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Effect of size and shape on the excitonic stimulated emission process in ZnO microstructures

Ryosuke Matsuzaki, and Takashi Uchino

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I. INTRODUCTION

Since the discovery of optically pumped lasing from polycrystalline ZnO,1,2 epitaxially grown ZnO thin films,3,4 and well-aligned ZnO nanowires5 at room temperature, a great number of studies have been carried out to investigate the underlying mechanism responsible for the lasing behavior.1-22 In particular, much attention has been devoted to Fabry-Perot nanowire laser5-11 and nanoparticle-based random laser.1,2,20-22 It has then been demonstrated that the lasing characteristics such as lasing threshold, lasing wavelength, and lasing modes are dependent not only on the crystallinity but also on the size, shape, and morphology of ZnO.5,6-10,20

Nanoparticle-based random laser is realized by recurring multiple scattering events of light in aggregated ZnO particles with sizes of several hundreds of nanometers.1,2,22 In these ZnO nanostructures, lasing spikes, i.e., discrete emission peaks with a linewidth of less than ~1 nm, are observed at pumping intensities over the threshold excitation for lasing. It has also been demonstrated that both localized and extended modes contribute to the generation of the lasing spikes from ZnO nanostructures.23 This indicates that random lasing occurs not only in strongly scattering systems but also in weakly scattering ones24-26 although the true physical origin of the narrow random lasing lines is still being debated.27

However, when the size of ZnO particles becomes larger than several micrometers, such narrow lasing spikes are not normally observed. It is hence probable that the conditions for realizing localized and/or extended modes are not reached in powders of micrometer-sized ZnO particles. Notwithstanding the absence of random lasing spikes, we can still expect the realization of feedback in the micrometer-sized ZnO particles. The relevant feedback in the ZnO microcrystals will not be coherent but can be used merely to return part of the energy or photons to the starting point, leading to energy or intensity feedback. This type of random laser is referred to as random laser with incoherent feedback,22 in contrast to the case of nanoparticle-based random laser with coherent feedback.22,26

Recently, we have demonstrated that the incoherent-feedback random lasing is likely to be realized in a film consisting of well-crystallized micrometer-sized ZnO grains. It should be stressed that room-temperature excitonic lasing is observed from the film of micrometer-sized grains without showing any symptoms of electron-hole plasma (EHP) emission. We have also found that the temperature-induced transition from the exciton-exciton (ex-ex) scattering to the exciton-electron (ex-el) scattering occurs at temperatures near ~150 K; the ex-el process continues to exist with further increasing temperature up to room temperature. The long carrier diffusion length and the low optical loss nature of the micrometer-thick ZnO films presumably play a key role in showing purely excitonic lasing at room temperature. In such micrometer-sized ZnO crystals, the concentration gradients of the photogenerated carriers created at the near surface will push them deeper into the sample, rapidly reducing their concentration below the Mott density even...
under highly excited conditions to allow pure excitonic lasing. These results will shed light on the nature of the room-temperature excitonic lasing in ZnO because its true physical origin, which was initially attributed to exciton-exciton (ex-ex) scattering process, is still a matter of discussion.

Although the ex-el scattering has been shown to be the principal gain process in ZnO microcrystals at room-temperature, the mechanism of the optical (mirrorless) feedback in these microstructured systems is still not well understood. To investigate this further, we perform systematic photoluminescence (PL) measurements of various ZnO microstructures with different size and shape. We show that excitonic lasing is observed exclusively from the sphere-like ZnO particles with a size larger than a few micrometers. Also, the temperature-induced transition between the ex-ex and ex-el processes has been shown to occur at $\sim 150$ K in these sphere-like ZnO microparticles, in agreement with the results observed from the ZnO film of micrometer-sized grains.

