Second-harmonic Generation and Multiphoton Induced Photoluminescence in ZnO

Noh Soo Han, Hyeong Seop Shim, Seung Min Park,* and Jae Kyu Song*

Department of Chemistry, Kyunghee University, Seoul 130-701, Korea
**E-mail: smpark@khu.ac.kr and jaeksong@khu.ac.kr*
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Among the II-VI semiconductors, zinc oxide (ZnO) has attracted considerable interest on account of its wide band gap (3.37 eV) and large exciton binding energy (60 meV).[1-3] The nonlinear optical responses of ZnO were investigated to better understand the nonlinear optical properties, such as second-harmonic generation (SHG) and third-harmonic generation (THG).[4-9] The non-resonant two-photon absorption (2PA) and three-photon absorption (3PA) processes were also examined by monitoring the multiphoton-induced photoluminescence.[4,10] However, there are few reports on the simultaneous measurements of harmonic generation (SHG and THG) and multiphoton absorption (2PA and 3PA),[4,11] although the competition between them is important for potential applications. In this Communication, we present the nonlinear optical properties of ZnO, which were examined by the nonresonant optical excitation of femtosecond laser pulses at a wavelength of 800 nm.

ZnO bulk powders (Fig. 1(a)) were purchased from Aldrich (#205532) and employed for measurements without further purification and annealing. The ZnO powders were drop-coated on glass substrates and excited with a He-Cd laser (325 nm, Kimmon) to obtain the photoluminescence spectrum (Fig. 1(b)). The emission peak in the UV region, which is attributed to exciton recombination,[1-3] is observed at 382 nm, while there is virtually no visible emission. Because the visible emission of ZnO is related to various defects,[1-3] the absence of visible emission suggests that this sample is suitable for a study of the nonlinear optical properties of ZnO without the perturbation of defects.

For measurements of the nonlinear optical response, ZnO was excited by the fundamental of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 800 nm, 150 fs) using a UV microscope objective (LUCPLFLN40X, Olympus, NA 0.6). The emission and SHG were collected by the same objective, resolved spectrally using a monochromator (SP-2150i, Acton Research Corp.), and detected by a photomultiplier (P2/PD-471, Acton Research Corp.). Figure 1(c) clearly shows the SHG at 400 nm (twice the photon energy of 800 nm), while the THG near 267 nm is barely observable (inset of Fig. 1(c)). The other peak at 382 nm, in the blue side of the SHG, appears to be from another nonlinear optical response, because the photon energy of 382 nm is significantly different from that of 800 nm and its multiple. In order to understand the mechanism for UV emission, the emission spectra were obtained as a function of the excitation intensity of 800 nm (Fig. 2(a)). UV emission and SHG increase nonlinearly with increasing excitation intensity, suggesting nonlinear optical responses. On the other hand, a closer examination reveals that the nonlinearity of UV emission is not identical to that of the SHG, which is observed more clearly in the normalized spectra (Fig. 2(b)). The ratio of the UV to SHG emission increases with increasing excitation intensity. In other words, the intensity of UV emission increases fast compared to SHG, suggesting a different order of nonlinear optical responses. The number of photons involved (n) is estimated using the equation, $I = cP^n$, where I is the signal intensity, c is a constant, and P is the power of the excitation pulse. In general, a two-photon-induced process shows a quadratic dependence (n = 2) on the excitation intensity, while a three-photon-induced process has a cubic dependence (n = 3). A logarithmic plot (Fig. 2(c))

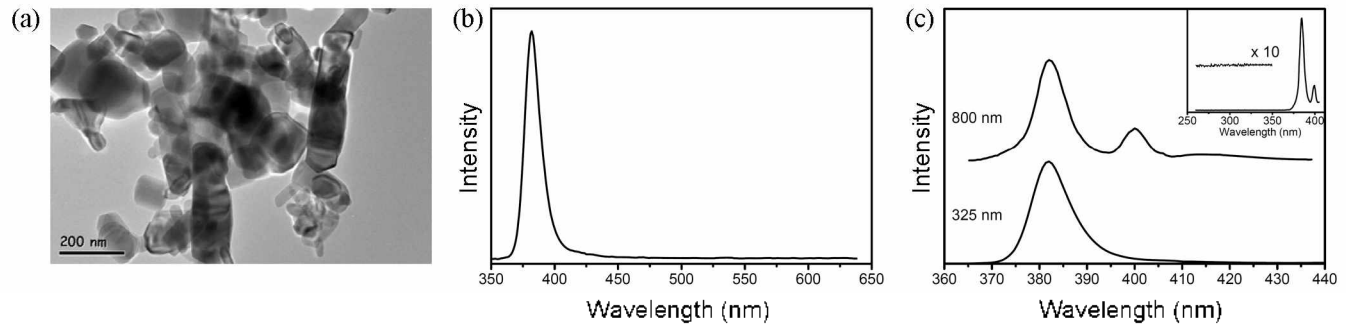

Figure 1. (a) The transmission electron microscopy (TEM) image of the ZnO powders used for the measurements. (b) Photoluminescence spectrum of the ZnO powders obtained with a He-Cd laser (325 nm). (c) Emission spectrum of the ZnO powders obtained with excitation of 800 nm. For comparison, photoluminescence spectrum obtained with excitation of 325 nm is also shown. The inset shows a wide wavelength range of the emission spectrum obtained with excitation of 800 nm.

