Two-photon-pumped stimulated emission from ZnO single crystal

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We report on two-photon-pumped stimulated emission (SE) from ZnO single crystal at low temperature. Under nanosecond pulse excitation, two-photon absorption induced SE with a threshold of 2.8 MW/cm^2 is observed, which is ascribed to the inelastic exciton-exciton scattering. The mechanism of the SE is further confirmed by temperature dependent photoluminescence spectra. However, it is interesting to find that under one photon pumping with the same power density, no SE is observed from the sample. Such unusual phenomenon is explained by the nonradiative surface recombination induced carriers depletion under single photon excitation. © *2011 American Institute of Physics*. [doi:10.1063/1.3628329]

Due to the large exciton binding energy (60 meV), ZnO could lead to stimulated emission (SE) based on exciton recombination even above room temperature (RT).[1] A notable discovery was the observation of the exciton–exciton (ex-ex) scattering induced SE in ZnO thin films at moderate pumping intensity.[2] Excitonic emission occurs at a threshold lower than the recombination of electron-hole plasma (EHP) and is, therefore, more desirable for the realization of low-threshold lasers.[3,4] Optically pumped SE has been observed in ZnO epitaxial thin films, ZnO/ZnMgO quantum wells, and nanostructures for their applications in integrated photonics and sensing.[1] However, in the previous works, the ex-ex scattering induced SE is always generated via one-photon excitation processes.[3–6] One-photon excitation requires UV laser source which could put some restraints on applying ZnO in biological science. On the other hand, ZnO crystals are easily exposed to an aqueous environment and lots of surface defects may form in the surface.[7] Due to the small penetration depth under the one-photon excitation, nonradiative processes from surface defects will greatly affect optical properties of ZnO single crystal. In comparison, two-photon excitation can circumvent the above limitations due to long penetration depth. Moreover, under two-photon pumping, the excitation wavelength is far away from emission wavelength, so the influence to the emission detection induced by the scattered light can be largely suppressed.[8] Two-photon-pumped lasing in ZnO nanocrystalline[8] and micro-needle[9] and photoluminescence (PL) in ZnO single crystal have been reported.[10] In this letter, we present our detailed study on the two-photon-pumped SE from ZnO single crystal at low temperature. The temperature dependent PL measurements further confirm that the origin of SE is due to the inelastic ex-ex scattering (P-band), but SE could not been observed under one-photon-pumping with similar density due to the carrier loss induced by nonradiative surface recombination.

The sample used herein is a ZnO single crystal ($10 \times 10 \times 1$ mm in size) grown by the hydrothermal method.[11] The temperature dependent PL measurements were performed within a helium closed-cycle cryostat. A fourth harmonic pulsed Nd:YAG (266 nm) laser and a cw He–Cd laser (325 nm) were used as the one-photon excitation source, while the second harmonic pulse Nd: YAG laser at 532 nm was used as the two-photon excitation source. The pulse width and repetition rate of the pulse laser are 1 ns and 30 Hz, respectively. All of the PL spectra are detected from the excitation side of the crystal surface, the so-called back-scattering geometry.

One- and two-photon-pumped PL spectra of ZnO single crystal at RT are comparatively shown in Fig. 1, with excitation power density of 0.2 and 4.1 MW/cm^2, respectively. The photon energy from the two-photon-pumped PL emission is smaller than that under one-photon excitation. Similar phenomenon was observed in previous work.[12] The inset in Fig. 1 logarithmically shows the PL intensity versus the excitation power of 532 nm laser. As can be seen, the plot has a slope near 2, which coincides with the requirement on two-photon excited PL.[13]

Figure 2(a) shows the power density dependent PL spectra of ZnO taken at 10 K. Under two-photon excitation with low power density, the PL emissions are dominated by bound-exciton complexes (BECs). When the excitation intensity increases up to 2.8 MW/cm^2, an emission peak at 3.18 eV emerges. When the power density is higher than 2.8 MW/cm^2, the integrated PL intensity of this peak increases superlinearly and its linewidth becomes as narrow as 0.61 nm. The integrated PL intensity versus the square of power density under two-photon excitation is shown in Fig. 2(b). Therefore, it is concluded that SE occurs under two-photon excitation. From this figure, the threshold of SE can be determined to be 2.8 MW/cm^2. In order to confirm the origin of two-photon-pumped SE, the one-photon-pumped PL spectrum under cw 325 nm excitation and the selected two-photon-pumped curves at 10 K are comparatively presented as shown in Fig. 2(c). For the PL spectrum under cw 325 nm excitation, it is dominated by free excitons (FX), longitudinal optical (LO) replicas of FX and BECs.[14] It can be seen that the two-photon-pumped SE, which appears under the