II. EXPERIMENTAL PROCEDURES

We prepared micrometer-sized ZnO particles by thermal decomposition of zinc acetate dihydrate, which is a simple but effective method to obtain variously sized and shaped ZnO particles. We first pre-annealed $\sim 2.6$ g of reagent grade zinc acetate dihydrate (Sigma-Aldrich, purity $\geq 98\%$), which was placed in an aluminum crucible covered with an alumina lid, in an electric furnace at 300°C for 12 h in air atmosphere. The resulting materials were washed with distilled water and dried in an oven at 90°C for 12 h. The dried samples were then post-annealed at 800 – 1100°C for 3 h in air. The resulting samples were stored in a desiccator for later characterization. Powder X-ray diffraction (XRD) patterns were obtained with a diffractometer (Rigaku, SmartLab) using Cu Kα radiation. Scanning electron microscopy (SEM) was conducted with a scanning electron microscope (JEOL, JSM-5510). PL measurements were carried out with a gated image intensified charge-coupled device (Princeton Instruments, PI-MAX:1024RB) and 1800 or 300 lines/mm grating by using the third harmonic (355 nm) of a Q-switched Nd:yttrium aluminum garnet (YAG) laser (Spectra Physics, INDI 40, pulse width $\sim 10$ ns, repetition rate 10 Hz) as an excitation source. During the PL measurements, the laser pulse was irradiated onto a quartz sample holder containing ZnO powder without focusing the laser beam (beam spot size of $\sim 7$ mm), and the emission signal from the front surface was monitored. The sample temperature was controlled in an optical cryostat system in the temperature region from 3 to 300 K.

III. RESULTS

Figure 1 shows the XRD patterns and SEM images of the samples post-annealed at different temperatures from 800 to 1100°C. Although all the samples have the hexagonal wurtzite structure of ZnO [Fig. 1(a)], the crystalline morphology varies from deformed rod-like ($\sim 100$ nm in diameter, $\sim 2$ µm in length) to irregular spherical shapes (typical size $\sim 2 – 3$ µm in diameter) with increasing annealing temperature, as shown in the SEM images in panels (b) to (e) in Fig. 1.

Room-temperature PL spectra of these micrometer-sized ZnO crystals for increasing optical excitation are shown in Fig. 2 in a semi-log plot. The near-band edge (NBE) emission of the 800°C sample exhibits a broad spectral feature under the excitation fluence $I$ ranging from 0.3 to 52 mJ/cm² [Fig. 2(a)], which broad NBE emission stems from the superimposition of the thermally broadened free exciton (FX) recombination and its longitudinal-optical (LO) phonon replica. Note also that this broad emission feature is observed from all the samples employed in this work [Figs. 2(b)–2(d)], indicating that this excitonic band is due to spontaneous emission and therefore occurs irrespective of the shape and size of the particles. Also, the PL spectra of the 800°C sample shows an almost linear increase in intensity and bandwidth with increasing $I$ up to $\sim 20$ mJ/cm², followed
by saturation at higher excitation fluences [Fig. 3(a)]. This result is consistent with the spontaneous emission scenario. However, the NBE emission of the samples prepared at temperatures higher than 900 °C exhibits spectral narrowing under highly excited conditions [Figs. 2(b)–2(d)], implying the occurrence of laser action. Indeed, as shown in Fig. 3(b), the spectral narrowing of the 1100 °C annealed sample is accompanied by a nonlinear increase in the integrated emission intensity with increasing $I$ [Figs. 2(b)–2(d)], thus supporting the lasing interpretation. The lasing threshold ($I_{th}$) can be defined as the pumping fluence at which the spectral narrowing initially sets in. We found that $I_{th}$ decreases with increasing post-annealing temperature, i.e., the $I_{th}$ values of the 900, 1000, and 1100 °C annealed samples are 31, 26, and 18 mJ/cm$^2$, respectively. Note, however, that the present lasing is most likely due to the random lasing.

FIG. 2. Excitation fluence dependence of the room-temperature PL spectra of the ZnO samples prepared at (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C. In (b) and (c), the threshold fluence for spectral narrowing ($I_{th}$) is shown.

FIG. 3. The excitation fluence dependence of the full width at half maximum (FWHM, right axis) and the spectrally integrated PL intensity (left axis) of the ZnO samples prepared at (a) 800 °C and (b) 1100 °C.
with incoherent feedback since no modal emission is observed, as will be discussed in more detail in Sec. IV. These observations suggest that ZnO particles with larger spherical shapes preferentially contribute to the narrowing behavior. It should also be worth mentioning that as shown in Figs. 2(b)–2(d), the peak energy and width of the observed lasing spectra are almost constant as \( I \) increases from \( \sim 10 \) to \( \sim 50 \text{ mJ/cm}^2 \). This indicates that bandgap renormalization due to many-body effects in an EHP does not occur in the sample under the present excitation condition. These results are quite similar to those reported previously for the ZnO film consisting of micrometer-sized grains.29

