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Multi-photon excitation UV emission by femtosecond pulses and nonlinearity in ZnO single crystal

Zhi-Wei Dong, Chun-Feng Zhang, Guan-Jun You, Xue-Qiong Qiu, Kang-Jun Liu, Yong-Li Yan and Shi-Xiong Qian[1]

State Key Lab for Surface Physics and Physics Department, Fudan University, Shanghai 200433, People's Republic of China

E-mail: sxqian@fudan.ac.cn

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Abstract

Optical nonlinearities and multi-photon ultraviolet (UV) excitation in ZnO single crystal were investigated by the z-scan method utilizing an intense femtosecond (fs) laser at different wavelengths. Based on the analysis of the experimental results at different excitation wavelengths near 800 nm, nonlinear optical effects that may emerge under an intense field are attributed to be responsible for the efficient two-photon absorption process under detuned excitation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO is a kind of II–VI compound wide-band-gap semiconductor with a direct band gap of 3.37 eV at room temperature and a large exciton binding energy of about 60 meV, which makes it a potential candidate for room-temperature ultraviolet (UV) laser diodes [1, 2]. Research on the photoluminescence (PL) properties of ZnO nanostructures has shown that, under high excitation conditions, exciton–exciton collision as well as the recombination of electron–hole plasma (EHP) is key process leading to stimulated emission and lasing [3–7], and that the nanostructures could serve as both an active gain material and an optical cavity [8–10]. These studies demonstrated the potential of using ZnO to fabricate room-temperature UV lasers. Besides the applications of ZnO in UV photonic devices, the nonlinear properties of ZnO are also very attractive for various applications. Efficient second-harmonic generation (SHG) has been observed in ZnO thin films [11]. High conversion efficiency of the third-harmonic radiation was also achieved [12]. Furthermore, nonlinear refraction of ZnO single crystal was measured under a GW cm^{-2} excitation intensity [13]. But, as far as we know, research

[1] Author to whom any correspondence should be addressed.

specifically on the nonlinear properties of ZnO single crystal under a higher excitation intensity regime is quite scarce.

Thanks to the development of laser technology, the emergence of ultrafast lasers, especially femtosecond (fs) laser sources with a low repetition rate, makes it possible to obtain an extremely intense field of above TW cm^{-2}, and this enables us to explore the interaction between condensed matter and an intense field. Under the action of an extremely intense field generated by fs laser pulses, nonlinear effects such as multi-photon absorption (MPA), the Stark effect and the Rabi effect have been observed in various kinds of materials, including molecules and semiconductors [14–16]. However, most PL research on ZnO material has been performed by utilizing linear optical pumping [3–7]. Only recently has research focused on the nonlinear excitation of ZnO with intense laser pulses been performed [17–20]. Therefore, further research on the nonlinear properties, especially the basic mechanisms of MPA-induced PL emission in ZnO under intense fs excitation, is meaningful.

In this paper, we report our research on PL emission by nonlinear excitation in ZnO crystal, and we find that intense PL emission is generated by intense near-infrared fs pulses. Our work reveals a novel nonlinear optical (NLO) route to generate photoluminescence in ZnO crystal.

2. Experimental details

A ZnO single-crystal slice with a thickness of 0.5 mm and a purity >99.99% was purchased from a commercial company in China. The laser source used in this experiment was a Ti:sapphire laser (Spectra-Physics Spitfire) operating at a repetition rate of 1 kHz with output pulses tuned from 780 to 820 nm and a full width at half-maximum of 150 fs.

In this work, we measured the nonlinear refraction of ZnO by using a single-beam z-scan technique at wavelengths of 800 and 400 nm. To further investigate the excitation process in ZnO, an open-aperture (OA) configuration z-scan was applied to measure the power-dependent transmission. The incident fs beam with wavelengths tuned at 780, 800 and 820 nm, respectively, was focused on the ZnO crystal, which was moved along the z-axis.

Degenerate optical Kerr effect (OKE) measurements were carried out at 800 nm to investigate the nonlinear optical properties further. A detailed description of the setup has been described elsewhere [21].

All the experiments were performed at room temperature.

3. Results and discussion

Figures 1(a) and (b) are the z-scan traces of ZnO single crystal with an excitation intensity of 320 GW cm^{-2} at the focal point with wavelengths of 800 and 400 nm, respectively. The squares represent closed-aperture (CA) experimental data, while the triangles are OA data. Circles are the results of dividing the CA value by the OA value to eliminate the effect of nonlinear absorption. In figure 1(a), the valley–peak configuration of the CA trace indicates that the ZnO single crystal has a positive nonlinear refractive index at 800 nm, while the peak–valley configuration in figure 1(b) indicates this index to be negative at 400 nm.

