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Dynamics of high-density excitons and electron-hole plasma
in ZnO epitaxial thin films

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Abstract

Time-resolved luminescence spectra due to an electron-hole plasma (EHP emission) and an exciton-exciton scattering process (P emission) were measured in ZnO epitaxial thin films under band-to-band excitation by the optical Kerr gate method. We found that both the EHP and P emissions emerge with a long time delay of a few picoseconds after the excitation. The time delay observed decreases quadratically with the excitation density below the critical Mott density. These results imply that the P (EHP) emission emerges after completing thermal cooling of excitons (electrons and holes) toward the exciton band bottom (renormalized bandgap) through multiple LO-phonon emissions. As the excitation density increases, the exciton-exciton scattering process also plays an important role on cooling and relaxation of high-density excitons.

Keywords: ZnO, electron-hole plasma, exciton-exciton collision, LO-phonon scattering, optical Kerr gate

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1. Introduction

Stimulated emission and lasing properties of highly excited ZnO-based II-VI compounds have been attracted much attention in optoelectronic device applications over the last decades, since ZnO has a large exciton binding energy (60 meV) and the exciton is stable even at room temperature. Under high excitation conditions, an exciton-exciton collision as well as recombination of an electron-hole plasma (EHP) is a key process leading to stimulated emission and lasing, and the luminescences due to the exciton-exciton collision process (P emission) and electron-hole plasma (EHP emission) have been extensively investigated in steady-state measurements so far [1-4]. To understand such luminescence properties, however, study on ultrafast dynamics and relaxation process of the high-density excitons and EHP is indispensable.

Recently, we first measured time-resolved luminescence spectra due to both the EHP and exciton-exciton scattering process from ZnO epitaxial films under resonant excitation of excitonic states by the optical Kerr gate (OKG) method [5,6]. At higher excitation density above the critical Mott density, luminescence due to the EHP instantaneously appears. It shows first a red shift with time due to thermal cooling toward a renormalized bandgap and then a blue shift due to recovery of the renormalized bandgap because of decrease of carrier density due to radiative recombination of electrons with holes. The EHP emission becomes replaced by the P emission after several picoseconds through a reverse Mott transition. At lower excitation density below the critical Mott density, on the other hand, the P emission emerges instantaneously and shows a red shift with time, implying that a thermal equilibrium process of excitons toward the bottleneck region takes place [6].

In the present work, we report on dynamics of highly excited ZnO epitaxial thin films under band-to-band excitation. Surprisingly, both the EHP and P emissions emerge with a long time delay of a few picoseconds after the excitation. We show that the time delay observed indicates that exciton-LO-phonon (carrier-LO-phonon) scattering process effectively

proceeds first and then the P (EHP) emission emerges after completing thermal cooling of excitons (electrons and holes) toward the exciton band bottom (renormalized bandgap) through multiple LO-phonon emissions.

2. Experimental

ZnO epitaxial thin films were fabricated on a sapphire (0001) substrate with/without an MgO buffer layer by a plasma-assisted molecular beam epitaxy method [7,8]. The typical sample thickness is 3800 nm. Time-resolved luminescence spectra were measured at room temperature by the OKG method [9,10]. The third harmonic pulses from a regenerative amplified mode-locked Ti:sapphire laser with a repetition rate of 1 kHz and a pulse duration of 100 fs were used as excitation pulses, while the fundamental ones used as gating pulses. The excitation energy of the third harmonics (4.65 eV) corresponds to band-to-band excitation of ZnO. We use a quartz plate having a 0.27mm-thickness as a Kerr medium and the overall time resolution of our system is about 400 fs. The experimental setup is almost the same as that reported in Ref. 10.

3. Experimental Results and Discussion

Figure 1 shows time- and spectral-resolved luminescence spectra of ZnO epitaxial thin films under band-to-band excitation at different excitation densities, (a) $8.0 \times 10^{19} \text{ cm}^{-3}$, (b) $3.5 \times 10^{19} \text{ cm}^{-3}$ and (c) $1.7 \times 10^{19} \text{ cm}^{-3}$. The time-integrated luminescence spectra are also shown in bottom of the figures. Above the critical Mott density ($3.7 \times 10^{19} \text{ cm}^{-3}$) [3], EHP emission is observed at $\sim 3.15 \text{ eV}$ as shown in Fig. 1(a). Below the critical Mott density, on the other hand, P emission is observed around $\sim 3.2 \text{ eV}$ as shown in Figs. 1(b) and 1(c), coming from an inelastic scattering process of excitons in which one of the two excitons scatters into a continuum state ($n=\infty$) and the other recombines radiatively. Surprisingly, both the EHP and P

emissions do not appear instantaneously after the excitation, but emerge with a long time delay of a few picoseconds.

