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Dynamics of high-density excitons in PbI_2 studied by two-photon absorption

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Abstract

Relaxation and diffusion processes of high-density excitons in layered type semiconductor PbI_2 have been investigated through femtosecond transient grating and time-resolved luminescence measurements under two-photon absorption. We observed two luminescence bands at low temperature; one is due to an exciton-exciton collision process, while the other originates from localized excitonic states. By utilizing the transient grating spectroscopy, the lifetime and diffusion coefficient of the high-density excitons in PbI_2 are estimated to be 72 ps and $4.6 \text{ cm}^2/\text{s}$, respectively. The lifetime observed is almost equal to the values of the decay time of the luminescence due to the exciton-exciton collision process and the rise time of the luminescence due to the localized excitons. This strongly shows that the decay of the exciton-exciton collision process is dominated by the exciton trapping to the localized states arising from potential fluctuations due to imperfection of crystal.

Keywords: exciton-exciton collision process, two-photon absorption, lead iodide

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1. Introduction

Photoluminescence properties in semiconductors under high density excitations have been attracted a great deal of attention in the fields of basic semiconductor physics and device applications. Under high density excitations, photoluminescence due to exciton-exciton collision process as well as biexcitons has been observed. In layered type semiconductor PbI_2 having a direct gap of ~ 2.5 eV, a variety of basic researches on relaxation processes of excitons has been performed so far [1-3]. When PbI_2 is highly excited at low temperature, biexciton luminescence is observed. On the other hand, luminescence due to the exciton-exciton collision process, which is generally observed in II-VI semiconductors, had not been observed, as far as we know. Very recently, we first report on the luminescence due to the exciton-exciton collision process in PbI_2 induced by two-photon absorption for band-to-band transitions [4].

In the present work, relaxation and diffusion processes of high-density excitons in PbI_2 are investigated through femtosecond transient grating and time-resolved luminescence measurements under two-photon absorption.

Experimental

The samples used in this study are 2H- PbI_2 single crystals grown from vapor phase. The typical thickness of the samples is 200 μm . A platelet-like single crystal is attached to a sample holder and kept at 20 K in a temperature-controlled cryostat. The relaxation and diffusion of the high density excitons in PbI_2 are studied by transient grating spectroscopy. Fundamental laser pulses (800 nm/1.55 eV) from a Ti:sapphire regenerative amplifier laser system with a repetition rate of 1 kHz and a pulse duration

of 100 fs are used as pump and probe pulses. To simplify the optical arrangement, we employ a phase mask to generate two pump pulses with equal intensities (+1 and -1 order diffracted beams) from a single pump pulse [5,6]. The ± 1 order diffracted beams are used as the pump pair to generate the population grating at the sample, while the other orders are blocked. The optically delayed probe pulse, which is spatially overlapped with the pump pair at the sample, reads out the decay of the produced grating as the diffracted signal. The diffracted signal is detected by a photodiode and analyzed by a lock-in amplifier. The typical time resolution of the system is 140 fs. The detailed experimental setup for the transient grating spectroscopy is reported in Ref. 6. Time-integrated and time-resolved luminescence spectra are measured by a monochromator with a CCD detector and a streak camera, respectively. The time resolution of the time-resolved luminescence measurements is 20 ps.

Results and discussion

Figure 1 shows emission spectra of PbI_2 under two-photon absorption with various excitation intensities at 20 K. Under weak excitation intensity (3.3 mJ/cm^2), a broad luminescence band B is observed around 2.45 eV, whose intensity quadratically increases with the excitation intensity. As the excitation intensity increases, a new luminescence band A suddenly emerges at the higher energy side of the B band, whose intensity follows 4th power law of the excitation intensity. The energy position of the A band is about 23 meV lower than the lowest exciton energy, and the value is equal to the energy difference between the $n=1$ and $n=2$ excitonic states of PbI_2 . Judging from these results, the A band observed originates from an exciton-exciton collision process, in which one of the two excitons scatters into the $n=2$ excitonic state and the other radiatively recombines [4]. On the other hand, the B band comes from excitons

localized by potential fluctuations caused by lattice imperfection [2].

To clarify relaxation and diffusion of the high density excitons in PbI_2 , the transient grating experiments were performed with the excitation intensity of 6.3 mJ/cm^2 . Under this excitation intensity, the luminescence due to the exciton-exciton collision process is dominantly observed as shown in Fig. 1. Figure 2 shows the typical diffracted probe signal of PbI_2 as a function of delay time in linear scale. The signal was measured by using a produced grating fringe spacing $\Lambda=5.8 \text{ }\mu\text{m}$. At time origin ($t=0$), a sharp peak corresponding to an instantaneous electronic response is observed. After the electronic response, the diffracted probe signal first increases and then decreases with time. The increase of the signal might correspond to formation of the high-density excitons, while the reduction of the signal originates from the relaxation and diffusion of the high-density excitons. The lifetime τ_G of the produced grating is given by the following equation,

$$\frac{1}{\tau_G} = \frac{1}{\tau_r} + \frac{4\pi^2 D}{\Lambda^2}, \quad (1)$$

where τ_r is the relaxation time, D the diffusion coefficient [5,6]. The first term in the right-hand of the equation (1) indicates reduction of the concentration of the high-density excitons, while the second term causes dissipation of the produced grating by the diffusion of the high-density excitons. Both terms contribute to reduction of the grating contrast, leading to the decrease of the diffracted probe signal. The value of τ_G is therefore experimentally obtained from the decay of the diffracted probe signal. By performing several experiments with different grating pitches, the lifetime and diffusion coefficient of the high-density excitons can be separately estimated. Figure 3 shows the

decay rate $1/\tau_G$ as a function of the grating pitch. Using the equation (1), the lifetime and diffusion coefficient of the high-density excitons at 20 K are determined to be 72 ps and 4.6 cm²/s, respectively.

Figure 4 shows the time evolution of the A and B bands measured by a streak camera. The luminescence intensity of the A band rises within a short time less than the instrumental time resolution and decreases exponentially with a decay time of 75 ps. On the other hand, the intensity of the B band increases with a rise time of 80 ps, then decreases exponentially with a decay time of 370 ps. The lifetime of the high-density excitons estimated from the transient grating spectroscopy is almost equal to the values of the decay time of the luminescence due to the exciton-exciton collision process and the rise time of the luminescence due to the localized excitons. This result strongly shows that the decay of the exciton-exciton collision process is dominated by the exciton trapping to the localized states arising from potential fluctuations due to imperfection of crystal.

In conclusion, we investigated relaxation and diffusion processes of high-density excitons in layered type semiconductor PbI₂ through femtosecond transient grating and time-resolved luminescence measurements under two-photon absorption. The lifetime and diffusion coefficient are estimated to be 72 ps and 4.6 cm²/s, respectively. The lifetime observed is nearly equal to the values of the decay time of the luminescence due to the exciton-exciton collision process and the rise time of the luminescence due to the localized excitons, suggesting that the decay of the exciton-exciton collision process is dominated by the exciton trapping to the localized states.

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Figure Captions

Figure 1

Emission spectra of PbI_2 under two-photon absorption with various excitation intensities at 20 K. The A and B bands originate from the luminescence bands due to the exciton-exciton collision process and the excitons localized by potential fluctuations, respectively.

Figure 2

Typical diffracted probe signal of PbI_2 as a function of delay time at 20 K in linear scale.

Figure 3

Decay rate of the produced grating as a function of grating fringe spacing. A solid line is given by a least square method.

Figure 4

Time evolution of the A and B luminescence bands at 20 K measured by a streak camera.

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Figure 3 T. Hosoya *et al.*

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