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Slow propagation of photon-like polaritons generated by exciton-exciton scattering in ZnO thin films

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Abstract. We report on the first observation of the thickness-dependent photoluminescence-decay time of exciton-exciton scattering in ZnO thin films, which indicates the slower propagation of photon-like polaritons compared to that in bulk by two orders magnitude.

The intense emission caused by exciton-exciton scattering, which is called P emission, is an interesting subject from an aspect of ultrafast phenomena leading to stimulated emission. Another attractive aspect of the P emission is that it enables us to access the related photon-like polariton state that can lead to slowdown of light propagation [1]. In the inelastic scattering process of two excitons in the first quantum ($n = 1$) state, one exciton is scattered into a higher excited state with $n \geq 2$, while the other exciton is scattered into a photon-like polariton state whose energy is lower than that of the $n = 1$ exciton state by the energy difference between the $n = 1$ and $n \geq 2$ states [2]:

$$Ex(n = 1, k_1) + Ex(n = 1, k_2) \rightarrow Ex(n \geq 2, k_1 + k_2 - k_{ph}) + \text{photon-like polariton}(k_{ph}), \quad (1)$$

where *Ex(n,k)* represents the exciton in n = i exciton state with a wavenumber of k. In the dynamical property of the exciton-exciton scattering, we have to take into account at least two processes on the basis of the exciton-polariton picture. First, in the exciton-exciton scattering process, the two exciton-polaritons are converted into a higher exciton and a photon-like polariton when the exciton density is higher than the threshold density. The rate of this collision process depends on the exciton density. The second process is the transformation of the polaritons into external photons on the crystal surface. The rate of this process is determined by [3]

$$\tau_d^{-1} = A \times v_g(E) \propto (1 - R) / L \times v_g(E). \quad (2)$$

Here, vg is the group velocity of the polaritons and R and L are the reflection coefficient and the film thickness, respectively. From Eq. (2), the lifetime of photon-like polariton is proportional to the group-velocity dispersion of the photon-like polariton branch. In our previous work, we reported that the decay time of the P emission changes with the detection energy and the energy dependence of that could be reproduced directly from the group-velocity dispersion of the photon-like polariton

branch [4]. However, the value of fitting parameter *A* obtained from the data fitting of experimental results is much smaller than that calculated from the values of *R* and *L* of the ZnO thin film. The detail of the relationship between the decay time of the P-emission and the lifetime of the photon-like polariton remain to be elucidated.

In this study, to understand the detail of the lifetime of the photon-like polariton state, we have investigated the ultrafast dynamics probed via the time-resolved PL spectra of the P emission process in ZnO thin films with the film thickness of 200 and 500 nm by using an optical-Kerr gating method at 10 K from the viewpoint of the propagation of the photon-like polaritons.

The samples used is a crystalline ZnO thin films grown on a (0001) Al_2O_3 substrate at 650 °C prepared by a pulsed laser deposition (PLD) method. Time-resolved PL spectra were measured by using the following optical-Kerr-gating method. The excitation energy and the excitation density were 3.59 eV and 65 μJ/cm^2, respectively. The detail of the experimental set up for OKG method is reported in Ref. 4.

Figure 1(a) and (b) shows the image plot of the time-resolved PL spectra in ZnO thin films with the film thickness of 200 and 500 nm, respectively. In the time-integrated PL spectra depicted by the solid curve, two PL bands labelled P and M were observed. From the emission energy, we decided that the P- and M-emission bands are originated from the exciton-exciton scattering and the biexciton in ZnO, respectively. Figure 2(a) and (b) show the decay profile of the P- and M-emission bands at the various detection energies in ZnO thin films with the film thickness of 200 and 500 nm, respectively. First, we focus on the decay profile at the detection energy of 3.345 eV whose energy is agree with the M-emission-peak energy, which shows in the bottom of Figure 2 (a) and (b). The decay time of M emission is estimated about 25 ps from the data fitting shown by the dashed line. This result indicates that the decay time of the biexciton is independent of the film thickness of 200 and 500 nm. On the other hand, the decay profile in the energy region observed the P emission change with the detection energy and the film thickness. In the detection energy from 3.305 to 3.265 eV, we found that the decay profile is composed of the fast and slow components in Figure 2(a) and (b). In this energy region, the P emission is main component of the time-resolved PL spectra. Therefore, the fast component is considered to be due to the P emission. Under the week excitation conditions, the low energy tail of the M emission is observed in the energy region located the P emission, which is not shown here. From this fact, the slow component is considered to be due to the M-emission. The decay time of the slow component becomes faster with a decrease of the detection energy. We consider that this result reflects the temporal change of the M-emission band, which will be reported elsewhere. Here, we focus on the decay time of the fast component originated from the P emission. The decay time of that becomes faster with a decrease of the detection energy. In addition, it is found that the decay time of the P-emission band of 200 nm thin film is shorter than that in 500 nm thin film at the same detection energy.