We fit the data in figures 1(a) and (b) (shown in solid curves) using the following formula for the CA configuration [22]:

$$T = 1 - \frac{4\Delta\Phi_0\,(z/z_0)}{\left[\left((z/z_0)^2 + 9\right)\left((z/z_0)^2 + 1\right)\right]} \tag{1}$$

where T is the normalized transmittance, z is the distance from the focus point, z_0 is the diffraction length of the laser beam, and $\Delta\Phi_0 = 12k\pi^2\varepsilon_0 I L_{\text{eff}}\gamma$. Here k, I, L_{eff}, ε_0 and γ

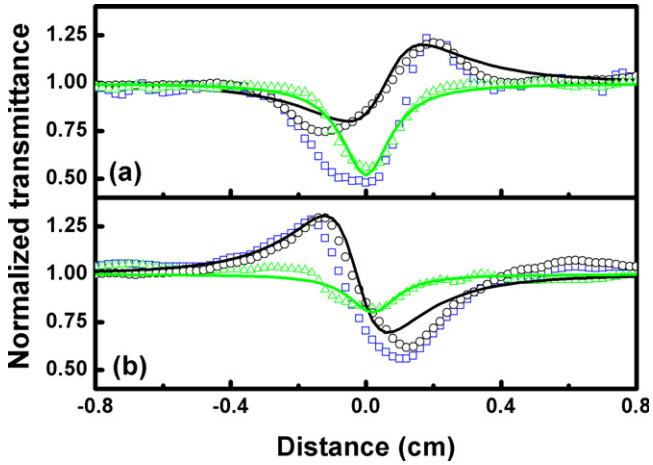

Figure 1. (a) The z-scan traces of ZnO crystal at 800 nm. Squares represent closed aperture data, triangles are open aperture data, and circles are the results of dividing the closed aperture value by the open aperture value. The solid curves are the fitting results. (b) The z-scan results at 400 nm.

are the wavevector of the light, the light intensity, the effective thickness of the sample, the vacuum permittivity, and the third-order nonlinear refraction index coefficient. Considering that k and I are determined, if L_{eff} is supposed to be 0.5 mm, we deduce γ to be 8.2×10^{-16} and -1.4×10^{-15} cm^2 W^{-1} at 800 and 400 nm, respectively. According to the two-parabolic-band (TPB) model, the nonlinear refraction of semiconductor materials will become negative when the excitation photon energy is tuned above $0.7E_{\text{g}}$ [23], which is the case in our experiment at 400 nm. Compared with relative research [24], the measured γ value in our experiment is one order less than their result, which may be caused by the high repetition rate of the laser pulses used in their experiment, because the thermal–optical nonlinearity will emerge when the thermal characteristic time ($t_{\text{c}} = \frac{\omega_0^2 \rho c_p}{4\kappa}$) is longer than the temporal interval of the laser pulses, where ω_0 is the beam radius, ρ is the density, c_p is the specific heat and κ is the thermal conductivity. Using the related parameters of ZnO [25], the thermal characteristic time is estimated to be 2 μs, which is much longer than the period of the laser pulses in [24] but shorter than that of 1 ms used in our fs z-scan experiment. This would result in the large discrepancy between the measured values.

The PL properties of ZnO single crystal excited by fs laser pulses at 800 nm were investigated and are shown in figure 2(a). There is a sharp peak in the UV region located at about 392 nm and a broad peak at about 550 nm. The near-bandgap UV emission is attributed to EHP emission under the intense excitation power used in our experiment [26]. Coulomb interactions in material with a large carrier population, which is called band-gap renormalization (BGR), cause the peak of the EHP emission to lie about 210 meV below the band gap [27]. The broad peak at about 550 nm is caused by defects in the ZnO crystal [28]. Compared with the UV emission, this weak peak in the PL spectra also implies good optical properties of the ZnO crystal.

