Upconversion luminescence of single-crystalline ZnO by femtosecond laser irradiation

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Near infrared to ultraviolet (UV) and visible upconversion luminescence was observed in ZnO single crystalline under femtosecond laser irradiation. The optical properties of the crystal reveal that the UV and visible emission band are due to the exciton transition (D_0X) bound to neutral donors and the deep luminescent centers in ZnO, respectively. The relationship between the upconversion luminescence intensity and the pump power of the femtosecond laser reveals that the UV emission belongs to three-photon simultaneous band-to-band excitation and the visible emission belongs to two-photon simultaneous defect-absorption-induced luminescence. The saturation effects are also found in the upconversion process of ZnO.

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Multiphoton (two, three, or more) excitation-related processes, materials, and applications have become more interesting in many research areas, such as infrared-pumped visible laser[1], frequency-upconversion imaging and microscopy[2], three-dimensional (3D) optical data storage and processing[3], 3D display[4], optical microfabrication[5,6], optical power limiting, optical stabilization, and reshaping[7]. Zinc oxide (ZnO) is a typical direct wide band-gap II-VI compound semiconductor. It has received a lot of attention in the past decade for its potential as a promising optoelectronic material in the ultraviolet (UV) for laser diodes and light-emitting diodes operating at room temperature[8,9]. The 60-meV exciton binding energy and the availability of large high-quality single-crystal substrates make ZnO interesting as a possible alternative to GaN. In the past several years, the optical properties based on single-photon absorption excited by UV laser in ZnO have been extensively investigated. But there are few investigations on the nonlinear optical properties in ZnO based on multiphoton absorption (MPA), especially MPA-induced luminescence[10]. We observed two- and three-photon absorption-induced visible and UV luminescence of ZnO single crystalline by femtosecond laser irradiation experimentally and found that the two- and three-photon absorption-induced luminescence in ZnO has saturation effects.

ZnO single crystal is a wurtzite hexagonal crystal. It was grown by the hydrothermal method. The crystal sample was cut and polished to a size of 5×5×1 (mm) with ⟨0001⟩ orientation. No inclusions or other light scattering centers were observed by the optical microscope. A regeneratively amplified 800-nm Ti:sapphire laser that emits 120 fs, 1 kHz, mode-locked pulses was used as the excitation source. The laser beams were focused into samples by objective lens with 100-mm focal length. The focus was inside the sample. The fluorescence spectra were recorded by a spectrophotometer of ZOLIX SBP300. The scanning rate of this spectrophotometer was 100 nm/min. The fluorescence spectra were measured at $\sim 90^\circ$ direction with respect to the pump beam. The fluorescence spectra excited by a 267-nm monochromatic light from a xenon lamp were measured by a JASCO FP6500 spectrophotometer. In addition, the absorption spectra were obtained by a JASCO V-570 spectrophotometer. All the measurements were performed at room temperature.

Under focused femtosecond laser irradiation, the ZnO sample shows a strong fluorescence near the focused spot. Figure 1 shows these emission spectra excited by the femtosecond laser with an average power of 20 mW. The emission spectrum excited at 267 nm is also shown in Fig. 1 for comparison. The spectrum of ZnO crystal irradiated by the femtosecond laser exhibits a broad emission band peaked at 500 nm and a narrow emission band peaked at 395 nm, which is similar to those of ZnO crystal excited by 267-nm monochromatic light. This result reveals that the 800-nm femtosecond laser can substitute for the 267-nm monochromatic light as excitation source to produce UV and visible luminescence in ZnO. The green emissions excited by femtosecond laser can all be assigned to transition between singly ionized oxygen vacancy and photoexcited hole[11] or between trapped electron at V_O^+ and a deeply trapped hole at V_{Zn}^-[12], while the UV emissions excited by femtosecond laser can be attributed to the exciton transition (D_0X) bound to neutral donors and their excited states[13].