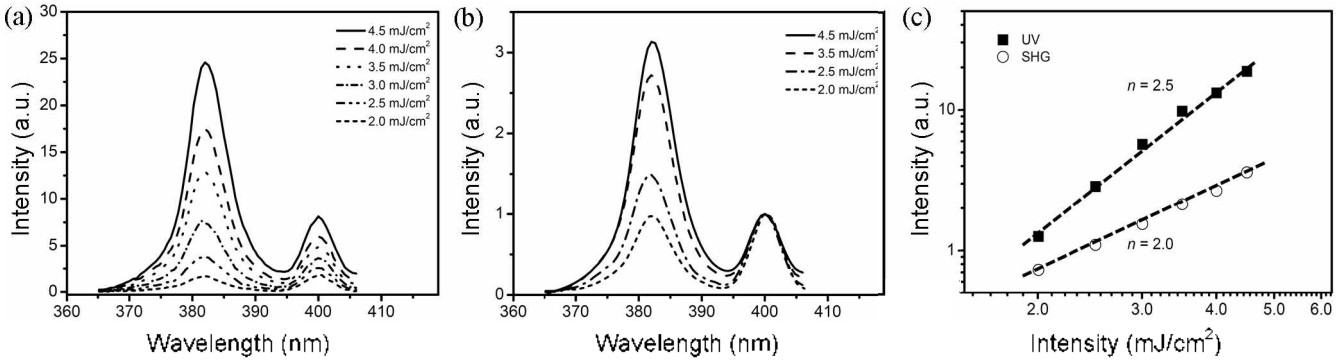

Figure 2. (a) Emission spectra of the ZnO powders as a function of the excitation intensity of 800 nm. From bottom to top, the intensities of UV emission and second-harmonic generation increase nonlinearly with increasing excitation intensity. (b) Emission spectra normalized to the intensity of the second-harmonic generation. (c) The logarithmic plot of the intensities of UV emission (UV) and second-harmonic generation (SHG) as a function of the excitation intensity. The number of photons involved (n) is ~2.5 for UV and ~2.0 for SHG.

shows that n is ~2.0 for SHG, which confirms that two photons are involved in SHG. However, n is ~2.5 for UV emission, which indicates a deviation from a simple power law. Because UV emission (exciton emission) originates from a band gap transition,[1-3] such a change in UV emission suggests a complicated scheme for the band gap excitation.

The 2PA process would not be effective under normal conditions, because the sum energy (400 nm, 3.10 eV) of two photons is less than the band gap of ZnO (368 nm, 3.37 eV). In extremely intense femtosecond laser excitation, on the other hand, the strong light-matter interaction can induce the 2PA process.[4] In this regard, a quadratic dependence (n = 2) of the UV emission intensity on the excitation intensity would be expected, if the 2PA process contributes to the band gap excitation. However, the observed power dependence (n = 2.5) that deviates from the expected one (n = 2) suggests that 2PA is not fully effective, mainly because the currently-employed power of 800 nm (10 - 30 GW/cm^2) is not as high as that reported previously (~100 GW/cm^2).[4] On the other hand, 3PA could also occur, leading to a cubic dependence (n = 3), because the sum energy (267 nm, 4.64 eV) of the three photons is larger than the band gap energy. However, the efficiency of 3PA is generally much lower than that of 2PA,[11] which indicates that 3PA cannot be the predominant scheme of the band gap excitation. The observed power dependence happens to be in the middle of the quadratic and cubic dependence, suggesting that both 2PA and 3PA processes play a role in the band gap excitation.

Presumably, a spatially inhomogeneous excitation is responsible for the coexistence of 2PA and 3PA in the band gap excitation. The beam quality might reduce the efficient homogeneous excitation, because a multimode laser beam can be considered as a beam with hot spots. A Gaussian-intensity-type profile is expected along the beam waist, even when a single-mode beam is employed for the excitation. Because the femtosecond laser pulses are focused to a spot size of ~3 μm, the powders (Fig. 1(a)) might be in the different excitation intensity regime. In the weak excitation intensity regime, the light-matter interaction cannot assist the 2PA process, leading to a cubic dependence (n = 3). However, 3PA is not also efficient in the weak intensity regime due to its low efficiency. At this point, we do not have direct information whether the relative contribution of 3PA decreases for the band gap excitation under the weak intensity. Therefore, further study using a high power from an amplified femtosecond laser system is needed to better understand the nonresonant band gap excitation. However, we note that 2PA as well as 3PA can contribute for the band gap excitation, while 2PA and 3PA take place only with the high excitation intensity.

In summary, the nonlinear optical properties of ZnO were examined by optical pumping of femtosecond pulses of 800 nm. In addition to SHG, exciton emission in the UV region was observed by multiphoton excitation of 800 nm. The power dependence suggested that SHG was a two-photon process and UV emission was affected by both 2PA and 3PA.

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