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Emission-energy dependence of ultrafast P-emission decay in ZnO from bulk to nanofilm

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ABSTRACT

We have performed time-resolved photoluminescence (PL) spectroscopy for ZnO thin films with thicknesses of 90, 460, and 2800 nm under intense excitation condition. We clearly observed the P emission due to inelastic exciton–exciton scattering. It was found that, in the 460- and 2800-nm thick samples, the decay time of the P emission considerably depends on the detection energy inversely proportional to the group velocity of the polariton in a bulk crystal with each factor of proportionality. In contrast, the energy dependence is less remarkable in the 90-nm thick sample. The decay times are basically shortened with a decrease in the film thickness. The thickness dependence of the P-emission-decay profiles is explained by considering the crossover from the polariton modes in the 2800-nm thick sample (bulk-like film) to the exciton-/photon-like modes in the 90-nm thick sample (nanofilm).

1. Introduction

Time-resolved photoluminescence (PL) spectral measurements are one of the most useful methods for understanding the dynamics of highly dense excitons. The intense emission called the P emission is caused by inelastic exciton–exciton scattering, which is an interesting subject from an aspect of dynamical processes of excitons and polaritons. In this scattering process, two excitons in the first quantized ($n=1$) state are scattered, and one exciton goes into a higher excited state with $n \geq 2$, while the other exciton is scattered into a photon-like polariton state with the energy lower than that of the $n=1$ state by the energy difference between the $n=1$ and $n \geq 2$ states. In this way, the dynamics of the P emission involves the polariton states; therefore, from the P-emission measurement, we can investigate the dynamical characteristics of the polaritons connected with the P-emission process. The temporal behaviors of the P-emission spectra have been investigated recently for CuI [1,2], ZnO [3–5], PbI_2 [6], $In_xGa_{1-x}N$ [7] and $Al_xGa_{1-x}As$ [8], and their decay times are generally shorter than the standard radiative recombination times of excitons. In contrast, the observed decay times of the P emission are two orders magnitude longer than those expected from a bulk-polariton propagation picture, the so-called wall collision model [9–11]. In addition, the decay time is independent of the pump power and can be thus considered apart from the early dynamics such as the P emission rise and cooling processes that have been observed to be much affected by the pump power [1,2]. Thus, it is expected that the observed decay time is closely related to the properties of the polariton state leading to the P emission. In this study, we have found that the decay time of the P emission at each detection energy is inversely proportional to the group velocity of the polariton state in ZnO thin films with thicknesses of 400 and 2800 nm, while the detection-energy dependence becomes less remarkable in a ZnO thin film with a thickness of 90 nm much shorter than the light wavelength of the P emission. We propose an interpretation that the thickness dependence of the decay time originates from the cross-over effect on the polariton state from bulk to nanofilm.

2. Experimental setup

The samples used are crystalline ZnO thin films grown on a (0001) Al_2O_3 substrate at 650 °C by a pulsed laser deposition (PLD) method. A commercially supplied ZnO ceramic plate with a purity of 99.99% was used as a target. A pulsed Nd:YAG laser was

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operated at a wavelength of 266 nm and a repetition rate of 10 Hz. The film thicknesses of the samples were 90, 460 and 2800 nm. It is obvious that the ZnO films have atomically smooth surface: The root mean square values of the surface roughness of $5 \times 5\ \mu m^2$ atomic force microscopy scan are $\sim$0.3, $\sim$0.9 and $\sim$1.6 nm in ZnO film with 90, 460 and 2800 nm thickness using the PLD, respectively. Time-resolved PL spectra were measured by using the optical-Kerr-gating (OKG) method. We used an yttria-stabilized zirconia (YSZ) single crystal as a Kerr-gating material. The time-gate width was 0.6 ps. The excitation energy and the excitation density were 3.59 eV and 72 $\mu J/cm^2$, respectively. The details of the experimental setup for the OKG method were reported in Ref. [1]. The sample temperature was kept at 10 K by a constant He-flow cryostat.

3. Results

Fig. 1 shows the time-integrated PL spectra (a–c) and the temporal profiles of the PL intensity at various detection energies (d–f), which the components of the M-PL band are subtracted on the basis of the spectral analysis in Ref. [4], in the ZnO thin films with (a, d) 90-, (b, e) 460-, and (c, f) 2800-nm thickness, respectively, under the excitation-power density of 72 $\mu J/cm^2$ at 10 K. In the time-integrated PL spectra, two PL bands labelled P and M were observed. Judging from the emission energy, we conclude that the P- and M-PL bands originate from the inelastic exciton–exciton scattering and the biexciton in ZnO [4,12], respectively. In Fig. 1(a–c), it should be noticed that the ratio of the intensity of the P-PL band to the M-PL band becomes higher in the samples with thinner thickness. In the 90-nm thick film, the P-PL band is observed as the main band, and the M-PL band is hardly observed. This result indicates that the density of excitons related to the P emission becomes more with decreasing the film thickness. It should be also noted that the rise time becomes shorter with decreasing the film thickness in Fig. 1(d–f). It is known that the inverse of the rise time of the P emission is proportional to the square of the exciton density in the bottleneck region [1]. Consequently, the intensity difference of the P-PL band is attributed to the difference of the exciton density related to the P emission.

