Efficient multiphoton-absorption-induced luminescence in single-crystalline ZnO at room temperature

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At room temperature, multiphoton absorption- (MPA-) induced photoluminescence in ZnO strongly driven by a femtosecond (fs) near-infrared laser is studied. Two-photon absorption and three-photon absorption are proved to be responsible for the intense luminescence, when the wavelength of the fs excitation laser is above and below the half-bandgap of ZnO, respectively. Strong MPA absorption in ZnO is unambiguously evidenced by the interferometric autocorrelation measurements of the luminescence signal. © 2005 Optical Society of America

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Recently ZnO has attracted renewed interest as a promising optoelectronic material in the UV for laser diodes and light-emitting diodes operating at room temperature owing to its wide bandgap and extremely large binding energy of free excitons.[1–4] In the past several years, spontaneous and stimulated emissions, the dynamics of photoexcited carriers, donor–acceptor pair recombination, and the dependence of photoluminescence (PL) on excitation power in ZnO and its microstructures have been extensively investigated.[5–9] All these studies were based on single-photon absorption induced by ultrafast UV lasers. Investigations of the nonlinear optical properties and ultrafast optical processes in ZnO based on two-photon and even multiphoton absorption (MPA), however, have been relatively few.[10–15] In particular, MPA-induced luminescence in ZnO has not been reported to our knowledge. Here we attempt to fill this void. Using a near-IR tunable-wavelength femtosecond laser, we observed efficient MPA-induced PL of ZnO at room temperature. The dependence on excitation power and the interferometric autocorrelation curves of the PL intensity were measured. Unambiguous experimental evidence for two-photon absorption (2PA) and three-photon absorption (3PA) was found when the photon energies of the excitation laser were higher and lower, respectively, than the half-bandgap of ZnO. In particular, the observation of efficient 3PA in ZnO is of scientific significance because this phenomenon is rarely reported in wide-bandgap semiconductor materials.

The sample used in this study is a wurtzite ZnO single crystal with thickness of ~1 mm. Its linear PL properties under excitation by a He:Cd cw UV laser (325 nm) are well characterized, and the results obtained agree well with those reported in the literature. The femtosecond laser source used in our experiments is a 10 W solid-state laser- (Millennia) pumped self-mode-locked Ti:sapphire oscillator (Tsunami). It delivers ~80 fs laser pulses with a repetition rate of 82 MHz. The tunable wavelength range of the pulses is 700–1000 nm, and their maximum output power can reach 1.7 W at 800 nm. During the measurements the excitation laser is almost normally incident onto the surface of sample. The luminescence signal from the sample is collected with a pair of lenses and is dispersed with an Acton SP300 monochromator equipped with a photomultiplier (Hamamatsu R928) detector. A blue band color filter is used to block the laser line. A standard lock-in amplification technique is employed for the PL measurements. For power-dependent measurements the intensity of the incident laser is controlled with a neutral-density metallic filter. The interferometric autocorrelation measurements of the sample PL signal are carried out with an experimental arrangement based on a Michaelson interferometer.[16] For the PL interferometric autocorrelation measurements the time delay between two collinear laser beams with identical intensity is determined with a time-delay translation stage (PI, Germany) that has sub-femtosecond time resolution. All the experiments are performed at room temperature.

Figure 1 shows representative MPA-induced PL spectra of ZnO excited by a femtosecond laser with several laser wavelengths at room temperature. There are two emission bands: a narrow UV band at 395 nm (3.14 eV) and a broad visible (VIS) band centered at ~492 nm (2.52 eV). The peaks marked by vertical arrows are the second-harmonic generation signals of the laser lines.[17,18] The UV emission band is due to electron–hole plasma emission, which is 230 meV below the bandgap, ~3.37 eV (368 nm) of ZnO at room temperature and is a result of bandgap renormalization that happens immediately after intense excitation and has been well discussed in the

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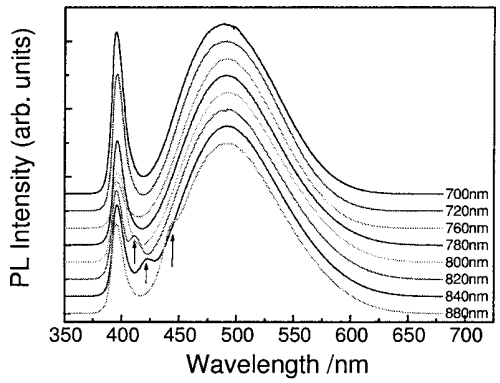

Fig. 1. MPA-induced PL spectra of ZnO at room temperature.

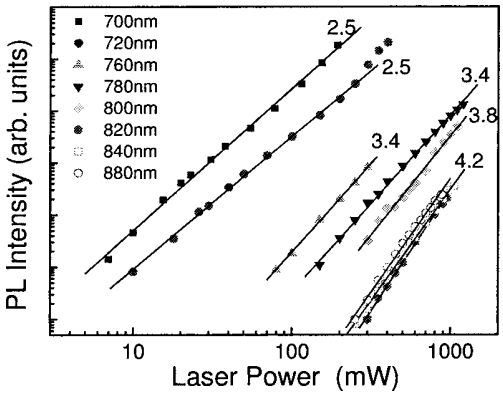

Fig. 2. Dependence on excitation power of the integrated intensity of the UV emission band. Solid curves are the results of fitting.

