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## Observation of optical bistability in a ZnO powder random medium

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Optical bistability has been observed in photoluminescence from a ZnO powder random medium. The emission spectra and the excitation intensity dependence of 420 nm emission clearly exhibit the existence of bistable steady states with changing excitation intensity. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338533]

Zinc oxide (ZnO) has been an attractive material, particularly over the past decade, because of its excellent high emission efficiency, good electrical conductivity, high binding energy, transparency in the visible region, and wide emission range (green to UV).<sup>1-5</sup> ZnO has therefore been investigated for various applications including photoluminescent or cathodoluminescent display elements and light sources, solar battery panels, photocatalysis, and thin-film transistors.<sup>6-12</sup> For improvements in performance and optical properties, technological developments have been mainly focused on the fabrication of high quality bulk ZnO single crystals. Meanwhile, size-reduction and morphological effects of ZnO have also been investigated to improve nonlinear performance. Lasing and stimulated emission have been reported in nanocrystalline thin films,<sup>2,4,5</sup> nanoparticles,<sup>7,10</sup> and nanorods<sup>13,14</sup> at room temperature in contrast to bulk ZnO. In this letter, we report observations of bistable photoluminescence from a random medium composed of ZnO nanoparticles at room temperature. In conjunction with the importance of and the significant attention paid to ZnO materials, this bistability is of great interest for technological applications for optical switching and photon manipulation.

ZnO powder (diameter <1  $\mu\text{m}$ , purity of 5N, Kojundo Chemical Lab. Co., Ltd.) and ZnO single crystal substrates (10 $\times$ 10 $\times$ 0.5 mm<sup>3</sup>, purity of 4N, Techno Chemicals, Inc.) were used in the study. The ZnO powder was dispersed in an ethanol solution and dropped on a cover glass. A ZnO powder film was formed by drying in air at room temperature, and the specimen was set on an optical microscope stage. Second harmonic pulses of a mode-locked Ti:sapphire laser (390 nm, 80 MHz,  $\sim$ 100 fs) were focused onto the sample under the microscope (spot size  $\sim$ 3  $\mu\text{m}$ , 40 $\times$  oil-immersion objective lens). Emission from the sample was collected by the same objective lens, passed through a pinhole (diameter  $\sim$ 3  $\mu\text{m}$  at the sample plane), and then detected by a spectroscopy equipped with a cooled charge-coupled device camera for spectral measurements. All measurements were performed in air at room temperature.

Figure 1 shows the typical observed emission spectra and the emission images obtained by changing the excitation intensity. At low excitation intensities, green emission around 550 nm was dominantly observed [curve (b) and image (d)]. This could be attributed to the green band emission usually observed for bulk ZnO. When the excitation intensity increased above a certain threshold, blue emission intensity around 420 nm suddenly increased and the peak position ap-

peared to be redshifted [curve (a) and image (c)], while the green emission spectra did not change. In contrast, when the excitation intensity decreased from an intensity higher than this threshold, we found that the blue emission intensity suddenly decreased and the emission spectrum reverted back to the spectrum of curve (b). The emission spectra exhibited similar behaviors at different locations in the same film, even though their thresholds were different. However, we also confirmed that the green emission did not exhibit such nonlinear behaviors at any location with changing excitation intensity, and the intensity distribution of the green emission is almost homogeneous everywhere in the ZnO powder film. Thus, the results suggest that position-dependent nonlinear phenomena of the blue emission, not the green emission, were induced in the ZnO powder film.

For confirmation of this behavior, we logarithmically plotted these blue emission intensities as a function of the excitation intensities, which were measured at two different locations (filled circles and squares in Fig. 2). The triangles indicate the intensities of the green emission from the same spot as the filled circle data for reference. The two solid lines with numbers in Fig. 2 indicate the slopes of the logarithmic plots. From the results, the thresholds for blue emission are clearly observed in the curves of the filled circles and squares, although the green emission linearly increases and is almost saturated. Above the threshold, the blue emission intensity exceeds the intensity of the green emission by about ten times, while the green emission is dominant at low excitation intensities. Thus, the change in the emission image shown in Figs. 1(c) and 1(d) was observed.

In particular, in the case of the filled circle curve, the spectra for which are shown in Fig. 1, we can observe the bistability with changing excitation intensity. In Fig. 2, it is

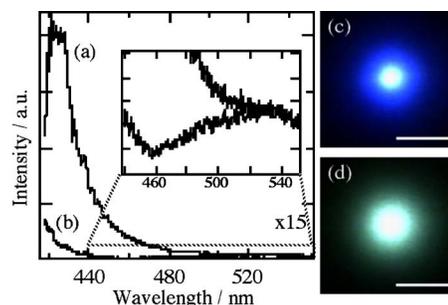


FIG. 1. (Color online) Emission spectra and images observed in the medium with [(a) and (c)] high and [(b) and (d)] low excitation intensities, respectively. White bars in (c) and (d) indicate the scale bar of 20  $\mu\text{m}$ . The inset shows the enlarged view of the green emission area.