Hereafter, we focus on the decay time of the P emission. The decay times (τ_d) of the P emission in the 90-nm thick sample at the detection energies of 3.20 eV, 3.24 eV and 3.28 eV have been observed to be the same of 0.9 ps, while ultrafast decay of 0.3 ps at 3.32 eV have been observed. The exciton-like polariton is considered to be less clearly determined in the region above around 3.3 eV because of the shortage of the thickness for photon–exciton interaction. The origin of such an ultrafast decay process remains as a future problem that should be addressed with further investigation. Therefore, apart from this unclear region, we focus on the energy region blow of 3.3 eV. The decay times (τ_d) of the P emission in the 460- and 2800-nm thick sample result in different

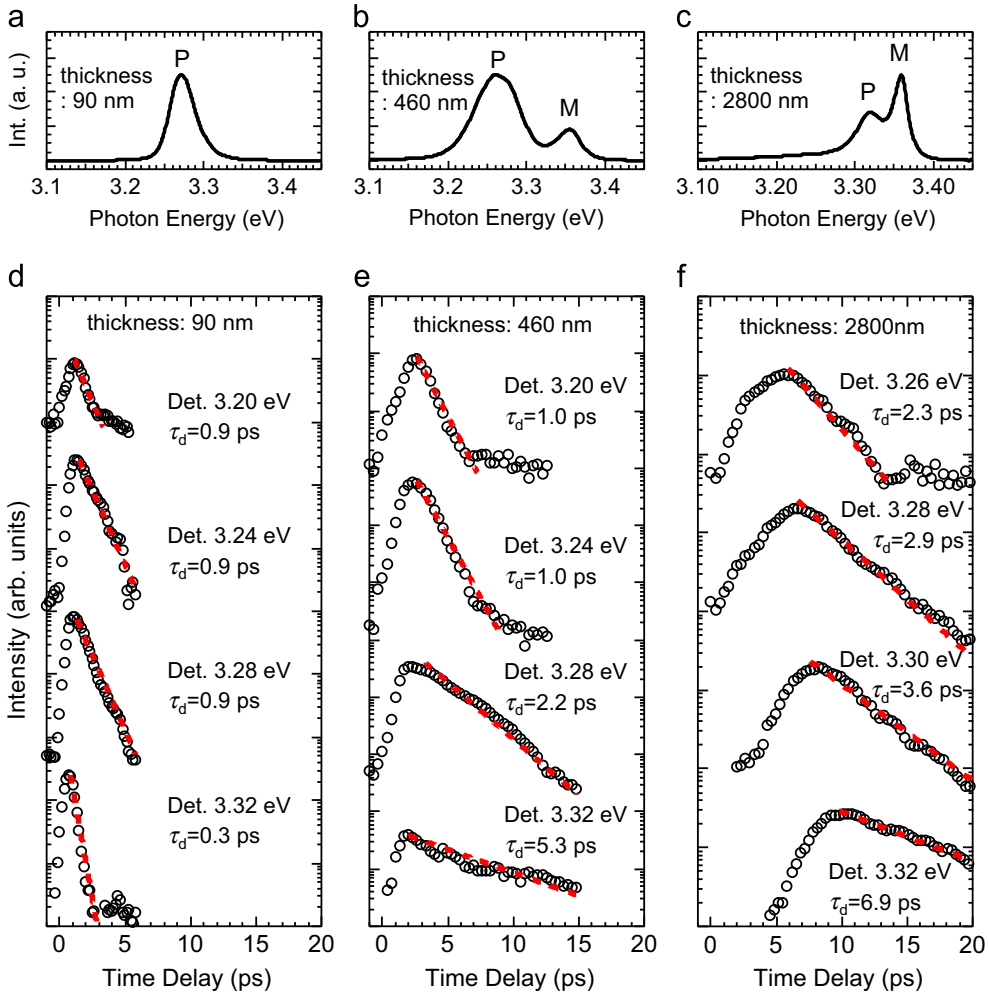

Fig. 1. Time-integrated PL spectra (a–c) and the temporal profiles of the PL intensity at various detection energies (d–f) in the ZnO thin films with (a, d) 90-, (b, e) 460-, and (c, f) 2800-nm thickness, under the excitation powers of 72 $\mu J/cm^2$ at 10 K. In the lower figures, the dashed lines show the fitted results to the temporal profile in the P-PL decay region.