Since the pump photon energy is 1.55 eV, which is much less than the band gap of ZnO, the excitation mechanism for PL emission must be MPA processes. Figure 2(b) shows the dependence of the intensity of the UV peak on the excitation intensity on a logarithmic scale. Because the slope is a little larger than two, this result indicates that two-photon absorption (2PA) plays an important role in the excitation process and that three-photon absorption (3PA)

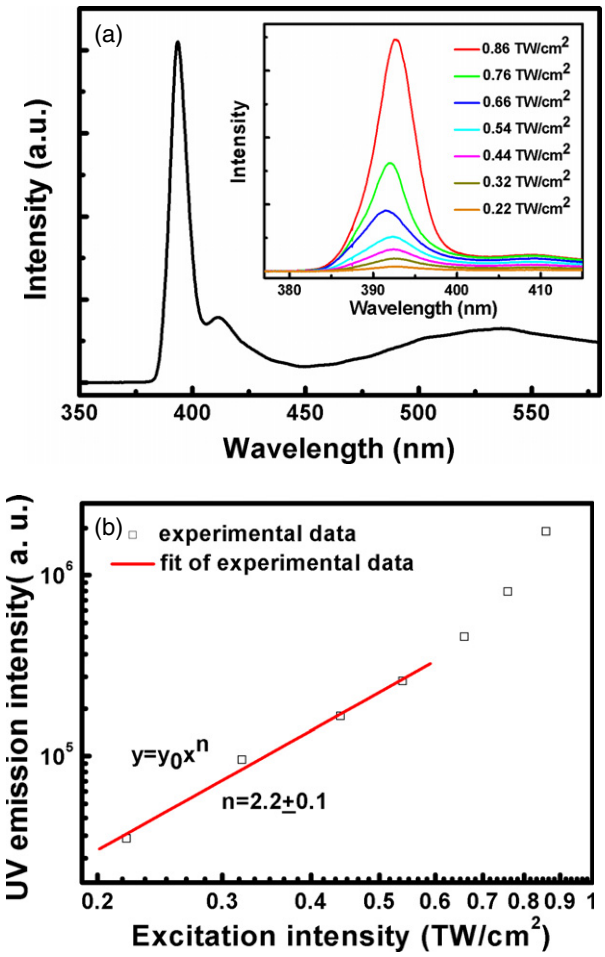

Figure 2. (a) PL spectrum in ZnO crystal excited by 800 nm fs pulses with an excitation intensity of 1.0 TW cm^{-2}. The inset shows the UV emission spectra at different excitation power densities. (b) Dependence of the UV peak intensity on excitation intensity on a logarithmic scale. The dots are experimental data and the solid line represents the fitting result.

would also contribute to the excitation process. With increasing excitation intensity, the index on a logarithmic scale increases obviously, indicating that a stimulated process may emerge.

Figure 3 is the OKE signal with the fitting results of autocorrelation due to 2PA. The symmetrical OKE signal in this figure implies that the response time in ZnO crystal is shorter than 500 fs under intense fs pulsed irradiation, and the fitting results also illustrate that the 2PA process is a reasonable mechanism for the excitation.

To investigate the MPA process in ZnO further, OA configuration z-scan experiments with different incident wavelengths centred at 780, 800 and 820 nm were performed. As the absorption of the MPA processes increases greatly with increasing incident power, the z-scan trace should show a valley at the focal point.

Under both the thin sample approximation and the slowly varying envelope approximation (SVEA), the wave equation for the incident beam can be described as follows:

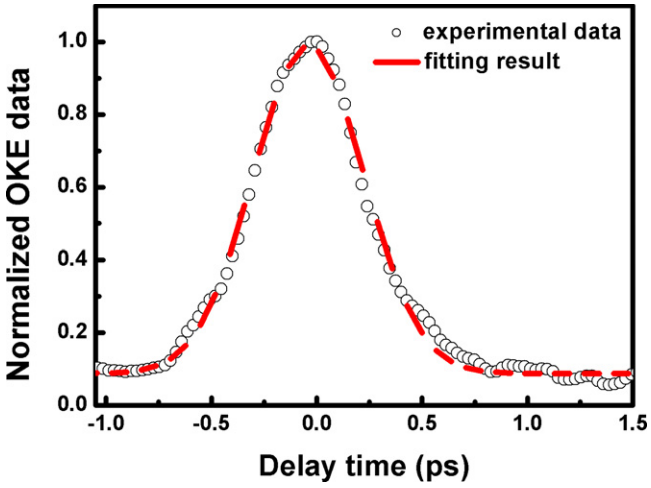

Figure 3. Normalized OKE signal and fitting results under an excitation intensity of 0.25 TW cm^{-2} at 800 nm.

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\left(\alpha_0 + \sum_{m=2} \alpha_m I^{m-1} + \sigma_\alpha N_{e-h}\right) I \tag{2}$$

where σ_α is the absorptive cross section, N_{e-h} is the number density of the photon-excited charge carriers, α_0 is the linear absorption coefficient, α_m is the MPA coefficient ($m = 2$ for 2PA; $m = 3$ for 3PA, and so on) and I is the intensity inside the sample. If we keep only the 2PA term and ignore all other terms on the right-hand side of (2), we can get the expression for the OA z-scan on 2PA as follows:

$$-\ln(T) \propto \alpha_2 I \tag{3}$$

where T is the normalized transmittance in the OA z-scan experiment.