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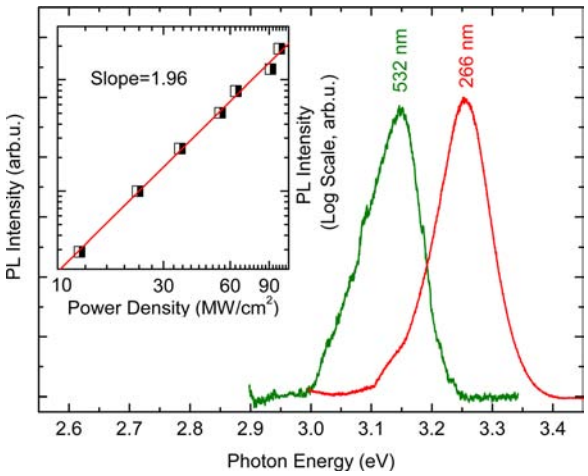

FIG. 1. (Color online) Comparison of one- and two-photon-pumped PL spectra at RT. Inset: measured relative emission intensity versus input pulse energy, showing the quadratic dependence.

excitation of 2.8 MW/cm^2, locates 45 meV below the FX line. At this power density, the SE emission band should be generated by ex-ex collision process where one of the excitons radiatively recombines to generate one photon and the other exciton is excited into the n_2 state (demoted as P_2).[2] It is also found that under the excitation of 4.1 MW/cm^2, two-photon-pumped SE locates 60 meV below the FX-line. Here, we denote the emission peak as P band.[2] This emission was generated by ex–ex collision process where one of the excitons radiatively recombines to generate one photon and the other exciton is excited into the continual band.[2]

To further confirm the recombination mechanism of two-photon-pumped SE, the measurements of SE peak positions under different temperatures were performed. Figure 3(a) shows temperature dependent PL spectra under an excitation density of 4.1 MW/cm^2. Please note that SE was not observed at temperature higher than 180 K due to the increase of pumping threshold. As the temperature increases, the SE band shifts towards lower energy due to the thermal dilation of the crystal lattice. A peak emerges with its energy 16 meV higher than that of donor-acceptor pairs (DAP) band is also observed at 120 K. That is due to the ionization of the

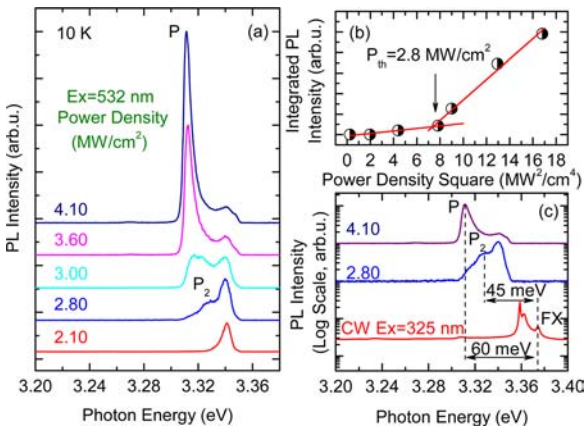

FIG. 2. (Color online) (a) Two-photon-pumped PL spectra of ZnO single crystal taken at 10 K for various excitation densities, (b) the integrated PL intensity versus the square of power density, and (c) the comparison of PL spectra under two-photon excitation and cw of 325 nm excitation.

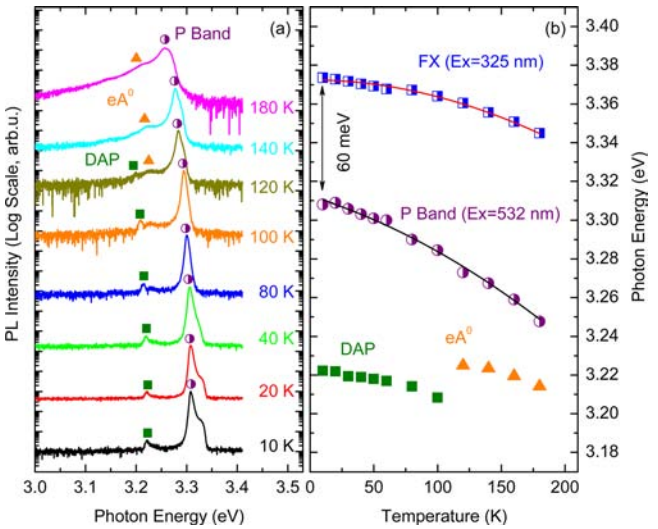

FIG. 3. (Color online) (a) Temperature dependent PL spectra of ZnO under 532 nm excitation, (b) FX energy under cw 325 nm excitation at different temperature, and the peak positions of P band, DAP, and eA^0 under 532 nm excitation.