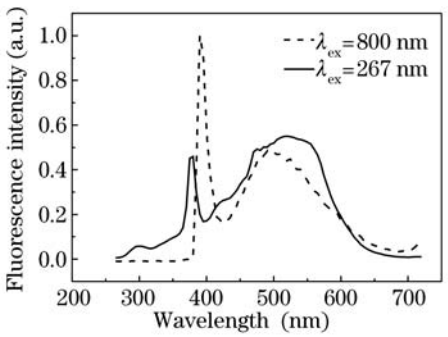

Fig. 1. Emission spectra of the ZnO crystal sample under focused femtosecond laser irradiation and 267-nm monochromatic light excitation.

In general, it is impossible to obtain a higher-energy photon via a lower-energy photon excitation. Therefore, the conversion of infrared radiation to the visible emission can be ascribed to a multiphoton absorption process. The upconversion-emission intensity $I_{\rm upcon}$ is dependent upon the pump power density $I_{\rm pump}$. Their relationship can be described as[14]

$$I_{\rm upcon} \propto I_{\rm pump}^{n}, \tag{1}$$

where n accounts for the number of pump photons involved in the upconversion excitation mechanism. The number of pump photons must satisfy that the total energy of n photons exceeds or equals to the excitation energy required by excited states. n can be experimentally determined from the slope coefficient of linearly fitted line of logarithmic plot of the pumping-power density and fluorescence intensity. The luminescence emission intensities of the 395- and 500-nm signals against the femtosecond laser power were investigated. The log-log relationship between pumping-power density of the femtosecond laser and fluorescence intensity of ZnO is shown in Fig. 2. At low pump power, the slope coefficient of the fitted line is 3.0 for the 395-nm signal and 1.7 for the 500-nm signal, but at high pump power it is reduced to 1.95 and 1.0, respectively. This reveals that three-photon absorption (3PA) induced photoluminescence is dominant for the 395-nm signals and two-photon absorption (2PA) induced photoluminescence is dominant for the 500-nm signals in the upconversion processes at low pump-power levels. When the excitation power gets higher, the upconversion process will be saturated. This saturation phenomenon can be explained as follows. Because the concentration of excitons and defects in ZnO crystal is dependent on the growth condition, the number of excitons and defects is constant for a certain ZnO sample. With the increase of pump laser power, the fluorescence intensity of ZnO at 395 and 500 nm will get a cubic and quadratic increase, respectively. When the excitation pump power reaches a certain level, the excitons and defects excitation will be saturated and the increase of the fluorescence intensity will become slower.

According to the electronic energy level of ZnO[12] (as shown in Fig. 3), the UV and visible upconversion luminescence under the femtosecond laser excitation may

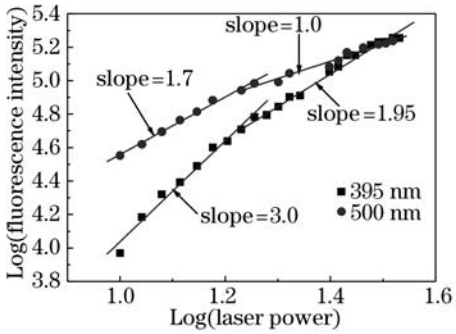

Fig. 2. Log-log plot of the upconversion emission intensity as a function of the femtosecond laser power at 800 nm. Laser power is in unit of milliwatt, and fluorescence intensity in arbitrary unit.

