assigned to the free-exciton emission. From the energy difference between the *X*-PL and *M*-PL bands, the *M*-PL band will be attributed to emission from the excitonic molecule (biexciton) or emission resulting from an exciton-exciton scattering process in the intra 1*s*-exciton state due to band filling. Until now, there has been no clear experimental evidence for the observation of the two emission processes even in a CuI bulk crystal; namely, the origin of the *M* band is now controversial. We, therefore, refer to the theoretical biexciton binding energy that is about 6 meV.[10] The energy spacing between the *M*-PL and *X*-PL bands almost agrees with the theoretical biexciton binding energy. For the intra 1*s*-exciton scattering process, there has been no theoretical and experimental report on such a process in cuprous halides. On the other hand, the biexciton PL is a usual phenomenon under high density excitation conditions.[5] Thus, at this stage, the origin of the *M* band is plausibly attributed to the biexciton PL. In CuCl and CuBr crystals, it is well known that there are two types of the biexciton PL: the so-called M_T and M_L bands.[5] The M_T (M_L) band corresponds to the emission from the biexciton to the transverse (longitudinal) exciton. In the present study, the M_T and M_L bands are not resolved. This may be due to a high-effective temperature leading to a broad PL shape in addition to a low spectral resolution. The energy spacing of 45 meV between *P*-PL and *X*-PL bands is almost equal to that between the $n=1$ and $n=2$ excitons in CuI.[5] Thus, the *P*-PL band is due to the P_2-emission process in the inelastic scattering of excitons from the $n=1$ state to $n=2$ state. Under the excitation power of 36 μJ/cm^2, the *P*-PL band is asymmetrically broadened and shifted to the lower energy side by about 18 meV, compared with that observed under the excitation power of 13 μJ/cm^2. In this case, the energy spacing of about 63 meV between the *P*-PL and *X*-PL bands is in almost agreement with the binding energy of the exciton of CuI.[5] Thus, the *P*-PL band under the excitation power of 36 μJ/cm^2 is attributed to the P_∞ emission accompanied with the inelastic scattering process from the $n=1$ state to the exciton-continuum state.

The image plots of the time-resolved PL spectra of the CuI thin film obtained under the excitation powers of 13 and 36 μJ/cm^2 are shown in Figs. 2(c) and 2(d), respectively. We can clearly observe the dynamical changes of the *M*-PL and *P*-PL bands under both the excitation conditions. The *P*-PL band quickly decays as compared with the *M*-PL band. The mean decay time of the *M*-PL and *P*-PL bands is about 60 and 8 ps, respectively. Moreover, it is noted that the *P*-PL band gradually rises after the irradiation of the excitation pulse, that is, there is a time lag until the *P*-PL band reaches the maximum intensity. The observed time lags under the excitation powers of 13 and 36 μJ/cm^2 are about 7 and 3 ps, respectively. The details of the time lag will be discussed later. The peak energy of the *P*-PL band observed under the excitation power of 36 μJ/cm^2 dramatically changes with the time delay, while that under the excitation power of 13 μJ/cm^2 hardly changes. The asymmetrically broadened *P*-PL band observed in the time-integrated PL spectrum shown in Fig. 2(b) reflects the temporal change of the peak energy of the *P*-PL band.

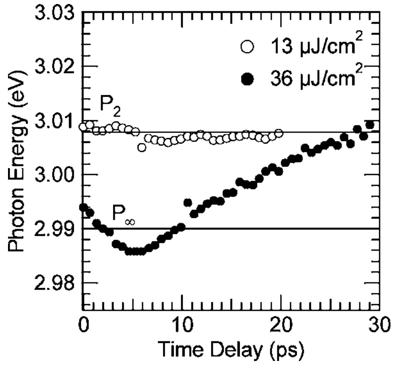

FIG. 3. Variation of the peak energy of the *P*-PL band as a function of time delay under the excitation powers of 13 and 36 μJ/cm^2. The solid lines indicate the energies of the P_2-emission and P_∞-emission bands obtained from the time-integrated PL spectra in Fig. 2.