impurity with smaller binding energy, and then the free electrons in conduction recombine with acceptors with larger binding energy (eA^0).[15] For convenient comparison, the peak positions of FX under cw 325 nm excitation, SE band, and DAP and eA^0 transitions under pulse 532 nm excitation are plotted in Fig. 3(b). FX peak energy decreases monotonically as the temperature increases, which can be well fitted by Varshni empirical equation, as indicated by the solid line.[16] It is well known that the energy of P band at different temperature can be described by the equation $P = E_{ex} - E_b^{ex} - (3/2)kT$, where P is the photon energy of P band, E_{ex} is the FX emission energy, E_b^{ex} is the exciton binding energy, and kT is the thermal energy.[2] We find that the track for SE band energy position can be well fitted by the above equation, as shown in the solid line of Fig. 3(b). Therefore, the two-photon-pumped SE can be further confirmed to be P band emission.

As is well known, the surface of ZnO single crystal can be easily contaminated, which will greatly affect its optical properties under one-photon excitation. It is beneficial to comparatively investigate the optical properties of the sample under one- and two-photon excitations. Therefore, we have also measured the one-photon-pumped PL spectra of ZnO single crystal at 10 K for various excitation densities, as depicted in Fig. 4. Though the excitation densities are comparably high as two-photon excitation, no SE is observed. Meanwhile, 7 meV peak redshift and band broadening have been observed at high pumping density due to thermal effect.[17,18] Regarding the absence of excitonic SE, it can be interpreted from the surface state defects induced nonradiative recombination. It is well known that the emission intensity of ZnO single crystal is related to the radiative and nonradiative transition.[19] The surface of ZnO single crystal is easily subject to atmospheric contamination which results in the formation of lots of defect states near the surface. These defect states may act as adsorption sites for O_2 and H_2O, which can trap FX and serve as nonradiative recombination centers. Therefore, the emission intensity from ZnO

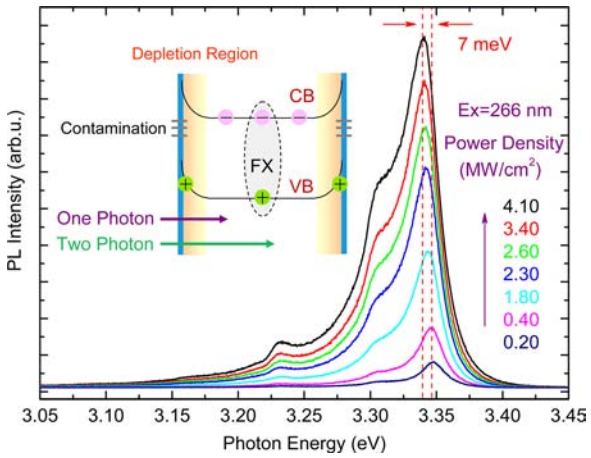

FIG. 4. (Color online) PL spectra of ZnO single crystal taken at 10 K for various excitation densities under 266 nm pumping. Inset: sketch of the energy band of the ZnO single crystal.

decreases. Surface state defects could lead to the generation of a surface depletion layer as illustrated in the inset of Fig. 4. The width of the depletion layer extends from the surface to the interior of ZnO bulk.[20] Liao *et al*. calculated the height of potential barrier (ϕ_s) to be in order of 0.5 eV by fitting the current–voltage (*I–V*) characteristics of ZnO at different ambiences (humid air, dry air, and vacuum).[21] Yang *et al*. calculated the width of depletion layer (69 nm) using the equation $d = [\frac{2\varepsilon_{ZnO}\varepsilon_0\phi_s}{e^2N_D^+(T)}]^{1/2}$, where ε_{ZnO} is the relative dielectric constant of ZnO, ε_0 is the permittivity of vacuum, and $N_D^+(T)$ is the temperature dependent activated donor concentration.[22] The width is comparable to the penetration depth of one-photon excitation (about 100 nm).[23] Therefore, the depletion layer will play an important role in affecting the PL properties under one-photon excitation. The photogenerated electrons and holes in the surface depletion layer can be effectively separated in the opposite directions by the built-in electric field, which will effectively hinder the generation of excitonic emission.[22,24] Due to above reasons, SE has not been observed under one-photon excitation.

In conclusion, we have studied on the two-photon-pumped excitonic SE of ZnO single crystal. Power density and temperature dependent PL measurements allow us to confirm that the origin of two-photon-pumped SE is P band emission. Due to nonradiative surface recombination induced carriers depletion, no SE is observed from the same sample under one photon pumping with the same power density. Our work will add to the application and scientific prospects of ZnO.

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