literature.[8,9] The broad VIS emission band is due to the deep luminescent centers in ZnO. As the energies of the excitation photons are well below the bandgap of ZnO, the observed luminescence bands are certainly due to MPA. To elucidate the MPA properties we measured the dependence of the UV emission band on excitation power for several laser wavelengths, and the results are shown in Fig. 2 on a logarithmic scale. The threshold of the excitation power for MPA and its wavelength dependence are apparently from the data in Fig. 2. Under the experimental conditions of the present study, the PL can be detected for excitation powers as low as 10 mW when the wavelength is less than 730 nm. However, if the wavelength of the excitation laser is longer than 780 nm, an excitation power as large as 200 mW is required for observation of the luminescence signal. As is discussed and evidenced below, 2PA and 3PA dominate for wavelengths of <730 and >780 nm, respectively. For the wavelength range 730–780 nm, 2PA and 3PA coexist. In Fig. 2 the solid curves are the results of fitting to the experimental data. The slopes obtained are 2.5 for 700 and 720 nm, 3.4 for 760 and 780 nm, 3.8 for 800 nm, and 4.3 for 820, 840, and 880 nm. It is known that the theoretical values are 2 and 3 for 2PA and 3PA, respectively. The deviation of the fitting results from the theoretical values may be attributed to the involvement of the defect states inside the bandgap in the multiphoton transition, which is also observed in GaN material.[19] The contributions of the defect states are not discussed here.

The interferometric autocorrelation technique is frequently used for quantitative characterization of MPA and ultrashort laser pulses.[16,20–24] To further investigate MPA in ZnO, we conducted the interferometric autocorrelation experiments for the UV emission band at 395 nm. The representative experimental curves are depicted in Fig. 3. Note that the signal intensity is normalized with respect to the background value that is the signal intensity when the delay time is long enough. If the wavelength of the excitation light is less than 730 nm (the corresponding photon energy is just above the half-bandgap of ZnO), only 2PA takes place. For 2PA the theoretical signal–background ratio should be 8:1. Measured values are in excellent agreement with theoretical predictions for wavelengths of 710 and 720 nm. When the laser wavelength is set at 760 nm, the recorded ratio reaches 10:1, which indicates the involvement of 3PA. As the wavelength is further increased, the ratio also increases. When the wavelength is increased to 775 nm, the ratio becomes $\sim 26:1$. This means that the contribution of 3PA increases, which is consistent with the data in Fig. 2. When the wavelength is beyond 778 nm the ratio is as high as 32:1, which is the theoretical value for 3PA. This result unambiguously shows that 3PA absorption occurs.

Now we discuss the relation of the VIS emission band to deep centers in ZnO.[7,8,25] Our group's detailed study of combined theory and experiment has shown that this broad VIS band is from the radiative transition of vibronic states owing to strong coupling between a deeply localized electron and a local oscillator phonon of ZnO. The deep center is located at ~ 0.52 eV below the bottom of the conduction band of ZnO. The corresponding wavelength of a direct optical transition from the deep center to the valence band of ZnO is ~ 435 nm. From Fig. 1 it can be seen

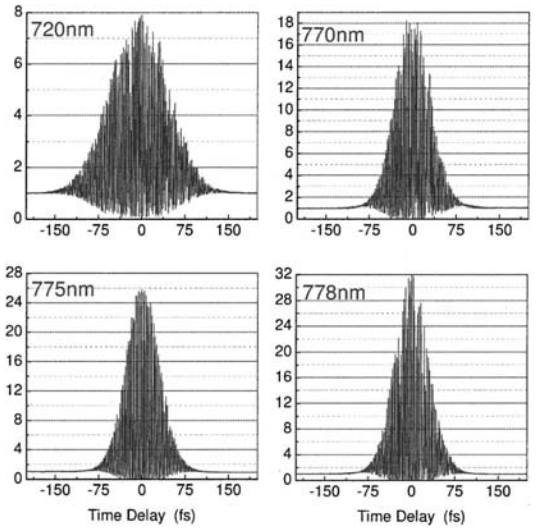

Fig. 3. Measured interferometric autocorrelation traces of the UV emission band of the sample excited by laser pulses of four wavelengths.

that the relative intensity of the VIS emission band with respect to the UV emission band is strongly dependent on the wavelength of the excitation laser and thus on the means of excitation. In the wavelength range where 2PA is dominant, the peak intensity of the VIS band is comparable with that of the UV band. However, for the longer wavelengths the VIS band becomes dominant. According to the discussion above, we know that the threshold wavelength of 2PA for the broad VIS band is ~870 nm, whereas the threshold wavelength of 2PA for the UV band is ~730 nm. Therefore, when the excitation wavelengths are >730 and <870 nm, the deep centers can be directly populated by electrons in the valence band by means of coherent 2PA. Note that 3PA absorption contributes mainly to the population of the conduction band and thus to the UV luminescence for this wavelength range. It is well known that the cross section of 2PA is much greater than that of 3PA. The population density is proportional to the cross section of absorption, which determines the luminescence intensity to a great extent. It is thus not difficult for one to understand that the VIS emission band becomes dominant when the wavelength of the excitation laser is longer than 730 nm.

We mention briefly the contribution of the deep centers to the UV emission. Some electrons already populated at the deep centers can be further excited to the conduction band by absorption of one photon of the excitation laser. In principle, this is a linear absorption process because the energy spacing between the deep centers and the conduction band is only 0.52 eV. However, populating the deep centers is a nonlinear 2PA. It is the contribution of the deep centers that gives the UV emission band a mixed character of 2PA and 3PA, as indicted by the data in Figs. 2 and 3.

In summary, multiphoton-absorption-induced luminescence in ZnO at room temperature has been studied by investigation of the power dependence and interferometric autocorrelation of the luminescence signal. We have demonstrated that two-photon and three-photon absorption are dominant while the excitation photon energies are above and below the half-bandgap of ZnO, respectively. The effects of defect states were also discussed. These results show that ZnO is a promising material for nonlinear optical applications.

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