In order to discuss the temporal change of the peak energy of the *P*-PL band, its peak energy is shown as a function of time delay in Fig. 3, where the open and closed circles indicate the experimental results obtained under the excitation powers of 13 and 36 μJ/cm^2, respectively. Under the excitation power of 13 μJ/cm^2, the peak energy of the *P*-PL band hardly changes in the whole time region. On the other hand, under the excitation power of 36 μJ/cm^2, the peak energy of the *P*-PL band is located at first between the energies of the P_2 emission and P_∞ one, and subsequently shifts to the lower energy side until about 5 ps. Moreover, the peak energy is shifts toward the energy of the P_2 emission after 5 ps. We consider that this temporal change of the peak energy results from the variation of the effective temperature of the excitonic system. The energy of the *P*-emission, $\hbar\omega_p$, due to the inelastic scattering of excitons is given by[11]

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

where σ is a positive constant smaller than 1, and T_{eff} is an effective temperature of excitonic system. Under the excitation power of 13 μJ/cm^2, the insignificant shift of the peak energy of the *P*-PL band around the energy of the P_2 emission indicates that the effective temperature of the excitonic system hardly changes with the time delay. On the other hand, under the excitation power of 36 μJ/cm^2, the low-energy shift of the *P*-PL band starting just after the irradiation of the excitation pulse is considered to be due to an increase of the effective temperature of the excitonic system. The initial energy of the *P*-PL band locates around the energy of the P_∞ emission. This means that the $n=2$ state is considerably occupied by hot excitons owing to a relatively high effective temperature. It is noted that the occurrence of the P_2 emission needs the condition that the $n=2$ state is unoccupied by excitons. The energy of the *P*-PL band is the lowest at ~5 ps as shown in Fig. 3, which corresponds to the fact that the effective temperature becomes the highest. In the time region after 5 ps, the peak energy of the *P*-PL band gradually shifts to the high-energy side. This behavior reflects the cooling process of the effective temperature. At the time of ~27 ps, the peak energy of the *P*-PL band reaches

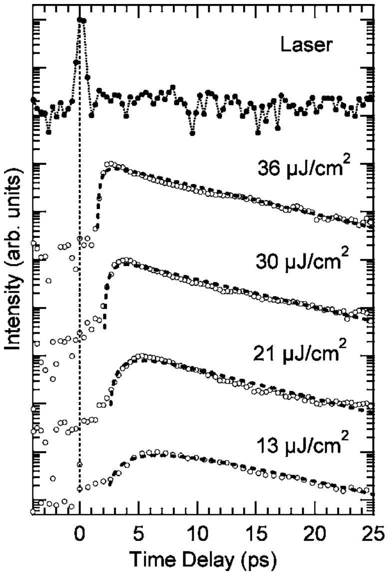

FIG. 4. Integrated intensity of the *P*-PL band as a function of time delay under various excitation powers. The top of the figure shows the time profile of the excitation pulse as a reference. The dashed curves indicate the fitted results to the time profile of the *P*-PL band with Eq. (2).

the energy of the P_2 emission, which indicates that the excitonic system is sufficiently cooled to the thermal condition that the $n=2$ state is not populated with hot excitons. Thus, the temporal peak shift of the *P*-PL band under the excitation power of 36 μJ/cm^2 shows a typical example of the dynamical change of the effective temperature in the *P*-emission process, which has not been reported until now.

Hereafter, we discuss the rise time and the decay time of the *P*-PL band. As shown in Figs. 2(c) and 2(d), the rise time changes with the excitation power. In order to reveal the excitation-power dependence of the rise time and the decay time of the *P*-PL band, the time-resolved PL spectra were measured by using the Kerr material of an SFS1 glass with the high time resolution of ~0.4 ps. Figure 4 shows the time profile of the *P*-PL band observed at various excitation powers, where the spectrally integrated intensity of the *P*-PL band is plotted on the logarithmic scale. The time profile of the excitation pulse is also shown on the top of Fig. 4 as a reference. The *P*-PL band is hardly observed at the time of the irradiation of the excitation pulse, and then that appears after several picoseconds. Moreover, the intensity of the *P*-PL band at each excitation power rises and decays almost exponentially. In order to estimate the mean rise and decay times of the *P*-PL band, the time profiles were fitted with the following equation, phenomenologically:

$$I(t) \propto -\exp[-(t-t_{onset})/\tau_{rise}] + \exp[-(t-t_{onset})/\tau_d]. \quad (2)$$