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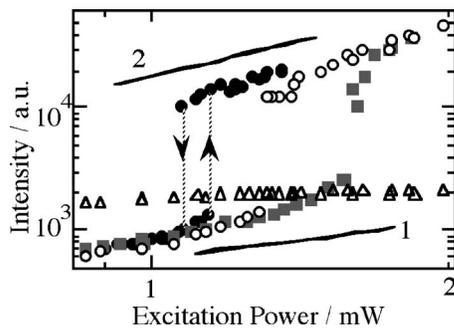


FIG. 2. Excitation intensity dependence of 420 nm emission intensity from a ZnO powder film. The filled circles and squares indicate blue emission intensities measured at different locations. Triangles represent the green emission measured at the same location as the filled circles. Open circles indicate blue emission intensities at the same location as the filled circles after high excitation intensity irradiation. The numbers and solid lines represent the slopes of logarithmic plots.

clearly seen that the intensity of the blue emission in a lower stable state suddenly jumps to a higher stable state when the excitation intensity increases to above  $\sim 1.14$  mW ( $16.1$  kW/cm<sup>2</sup>). Adversely, the higher stable state is maintained when the excitation intensity decreases to  $\sim 1.03$  mW ( $14.6$  kW/cm<sup>2</sup>). When the excitation intensity was set between the two thresholds and the sample was kept in the lower or higher stable state, we confirmed that this lower stable state was maintained for more than 1 h. Therefore, the bistability likely did not originate from heating effects. In addition, the repeatability of the bistability was also confirmed in the region of the measured excitation intensity.

In order to explain the bistability, we need to consider the blue emission mechanism and the effect of the random medium. In Fig. 2, as the slopes of the blue emission changed from the first (lower stable state) to the second (higher stable state) order over the threshold, blue emission would be induced by a two-photon excitation process. Meanwhile, the slope of the green emission exhibited the first order and then saturated at higher excitation intensities. These results and the fact that the bistability is strongly position dependent yield clues for understanding the origins of the blue emission around 420 nm and the bistable photoluminescence. Based on previous studies,<sup>1,2,4</sup> in which 420 nm emission was reported as electron-hole plasma (EHP) state at higher excitation intensity and depended on the square of the excitation intensity, we considered that the reason for the change in the slope would be related to the EHP state. However, it is worth noting that, in recent works on photoluminescence measurements of ZnO nanostructures at weak excitation intensity, 420 nm emission was identified as shallow defects.<sup>15,16</sup> Unfortunately, as we have no sufficient data to determine the origins of the 420 nm emission and the sudden increase and since 420 nm emission has hardly been reported, we have to note that the origin of this strange behavior is still uncertain and requires further study. In any case, we considered that some nonlinearity (absorption saturation, spectral change, lasing, or two-photon excitation) should be included in order to explain the observed strange behaviors, and the emission or excitation process would be strongly affected by the random medium, and consequently the position dependence would occur.

By repeating the measurements of the excitation intensity dependence at different locations in the ZnO powder

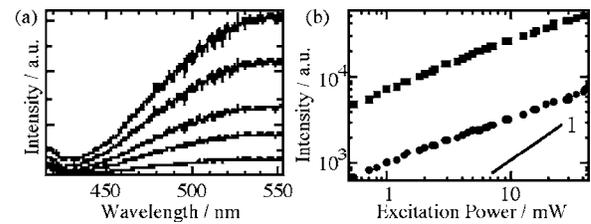


FIG. 3. (a) Emission spectra and (b) excitation intensity dependence of a ZnO single crystal. Squares and circles indicate the dependence of the green and blue emissions, respectively. Solid line with number indicates the slope of the first power of the excitation intensity.

film, we found that such optical bistability could be observed at any location, but with different thresholds, as long as the excitation intensity did not exceed a certain damage threshold, which was also dependent on the location. For instance, open circles in Fig. 2 show the excitation intensity dependence after strong irradiation with excitation laser [ $\sim 3.6$  mW ( $50.9$  kW/cm<sup>2</sup>)] measured at the same location as the filled circle data. An increase in the threshold and the disappearance of the bistability can be clearly observed. However, the shapes of the emission spectra above and below the new threshold did not change from those before the strong excitation. By observing scanning electron microscope (SEM) images of the sample, we found that the scanned area with excitation intensity over the damage threshold was clearly changed when compared to the surrounding area and formed a V-shaped groove. The surface of the V-shaped groove was not melted because we could clearly see nanoparticles at the surface of the groove in SEM images. From this result, it is clear that photodecomposition of the ZnO nanoparticles would occur under excitation intensity over the damage threshold and result in irreversible morphological changes in the ZnO powder film. Therefore, when the morphological change was irreversibly induced, the local field enhancement due to multiple light scattering would decrease, resulting in an increase in the threshold and disappearance of the bistability.

In order to further confirm the importance of the random structure and the form of the ZnO (nanoparticles, not the bulk), the same measurements were performed using a ZnO single crystal for comparison. Figure 3 shows the emission spectra and the excitation intensity dependence and the solid line with a number indicates the slope of the first power of the excitation intensity. Only green emission was dominantly observed in the measured excitation intensity range, and the spectral profiles were not changed as a function of the excitation intensity. The threshold and bistability were not observed, even when the excitation intensity was increased to  $\sim 40$  mW ( $\sim 0.56$  MW/cm<sup>2</sup>). Thus, we consider that the morphological properties of the random structure and ZnO nanoparticles are important features to induce bistable photoluminescence in the ZnO powder film.

In summary, we have demonstrated optical bistability of blue emission from the ZnO powder random medium, whose repeatability could be confirmed as long as the excitation intensity was lower than the damage threshold. From the results, we considered that the morphological properties of the random structure and the ZnO nanoparticles play a key role in achieving bistable photoluminescence. As the conclusive evidence to explain the observed phenomena is still uncertain, further studies of ZnO nanoparticles are needed for

future work. However, considering the wide use of ZnO materials for various applications, this bistability observed in the ZnO powder film has the potential for technological applications related to optical or electro-optical switching and photon manipulations in microcavity structures.

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