To further investigate the lasing characteristics of the micrometer-sized ZnO particles, we next carried out low-temperature PL measurements for the 1100 °C sample. Figure 4 shows the excitation-fluence-dependent PL spectra measured at 3 K. The PL spectrum obtained under the lowest excitation fluence \( (I_{\text{exc}} = 0.1 \text{ mJ/cm}^2) \) shows several emission lines at 3.360, \( \sim 3.31, \sim 3.29, \) and \( \sim 3.22 \text{ eV} \). The peak at 3.360 eV is attributed to a donor bound exciton emission \( (\text{D}^0\text{X})_{36,37} \) and the two lower energy peaks at \( \sim 3.29 \) and \( \sim 3.22 \text{ eV} \) to its first and second longitudinal optical (LO) phonon replicas \( (\text{D}^0\text{X}-\text{LO} \text{ and D}^0\text{X}-2\text{LO}) \), respectively.37

The \( \sim 3.31-\text{eV} \) band is likely to result from the stacking fault related transition \( (n=2,3, \ldots \infty) \). As the excitation fluence increases, one finds that two additional peaks grow on the lower energy side of the \( \text{D}^0\text{X} \) band. One is the peak at 3.353 eV, which can be recognized in the PL spectra obtained at \( I = 0.3 \text{ mJ/cm}^2 \) or higher. This emission is tentatively attributed to the donor-bound biexciton \( (\text{D}^0\text{M})_{51,42} \) when \( I \) exceeds \( \sim 4 \text{ mJ/cm}^2 \), the other peak develops in the 3.32–3.33 eV region [see the pink-colored area in Fig. 4(a)]. This peak dominates the entire spectrum for \( I \geq 10 \text{ mJ/cm}^2 \) and shows a slight red shift with a further increase in \( I \). The integrated emission intensity shows a nonlinear increase with increasing excitation fluence with an excitation threshold of \( \sim 7 \text{ mJ/cm}^2 \) [Fig. 4(b)]. This newly developed peak can be attributed to the stimulated emission induced by ex-ex scattering, in which one exciton recombines radiatively, while the other is scattered into a higher state \( (n=2,3, \ldots \infty) \). The emission maxima of the ex-ex process can be given by

\[
\hbar \omega_{\text{ex-ex}}(T) = E_{\text{ex}}(T) - E_{\text{b}} \left( 1 - \frac{1}{n^2} \right) - \frac{3}{2} k_BT,
\]

where \( E_{\text{ex}}(T) \) is the free exciton transition energy at a temperature \( T \), \( E_{\text{b}} \) is the binding energy of the exciton (60 meV), and \( k_B \) is the Boltzmann constant. When we assume that \( E_{\text{ex}}(T) = 3.377 \text{ eV} \) at 3 K, \( n=2 \) and \( \infty \) predicted from Eq. (1). One sees from Fig. 4(b) that in the temperature range from 3 to \( \sim 150 \text{ K} \), the observed peak energy lies within the energy range predicted for the ex-ex scattering process. At temperatures above \( \sim 150 \text{ K} \), however, the observed peak energy shows a substantial deviation from the energy range of the ex-ex scattering, implying the onset of an alternative emission process. We found that similar to the case of the ZnO film of micrometer-sized grains,29 the temperature dependence of the expected alternative process is well described by that of the exciton-electron (ex-el) scattering process, which is given by \( \text{Eq. (1)} \).
where $\gamma$ is a constant related to the ratio of exciton effective mass over electron effective mass. The fitting with Eq. (2) was performed for the data points in the 160–300 K range, and the result of fitting is shown in Fig. 5(b) as a solid (blue) line. The best fitted value of $\gamma$ is 5.5, which is slightly smaller than the one obtained for the ZnO film of micrometer-sized grains ($\gamma = 6.1$) but is still in reasonable agreement with the predicted value of $\gamma = 7$.\(^{33,44}\)

**IV. DISCUSSION**

We have shown that the ZnO aggregates obtained by post-annealing at 800 °C did not show any lasing action [see Fig. 2(a)]. This is probably due to their highly deformed and ill-crystallized structures, in which the optical loss and surface recombination of these small grains are too large to exhibit a practical laser action. As the post-annealing temperature increases, the ZnO aggregated particles tend to become large and spherical although still deformed. Accordingly, one can recognize the lasing behavior, i.e., the appreciable spectral narrowing and nonlinear intensity enhancement of the luminescence, for the samples obtained by post-annealing at temperatures above 900 °C [Figs. 2(a)–2(c)]. It can hence safely be assumed that the low-loss feedback condition is achieved in the large spherical ZnO grains. Note, however, that the spatial resonances for the electromagnetic field are likely to be absent because light will not necessarily return to its original position after one round trip in these deformed particles. We hence consider that the feedback is non-resonant and is used only to return part of the photon energy to the gain medium, resulting only in incoherent energy feedback.\(^{22,24}\) Indeed, we did not observe a spiky feature, which is an indication of coherent feedback.\(^{22,26}\) and it is absent in the present lasing spectra. In such an incoherent energy feedback system, the mean frequency of laser emission does not depend on the dimensions of the gain medium but is determined only by the center frequency of the amplification line.\(^{46}\) This can explain the observation shown in panels (b), (c), and (d) in Fig. 2 that the present ZnO microparticles prepared after different post-annealing temperatures exhibit basically the same lasing peak at 3.17 eV at room temperature.