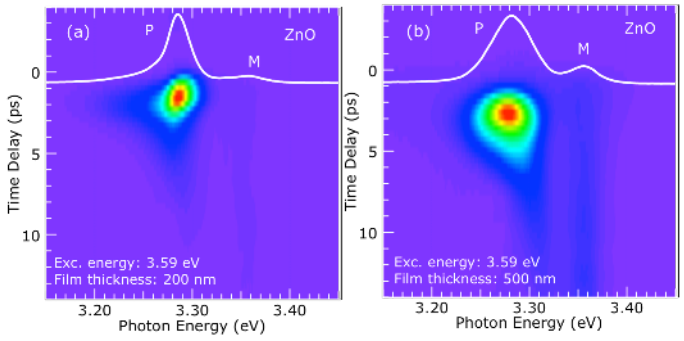

Fig. 1. Image plot of the time-resolved PL spectra in ZnO (a) 200 nm and (b) 500 nm thin films under the excitation power of 65 μJ/cm^2. The solid curve indicates the time-integrated PL spectra.

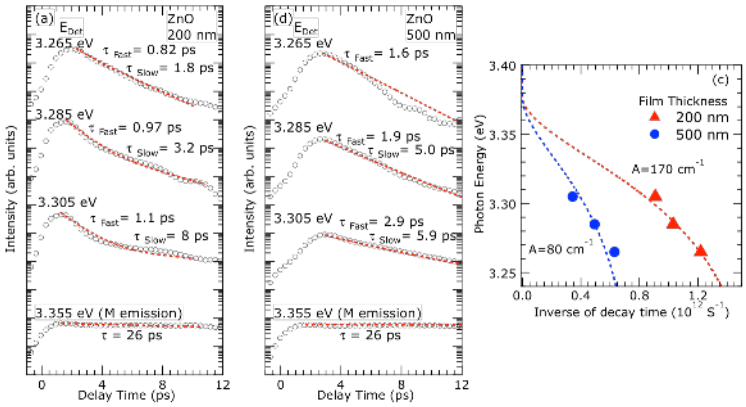

Fig. 2. The temporal profile of the PL intensity at various detection energies in (a) 200 nm and (b) 500 nm thin films. The dashed lines show the fitted results to the temporal profile in the PL decay region. (c) Relation between the inverse of the decay time of the P emission and the group velocity of the photon-like polariton. The dashed curve depicts the fitted result of the energy dependence of the group velocity on the basis of Eq. (2).

In order to elucidate the above properties of the decay profiles of P emission, we discuss the relation between the decay time of the P emission and the group velocity of the photon-like polariton based on Eq. (2). In Figure 2 (c), the circles and triangles indicate the inverse of the decay time of the P emission in 200 and 500 nm thin films, respectively, while the dashed curves show the fitted results of the energy dependence of the group velocity calculated from Eq. (2) with the fitting parameter A of 170 cm^{-1} for 200 nm thin film and 80 cm^{-1} for 500 nm thin film. The excellent agreement exists between the calculated values of the scaled v_g(E) based on Eq. (2) and the inverse of the P-emission decay time. On the basis of Eq. (2), the reflection coefficient of R is calculated to be ~0.99 in both film thickness samples. This result means that the photon-like polaritons are strongly confined in the ZnO thin film. However, this large reflection coefficient is a curious value because the low energy side below the lowest exciton-absorption band is considered to be the transparency region for photons. Now, we focus on the group velocity of the polaritons. In the ZnO bulk crystal, the group velocity of exciton-photon polariton at 3.285 eV is calculated 6.4×10^9 cm/s. On the other hand, the group velocity of that in 200 and 500 nm thin films is estimated 2.9×10^7 cm/s and 3.6×10^7 cm/s, respectively, from Eq. (2) by using the observed decay time (τ_d) and the reported value of the reflection coefficient (R) of 0.3 [5] and the sample thickness (L). This result demonstrates that the group velocity of the photon-like polariton generated by the exciton-exciton scattering in the ZnO thin film is two orders of magnitude slower than that calculated from the exciton-polariton dispersion in ZnO bulk crystals.

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