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Pump power dependence of the electron-hole plasma luminescence in Ga-doped ZnO film

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ABSTRACT

Time resolved two-photon absorption induced electron-hole plasma (EHP) luminescence of Ga-doped ZnO thin film was measured by an ultrafast optical Kerr gate (OKG) in femtosecond time regime. Experimental results showed that the buildup time of the EHP luminescence was strongly dependent on the excitation fluence. The dependence of the buildup time of EHP on excitation fluence probably arose mainly from the relaxation of the hot carriers due to the carrier–carrier interaction, which increased with the increase of excitation fluence.

1. Introduction

Zinc oxide (ZnO) is one of the most attractive semiconductors with wide band gap (3.37 eV) and high exciton binding energy (60 meV) at room temperature, promising for ultraviolet (UV) photonic devices [1–4]. Room temperature lasing from an exciton–exciton collision process or an electron-hole plasma (EHP) state with a low threshold was observed in ZnO epitaxial thin film [5–7]. Production of high-quality doped ZnO films is indispensable for the device application. The carrier concentration of n-type ZnO films increases largely by doping with Ga compared to that of an undoped ZnO films. Besides, a slightly smaller bond length of Ga-O than that of Zn-O is expected to make the deformation of the ZnO lattice small even in the case of high Ga concentration [8,9]. Therefore, Ga-doped ZnO (ZnO:Ga) film may be a promising material in the applications of the ultraviolet photonic devices, and have more superiorities comparing with the undoped one. Time resolved absorption and photoluminescence (PL) spectra using subpicosecond or femtosecond pulse laser have been extensively researched [10–17]. Investigation on the PL properties of ZnO has shown that, under high excitation conditions, exciton–exciton scattering as well as the recombination of EHP is the key process leading to stimulated emission and lasing [10–13].

Several cooling processes of the hot electron including carrier-LO-phonon interaction and carrier–carrier interaction in ZnO have been investigated with large interests [18,19]. Up to date, most studies on the time resolved spectra of EHP in ZnO were conducted through UV excitation, in which the electron relaxation in ZnO was attributed to the carrier–carrier and carrier-LO-phonon interaction [18]. When the electrons were excited by UV, the relaxation of the free carriers was mainly due to the carrier-LO-phonon interaction [19]. Under two-photon excitation of 800 nm, the carriers were excited into near-band-edge, in which the contribution of carrier–carrier interaction may be dominated, although the PL peak of the EHP emission in ZnO was the same for UV excitation and two-photon excitation [3–5]. The time resolved spectra and dynamic behavior of EHP through near-band-edge excitation have not yet been investigated.

In this paper, time resolved two-photon absorption induced electron-hole plasma (EHP) luminescence of Ga-doped ZnO thin film was measured by an ultrafast optical Kerr gate (OKG) in femtosecond time regime. Experimental results showed that the buildup time of the EHP luminescence was strongly dependent on the excitation fluence. The dependence of the buildup time of EHP on excitation fluence probably arose mainly from the relaxation of the hot carriers due to the carrier–carrier interaction, which increased with the increase of excitation fluence.

2. Experiments

The ZnO:Ga film was fabricated by radiofrequency (rf, 13.56 MHz) magnetron sputtering technique. The target for the RF magnetron sputtering process have been prepared by cold pressing and subsequent sintering of a mixture ZnO and Ga_2O_3 powders (both 5 N) with a 95:5 molar ratio of Zn and Ga in a oxygen atmosphere at 1050 °C for 12 h. The process chamber was a custom-built RF magnetron sputtering chamber with a base pressure of 6.67×10^{-5} Pa. The ZnO:Ga target was used for sputtering with flux ratio of $Ar:O_2=3:1$, the rf power was 150 W. The distance between the substrate and target was 12 cm. The deposition rate was about 22 nm/min (the rf power was 150 W). The double smoothed sapphire substrate were degreased in acetone, methanol, each for 10 min at room temperature, then etched in HF

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for 1–2 s, followed by a rinse in deionized water and dry with a 5 N nitrogen. After a thermal cleaning of the sapphire substrate at 600 °C, a 100 nm thick ZnO:Ga buffer layer was deposited at the rf power of 100 W on a double smoothed and cleaned sapphire substrate. The buffer layer sputtering was carried out at room temperature, and the chamber deposition pressure was 1 Pa. And then a 2 μm thick ZnO:Ga was deposited on the buffer layer using RF magnetron sputtering technique at 350 °C substrate temperature. Finally, the substrate temperature was increased to 600 °C, the ZnO:Ga film was annealed at 600 °C under a 1 Pa nitrogen pressure for 40 min and then cooled down under it. The structure properties of the sample are investigated by X-ray diffraction (XRD) with Cu Kα (1.5406) source.