Similarly, for 3PA, it is

$$-\ln(T) \propto \alpha_3 I^2. \tag{4}$$

This enables us to identify 2PA or 3PA process by fitting the plot of $-\ln(T)$ versus I_0, as shown in figure 4. The normalized transmittance is found to be approximately linearly proportional to the excitation intensity. These results confirm the above PL experiment and indicate that the 2PA process dominates the excitation process when the incident fs wavelength is around 800 nm.

Because the excitation photon energy is only 1.55 eV, which is still less than half the band gap of ZnO, generally 3PA should dominate the excitation process, as has been reported in previous research reports [24, 29]. But, from our study, it is found that 2PA excitation is very efficient in the excitation process. We attribute this to the effects emerging under the intense field generated by ultrafast femtosecond pulses with a low repetition rate (Spectra-Physics Spitfire). According to the treatment for ZnO nanowire [30, 31] with an excitation intensity higher than hundreds of GW cm^{-2}, nonlinear optical effects such as the Stark effect and the Rabi effect may emerge. These effects can make the band gap of the semiconductor decrease by up to hundreds of millielectronvolts under an extremely high laser field [32, 33], which would dramatically reduce the detuning and enhance the excitation via the 2PA process. Generally speaking, the absorption cross-section of the 2PA process is orders of magnitude larger than that of 3PA; in that case, 2PA, not 3PA, would play an important role in the excitation process

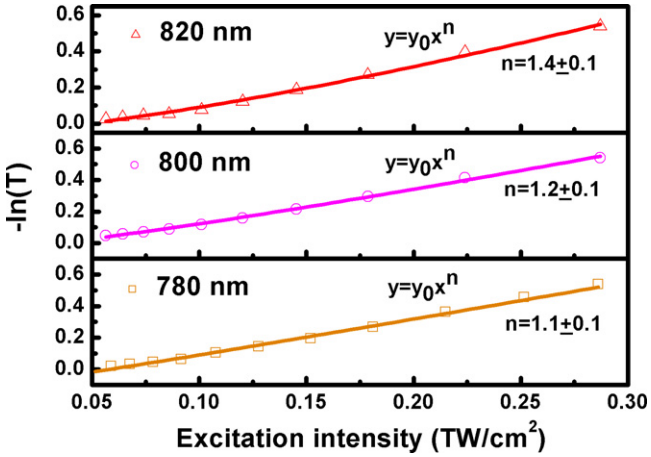

Figure 4. The logarithmic transformation of normalized transmittance versus incident intensity at wavelengths of 780, 800 and 820 nm, respectively. The dots are the experimental data and the lines represent the fitting results with the function $y = y_0 x^n$.

under very intense excitation [34]. In order to verify this, we fit the z-scan results for the 2PA coefficient β at 800 nm under different excitation intensities, as follows:

$$T = \frac{\ln(1+q)}{q} \tag{5}$$

where $q = \frac{IL_{\text{eff}}\beta}{1+z^2/z_0^2}$. β is determined to be 7.1×10^{-11} and 9.0×10^{-11} cm W^{-1} under excitation intensities of 0.32 and 1.3 TW cm^{-2}, respectively. The fact that the value of β increases with the increase in excitation intensity demonstrates that high excitation intensity indeed helps to improve the 2PA efficiency. Though the Rabi effect would reduce the detuning and make the 2PA process effective, with increasing detuning, the 2PA efficiency would gradually reduce and 3PA would become more important in the excitation process. As shown in figure 4, when the incident wavelength was tuned to the red side, the fitting index for the normalized transmittance increases, indicating the obvious participation of the 3PA process in the excitation process at large detuning of 2PA. Based on the above analysis, we conclude that under intense excitation, nonlinear optical effects such as the two-photon Rabi effect and the Stark effect should assist the off-resonant 2PA process to make more of a contribution to excitation in ZnO crystal.

4. Conclusion

The optical nonlinearities of ZnO single crystal were investigated by the z-scan method, applying a femtosecond laser at different wavelengths near 800 nm. Multi-photon excitation in ZnO crystal was clearly observed. Under the intense field generated by fs pulses around 800 nm, the 2PA process is found to be very efficient in exciting band-edge emission from ZnO crystal under detuning conditions. Nonlinear optical effects such as the Stark effect and the Rabi effect, which may emerge under an intense field, are suggested to be responsible for this efficient excitation via the 2PA process. We consider that this NLO route for generating photoluminescence in ZnO crystal is meaningful for research in the blue-violet semiconductor laser field.

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