Here, τ_{rise} is the mean rise time, τ_d is the mean decay time, and t_{onset} is the onset time of the *P*-PL band. The fitted results shown by the dashed curves in Fig. 4 are in agreement with the experimental results. The best-fit value of the onset time, t_{onset}, is about 2 ps under all the excitation conditions. Since the excitation pulse with the energy of 3.2 eV is about 150 meV higher than the $n=1$ exciton energy generates excitons in the exciton-continuum state, the intially generated exciton will need a finite time to relax to the $n=1$ exciton state. Then, the onset time is considered to be related to the relaxation time of excitons from the exciton-continuum state to the $n=1$ exciton state. The mean decay times of the *P*-PL band are 7.6, 7.5, 7.2, and 8.2 ps at the excitation powers of 36, 30, 21, and 13 μJ/cm^2, respectively; namely the mean decay time hardly changes with the excitation power. Here, we discuss the reason why the decay time of the *P*-PL band is independent of the excitation power and much shorter than that of an ordinary excitonic PL band. From an excitonic-polariton picture, the decay time of the *P*-PL band is dominated by the radiative lifetime of the photonlike polariton that is the final state in the exciton-exciton scattering process. Although the *P*-PL band usually appears under occurrence of stimulated emission,[1,7] the exciton-exciton scattering process can be treated as a Boson framework,[1] which is quite different from stimulated emission due to electron-hole plasma, which is a Fermion system, in a semiconductor. It is well known that the radiative lifetime in the polariton-bottleneck region producing ordinary excitonic PL is governed by acoustic phonon scattering that leads to remarkable slowdown of the radiative process. On the other hand, the *P* emission originally belongs to the photonlike polariton that is lower in energy than the polariton bottleneck; therefore, it is expected that the radiative lifetime is much faster than that of the excitonic polariton. Furthermore, the lifetime of the photonlike polariton is an intrinsic character of the CuI crystal; namely, that is not influenced in principle by the excitation power. This consideration is consistent with the fact that the observed decay time of the *P*-PL band is independent of the excitation power. Thus, the fact that the decay time of the *P*-PL band hardly depends on the excitation power suggests the appropriateness of the assumption related to the photonlike polariton described above.

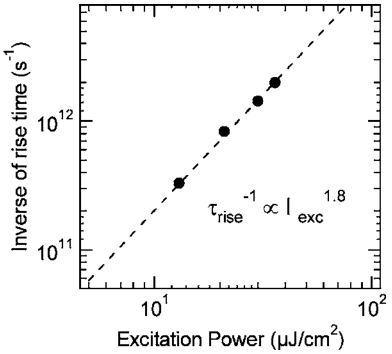

FIG. 5. Inverse of the rise time of the *P*-PL band as a function of excitation power. The dashed line indicates the superlinear relation of the inverse of the rise time, τ_{rise}, to the excitation power, I_{exc}.

We finally focus on the excitation-power dependence of the rise time of the *P*-PL band in order to clarify the origin of the rise time. Figure 5 shows the inverse of the rise time of the *P*-PL band as a function of excitation power. The inverse of the rise time of the *P*-PL band, τ_{rise}^{-1}, apparently indicates the superlinear dependence on the excitation power, I_{exc}: $\tau_{rise}^{-1} \propto I_{exc}^{1.8}$. Since the exciton density, N_{ex}, is proportional to the excitation power, the inverse of the rise time exhibits almost quadratic dependence on the exciton density. This superlinear dependence is analogous to the characteristics of forming excitonic molecules due to exciton-exciton collisions. Here, we assume that the inverse of the rise time originates from the scattering rate of excitons. The scattering rate of excitons, $R_{ex\text{-}ex}$, is given by[12,13]

$$R_{ex\text{-}ex} \propto |M|^2 N_{ex}^2, \tag{3}$$

where M is the matrix element of exciton-exciton scattering. Equation (3) implies that the scattering rate of excitons exhibits the quadratic dependence on the exciton density, which is consistent with the experimental result shown in Fig. 5. This consistency supports that the inverse of the rise time of the P-PL band corresponds to the rate of the exciton-exciton scattering in the $n=1$ exciton state.

IV. CONCLUSION

We have investigated the time-resolved PL spectra in CuI thin films under intense-excitation conditions by using the OKG method. We demonstrate two characteristics of the P-emission band due to the inelastic scattering of excitons: the temporal change of the peak energy of the P-emission band and the rise time of the P-emission band dependent on the excitation power. The temporal change of the peak energy of the P-emission band reflects the variation of the thermal distribution of the excitons under nonequilibrium conditions. The decay time of the P-emission band hardly changes with the excitation power. This suggests that the decay time is determined by the lifetime of the photonlike polariton. The inverse of the rise time exhibits almost the quadratic dependence on the excitation power, which means that the inverse of the rise time corresponds to the rate of the exciton-exciton scattering.

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