The experimental setup is shown in Fig. 1. The multi-pass amplified Ti:sapphire laser, which emitted 30 fs, 800 nm laser pulses at a repetition rate of 1 kHz, was split into two beams. One beam which had 30% of the total power was focused into a ZnO film with 2 μm thickness by a 10-cm focal-length lens, the generated luminescence was first polarized through polarizer and then served as probe beam. The other beam (pump beam), which had 70% of the total power, passed through a time-delay device and a λ/2 plate to control the path length and polarization of the pump beam, respectively. Both of beams were focused by lenses before they passed through the Kerr media. The centers of the pump beam and the generated luminescence spatially overlapped at the Kerr media at an angle of 25°. A polarizer was placed behind the Kerr media in a cross-Nicol configuration, so that the polarized luminescence could not pass through the polarizer without the pump beam. The luminescence transmitted after the Kerr media was collimated with a 100 mm focal-length lens before passing through the analyzer. The polarization of the pump beam was rotated 45° by λ/2 plate from that of the luminescence to optimize the intensity of the Kerr signals. A time-delay device, which was controlled by a computer, was used to adjust the timing of pulse collisions. The Kerr media we used here was quartz glass with a thickness of 1 mm. A low-pass filter was used to remove the 800 nm beam mixed in luminescence. As time-delay device moving, the temporal signals and spectral signals were detected by the photomultiplier tube (PMT) and the optical multichannel analyzer (OMA), respectively. The instrument response function of this system was about 100 fs.

3. Results and discussions

Fig. 2 shows the XRD pattern of the ZnO:Ga film. From the XRD pattern, we can see only two diffraction peaks indexed as (0002) and (0004) of the ZnO:Ga with wurtzite structure besides the peak (0006) from the sapphire (Al_2O_3) substrate. No characteristic diffraction peak corresponding to Ga or Ga compound impurity phase is observed. The full width at half maximum (FWHM) of the peak at 34.4° is 0.19°,

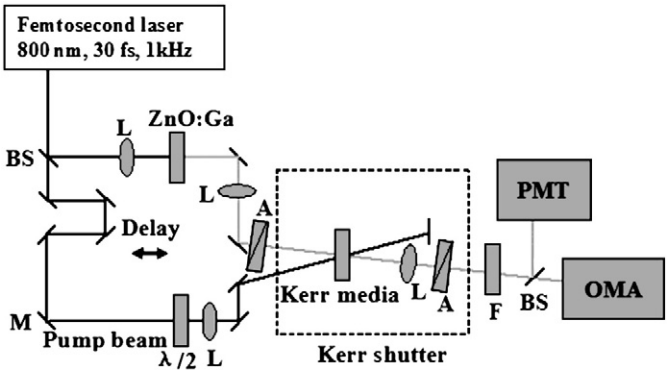

Fig. 1. Experimental setup of time resolved photoluminescence using the OKG method. BS: beam splitter; L: lens; M: mirror; A: analyzer; F: 800 nm filter; PMT: photomultiplier tube; OMA: optical multichannel analyzer.

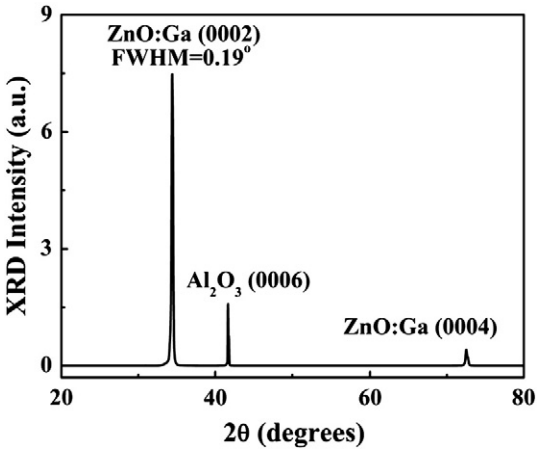

Fig. 2. XRD pattern of the ZnO:Ga film.

which indicates that the ZnO:Ga film is strongly c-oriented. We measured time resolved luminescence spectra of the ZnO:Ga film at different excitation fluences using ultrafast OKG. The results are shown in Fig. 3. From Fig. 3, we can see that the PL peak shifts from 397 nm to 403 nm with increasing excitation fluence. The onset wavelength of the EHP luminescence are 406, 411, 413, and 415 nm for the excitation fluence 160, 185, 210, and 220 mJ/cm^2 on the ZnO:Ga film, respectively. The PL is originated from the EHP emission. Coulomb interactions in material with a large carrier population,