It should also be worth mentioning that the excitonic lasing behavior of the present ZnO microparticles is quite similar to that of the ZnO film of micrometer-sized grains.\(^{29}\) Both the samples not only exhibit a transition from ex-ex to ex-el processes at ~150 K but also demonstrate no signs of EHP emissions under the present excitation conditions (±50 mJ/cm\(^2\)). The only apparent difference between the two samples is the excitonic lasing threshold $I_{EX}^{EX}$; the $I_{EX}^{EX}$ values for the film and the particle samples are ~2 mJ/cm\(^2\) (or ~200 kW/cm\(^2\)) and ~20 mJ/cm\(^2\) (or ~2 MW/cm\(^2\)), respectively, at room temperature. We suggest that the higher threshold of the particle samples results from the low efficiency of the energy feedback because of their irregular shape and high optical loss. However, the absence of the EHP emission implies that the density of electron-hole pairs $n_p$ is still below the Mott density at $I_{EX}^{EX}$ even for the present particle samples. It is hence interesting to estimate the $n_p$ values at $I_{EX}^{EX}$ for these samples. When the sample size $d$ is comparable to or larger than the diffusion length $l_D$ (~3 μm) of the excited carriers, which is the case for the present micrometer-sized ZnO crystals, $n_p$ can be estimated by\(^{17}\)

$$n_p = \frac{P \tau}{h \omega l_D},$$

where $P$ and $h \omega$ are the excitation power (in W/cm\(^2\)) and the photon energy (in J) of the light source, respectively, and $\tau$ is the decay time of the stimulated emission (4 ps).\(^{29}\)
mentioned in Ref. 29, \( n_p \) of the ZnO film of micrometer-sized grains at the lasing threshold (\( P = 200 \text{ kW/cm}^2 \)) is estimated to be \( \sim 5 \times 10^{15} \text{ cm}^{-3} \), which is two or three orders of magnitude lower than the reported value of the Mott density \((\sim 10^{19} \text{ cm}^{-3})\). On the other hand, \( n_p \) of the micrometer-sized ZnO particles at the threshold (\( P = 2 \text{ MW/cm}^2 \)) is calculated to be \( \sim 5 \times 10^{16} \text{ cm}^{-3} \). The resulting electron-hole density is still at least an order of magnitude lower than the Mott density. Thus, the evaluation of \( n_p \) allows us to confirm that the room-temperature lasing of the micrometer-sized ZnO particles observed under the present excitation condition is of excitonic origin. It is hence most likely that the low-loss feedback condition is satisfied, micrometer-sized ZnO structures can exhibit common excitonic lasing behaviors in a wide temperature region, including room temperature.

V. CONCLUSIONS

We have carried out systematic PL measurements of the differently sized/shaped ZnO particles. The lasing threshold, which corresponds to a condition in which the photon loss rate is balanced by the photon generation rate in the amplifying region, decreases as the particles grow into sphere-like structures with the size of a few micrometers. It is most likely that the incoherent energy feedback is responsible for the observed lasing action. As for these sphere-like particles, the gain mechanism is changed from the ex-ex scattering (below \( \sim 150 \text{ K} \)) to the ex-el scattering (above \( \sim 150 \text{ K} \)) with increasing temperatures. The density of electron-hole pairs at the room-temperature lasing threshold is an order of magnitude lower than the Mott density, confirming that the EHP at the room-temperature lasing threshold is an order of magnitude lower than the Mott density. Thus, the evaluation of \( n_p \) is still at least an order of magnitude lower than the Mott density, confirming that the EHP at the room-temperature lasing is an order of magnitude lower than the Mott density. Thus, the evaluation of \( n_p \) is still at least an order of magnitude lower than the Mott density, confirming that the EHP at the room-temperature lasing is an order of magnitude lower than the Mott density.