have three possible mechanisms. 1) Two-photon exciton-absorption process. In this case, an electron in valence band of ZnO can absorb two pump photons, then is nonresonantly excited to the exciton state[15] and form a free exciton with the hole in valence band of ZnO. The free exciton can emit a photon with 375 nm directly or be trapped by some defect pairs and become an exciton bound to neutral donors (D_0X), from which, the characteristic emission at 395 nm occurs. In the emission spectra (Fig. 1) excited by the 800-nm femtosecond laser, there is no emission at 375 nm, in addition, the three-photon excitation predominates in the upconversion emission at 395 nm, so the possibility of two-photon exciton-absorption-induced luminescence at 395 nm is very little. 2) Two-photon defect-absorption process. In this process, an electron in valence band can be excited to oxygen vacancy energy level ($V_{\rm O}^{+}$) by absorption of two pump photon, then either recombines with the hole trapped by zinc vacancy ($V_{\rm Zn}^{-}$) and emit a photon at 500 nm, or nonradiatively relaxes to localized donor center, from which, the electron recombines with the hole in valence band and emit a photon at 500 nm. This two-photon excitation process may have two possible ways. One is the one-photon excitation to a real level followed by another photon absorption. Another is the two-photon simultaneous excitation. In the first case, the material should have absorption at about 800 nm. In order to elucidate the actual two-photon-excited upconversion mechanisms, the absorption spectrum of the sample was measured and is shown in Fig. 4. It can be seen that there is a strong absorption band below 450 nm, corresponding the intrinsic absorption and absorption edge of ZnO. At the other spot, there is almost no absorption. Therefore, the first case of one-photon excitation to a real level should be ruled out due to the absence of the absorption at about 800 nm and the two-photon simultaneous absorption can be considered to be responsible for the defect-absorption process. 3) three-photon band-to-band excitation process. In this process, an electron in valence band of ZnO can be promoted to the conduction band by absorbing three pump photons and then nonradiatively relaxes to either exciton state or defect state, from which, the characteristic emission at 395 and 500 nm occurs. The three-photon band-to-band excitation may have three possible ways. One is the one-photon excitation to a real level followed by a two-photon absorption. Another is the two-photon simultaneous excitation to a real level followed by a one-photon absorption. The third is the three-photon simultaneous absorption. The first case has been ruled

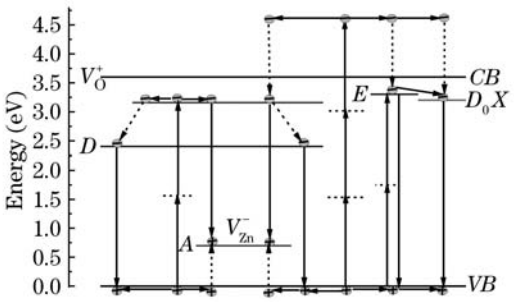

Fig. 3. Energy-level diagram for ZnO crystal upconversion process pumped at 800 nm.

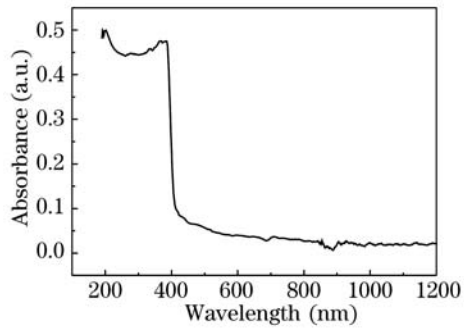

Fig. 4. Absorption spectrum of the ZnO crystal sample.

out due to the absence of the absorption at about 800 nm. In the second case, the fluorescence intensity at 500 nm should be stronger than that at 395 nm, but we have observed the opposite phenomenon, in addition, the two-photon excitation predominates in the upconversion emission at 500 nm, therefore, there is little possibility for the two-photon simultaneous excitation to oxygen vacancy energy level ($V_{\rm O}^{+}$) followed by a one-photon absorption. The three-photon simultaneous absorption can be considered to be responsible for the band-to-band excitation process. All above analyses indicate that two-photon simultaneous defect-absorption predominates in the upconversion emission at 500 nm and three-photon simultaneous band-to-band absorption predominates in the upconversion emission at 395 nm.

In summary, the UV and visible upconversion luminescence in ZnO single crystal has been observed under focused infrared femtosecond laser irradiation. The dependence of the fluorescence intensity of ZnO on the pump power shows that the upconversion luminescence at 500 and 395 nm is dominated by 2PA and 3PA absorption, respectively. The saturation effects are also found in the upconversion process of ZnO. The analysis reveals that the 2PA is a simultaneous defect-absorption process rather than a two-photon exciton-absorption process and 3PA is a three-photon simultaneous band-to-band absorption process rather than a sequential process. This result provides a promising method to obtain ultraviolet or visible emission from infrared pumping light in solid-state crystals, and has potential applications in visible lasers, high-resolution optical data storage, 3D displays, etc..

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