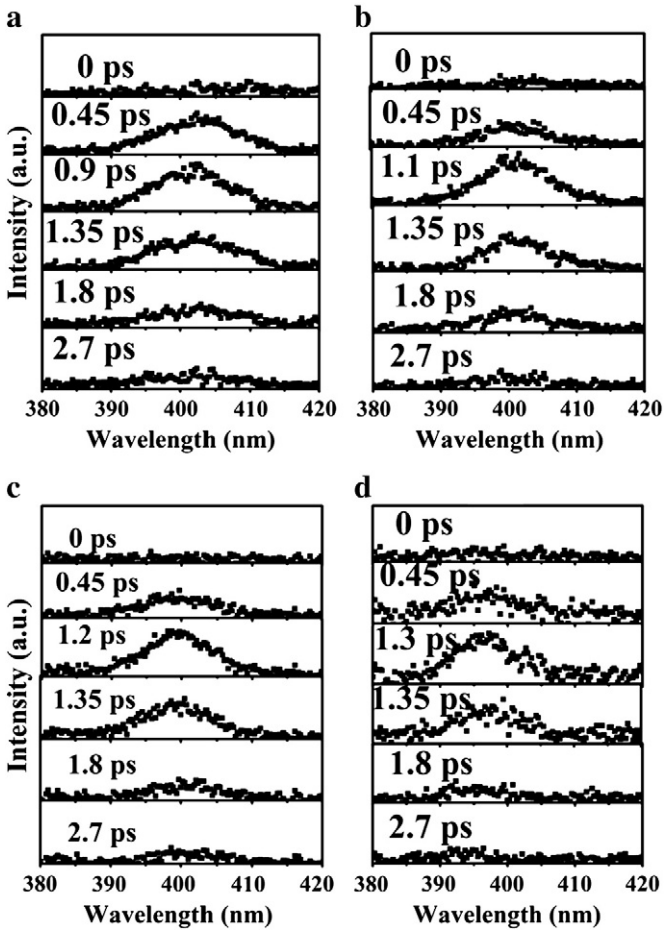

Fig. 3. Time resolved luminescence spectra of the ZnO:Ga film at different excitation fluences. The excitation fluences in (a), (b), (c), and (d) are 220, 210, 185, and 160 mJ/cm^2, respectively.

which is called band gap renormalization (BGR), cause the peak of the EHP emission (~400 nm) to locate below the band gap and redshift [5]. The short buildup time of the EHP emission (~1 ps) is in agreement with previously reported results [5,10,15,18]. However, the buildup time of the EHP emission becomes obviously faster with increasing excitation fluence on the ZnO:Ga film.

Fig. 4(a) shows time evolution of the EHP emission in ZnO:Ga film, which was measured using OKG. From Fig. 4(a), the buildup time becomes obviously faster with increasing excitation fluence. Also, the buildup time for EHP emission decrease from 1.3 to 0.9 ps as the excitation fluence on ZnO:Ga film increases from 160 to 220 mJ/cm^2 in Fig. 4(b). The single exponential decay fits reveals the EHP recombination times as 1.09, 1.07, 1.07, and 1 ps for the excitation fluence 160, 185, 210, and 220 mJ/cm^2 on the ZnO:Ga film, respectively. It indicates that the decay time of EHP emission keeps nearly invariant, while the buildup time of EHP emission is strongly influenced by the excitation fluence. It is well known that the buildup time for EHP emission in ZnO is related to the time needed for cooling of the hot carriers to a quasi-thermal equilibrium. It suggests that the cooling of the hot carriers to a quasi-thermal equilibrium is strongly influenced by the excitation fluence on the ZnO:Ga film.

In contrast to the pure ZnO, the Ga atoms work as donors and increase the density of electrons in the conduction band. Ga-doped in ZnO film increases band gap energy. Randomly distributed Ga in ZnO film unavoidably give rise to potential fluctuation or tail states of band edges, resulting in the broadening of luminescence line [20]. In our work, the buildup time of the EHP emission becomes obviously faster with increasing excitation fluence on the ZnO:Ga film. The similar dependence of the buildup time of the EHP emission on the excitation intensity in the EHP region has been also observed in pure ZnO epitaxial thin film, in which UV excitation was adopted in ref. [21]. It suggests that the presence of the Ga atoms doped in ZnO film has no influence on the pump power dependence of the buildup time of the EHP emission. The same cooling mechanism of the hot electron in the EHP region may exist in pure ZnO and ZnO:Ga film. Although the phenomenon for the pump power dependence of the buildup time of the EHP emission has been observed in ref. [21], the origin of the phenomenon has not been discussed.