The EHP emission first shows a red shift toward the renormalized bandgap energy, and then a blue shift to higher energy with time. Finally the EHP emission becomes replaced by the P emission through a reverse Mott transition. On the other hand, the P emission shows a slight red shift and a small decrease of the full-width at half maximum (FWHM) with time. The peak energy and FWHM in ~ 10 ps after excitation become close to constant values of 3.18 eV and 30 meV, respectively, which are the values observed in the steady-state experiment [11]. Except for the observed time delay of the EHP or P emission, the dynamics of highly excited ZnO seems to be essentially the same as that observed under the excitonic resonant excitation [6].

Figure 2 shows the inverse of the observed time delay as a function of excitation density in a log-log plot. ‘Time delay’ was decided time that the luminescence of strength of 1% of the maximum value of the luminous intensity appeared in 3.18eV after excitation. The vertical dotted line shows the critical Mott density of ZnO, and separates the high-density exciton region (P region) from the EHP region. The inverse of the time delay increases almost quadratically with the excitation density in the high-density exciton region as shown in a dotted line, while it shows a weak dependence on the excitation density in the EHP region.

To explain the above experimental results qualitatively, we take account of both exciton-LO-phonon (or carrier-LO-phonon) and exciton-exciton scattering processes occurring through cooling of excitons (carriers). Under the band-to-band excitation, at the excitation density below the critical Mott density, free electron-hole pairs are created by excitation pulses and instantaneously convert into excitons having high energy. Since the exciton-LO-phonon scattering process is most effective for cooling and relaxation of high energy excitons, the excitons relax toward the exciton band bottom along the lower polariton branch through cascade emission of multiple LO-phonons. When the exciton reaches to the bottleneck region, the exciton-LO-phonon scattering process is suppressed due to small density of final states to

scatter, and then the exciton-exciton scattering processes become dominant. Thus the P emission emerges after a long time delay of a few picoseconds accompanied with a slight red shift and a small decrease of the FWHM.

As the excitation density increases in the high-density exciton region, not only the exciton-LO-phonon scattering but also the exciton-exciton scattering must play an important role on relaxation and cooling of high-density excitons at the beginning, which causes shortening of the time delay. Since the exciton-exciton scattering rate is proportional to square of exciton density [12,13], the inverse of the time delay might quadratically increase with the excitation density in the high-density exciton region.

At the excitation density above the critical Mott density, electrons and holes with high energy are created by excitation pulses and form the EHP. Since the carrier-LO-phonon scattering more effectively takes place than radiative recombination of electrons with holes, the hot carriers relax toward the renormalized bandgap by emitting multiple LO-phonons. After completing the cooling toward the renormalized bandgap, the EHP emission emerges, leading to the time delay observed. Because the interaction between the ionized carrier (electron and hole) and LO-phonon is stronger than that between the neutral exciton and LO-phonon, the observed time delay in the EHP region might become shorter than that in the high-density exciton region. But the time delay in the EHP region weakly depend on the excitation density, we can't understand the cause.

In conclusion, we measured time-resolved luminescence spectra due to an electron-hole plasma and an exciton-exciton scattering process in ZnO epitaxial thin films under band-to-band excitation by the optical Kerr gate method. We found that both the EHP and P emissions emerge with a long time delay of a few picoseconds. This result shows that the P (EHP) emission emerges after completing thermal cooling of excitons (electrons and holes) toward the exciton band bottom (renormalized bandgap) through multiple LO-phonon emissions. As the excitation density increases, the exciton-exciton scattering process also plays an important role on cooling and relaxation of high-density excitons.

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Figure captions

Figure 1

Time- and spectral-resolved luminescence spectra of the EHP (a) and P (b and c) emissions under band-to-band excitations as shown in contours. Time-integrated luminescence spectra are also shown in the bottom of figures. The thick broken curves show the peak energy shift of the EHP and P emissions.

Figure 2

Inverse of the observed time delay as a function of excitation density in a log-log plot. A vertical dotted line shows the critical Mott density of ZnO.

Figure 1 *N. Arai et al.*

Figure 2 *N. Arai et al.*