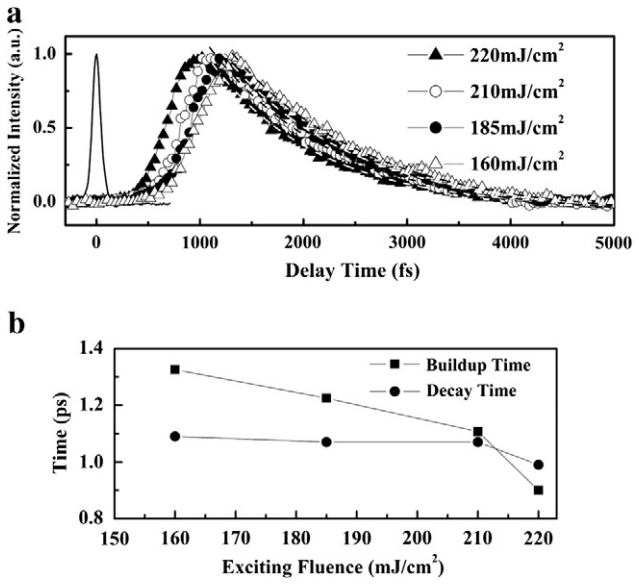

Fig. 4. (a) Time evolution of luminescence of the ZnO:Ga film at different excitation fluences. The inset shows the different excitation fluences on the ZnO:Ga film. The broken lines show the fitting results. The instrumental response is also shown by a solid line. (b) The buildup time and the decay time of the luminescence of the ZnO:Ga film at different excitation fluences.

To understand the dependence of the cooling of the hot electron on the excitation fluence, we investigate the excitation mechanism for EHP emission. The dependence of the intensity of the UV peak on the excitation intensity on a logarithmic scale is shown in Fig. 5. We can see that when the excitations exceeded a threshold of ~185 mJ/cm^2, the index on a logarithmic scale increases obviously. The slope is a little larger than two, this result indicates that the two-photon absorption plays an important role in the excitation process and that three photon absorption would also contribute to the excitation process.

The onset wavelength of the EHP luminescence, which corresponds to the renormalized band gap, is located at ~410 nm (~3.02 eV) depending on the excitation fluence. The excess energy of the hot carrier excitated by the 800 nm two-photon (3.1 eV) is higher than the LO-phonon emission energy (72 meV). Since the carrier-LO-phonon scattering takes place more effectively than radiative recombination of electrons with holes, the hot carriers relax toward the renormalized band gap by emitting LO-phonon. However, the buildup time for EHP emission is delayed due to the contribution of the carrier-LO-phonon interaction as the excitation fluence increases, which is not consistent to the experimental results shown in Fig. 4. According to the experimental results that the buildup time for EHP emission decreases with the increase of the excitation fluence, we suppose that the cooling of the hot electrons probably arises mainly from carrier–carrier scattering.

The buildup time for EHP emission is strongly dependent on the excitation fluence as is shown in Fig. 4. As carrier–carrier scattering dominates the energy relaxation path, more electrons contribute to higher scattering rate, causing shorter cooling time due to higher carrier density, which is consistent to the experimental results in Fig. 4. It suggests that, under the condition of the band edge absorption and high carrier concentration, the carrier–carrier interaction is the most important factor in influencing the hot electron cooling rate. This can be understood from the fact that, the carrier–carrier scattering rate increases with the increase of the carrier concentration [22], so that at high concentrations the collisions occur more frequently, resulting in energy transfer in plenty of carriers, even though the energy transfer in a single collision is small.

4. Conclusion

In this paper, time resolved two-photon absorption induced electron-hole plasma (EHP) luminescence of Ga-doped ZnO thin film was measured by an ultrafast optical Kerr gate (OKG) in femtosecond time regime. Experimental results showed that the buildup time of the EHP luminescence was strongly dependent on the

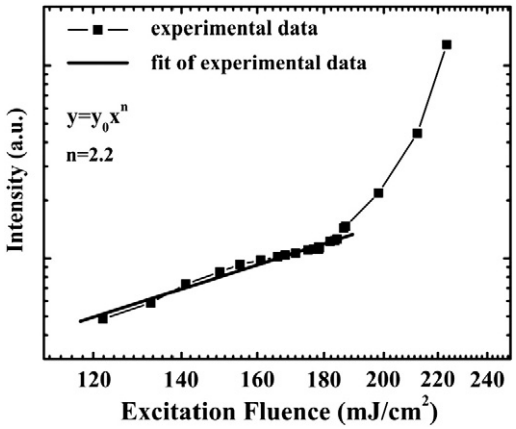

Fig. 5. Dependence of the UV peak intensity on excitation intensity on a logarithmic scale. The circle dots are experimental data and the solid line represents the fitting result.

excitation fluence. The dependence of the buildup time of EHP on excitation fluence probably arose mainly from the relaxation of the hot carriers due to the carrier–carrier interaction, which increased with the increase of excitation fluence.

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