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Electric-field effect of near-band-edge photoluminescence in bulk ZnO

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Abstract We have studied the effect of electric fields on the near-band-edge (NBE) emissions in bulk zinc oxide (ZnO) by using photoluminescence and photocurrent (PC) spectroscopy simultaneously. The intensity-quenching and peak-shift effects of the free exciton spectra were observed with increasing electric field. From the PC result, we find out that the free excitons are disturbed by the PC carriers of the photo-created electrons and holes. This disturbance reduces the recombination ratio and the lifetime of free excitons. Therefore, the intensity-quenching effect was attributed to the decrease in the recombination of free excitons. Thus, the shift of the free exciton peaks was related to Stark effect induced by electric field. As a result, we have found that these phenomena are caused to the exciton–electron scattering due to a strong interaction between the excitons in the conduction band and the photo-generated electron carriers with increasing the applied electric field.

Introduction

Zinc oxide (ZnO) has a direct transition and a wide band gap of 3.37 eV at room temperature (RT) [1]. Therefore, it is an attractive material for blue and ultraviolet (UV) light-emitting diodes (LEDs). Ultimately, it is expected that the materials related ZnO can replace the GaN materials currently used for blue and UV LEDs. Furthermore, the research on ZnO has been actively attempted for use in transparent conducting electrodes on laser diodes, field-effect transistors, and solar cells [2–7]. For these applications, it is important to understand the effect of the electric field on the optical properties of ZnO because the electric field perturbs the optical properties of a semiconductor [8]. The applied electric field can accelerate free carriers and increase the number of carriers due to impact ionization. The electric field dependence on the photoluminescence (PL) properties of Schottky diode fabricated on the CdS and GaAs bulks has previously been examined [9, 10]. The electric field dependence on the excitons of Si, Ge, InP, GaAs, and GaN has been reported by using PL spectroscopy [11–16]. However, the electric field effect on ZnO was only reported by a few researchers. Korsunska et al. observed that the external electric field influenced the green luminescence of a ZnO single crystal only under high temperatures [17]. Also, Yi et al. reported experimental luminescence data for the field effects on Zn-rich ZnO thin film [18]. Generally, PL spectroscopy measurement under the electric field is one technique of great importance in understanding the optical and electronic properties of the material, both fundamental properties and defects [19]. Therefore, it is useful in obtaining the information about the mechanism of PL quenching and recombination processes.

In this study, we investigated the electric-field-induced quenching phenomena of near-band-edge (NBE) PL in bulk ZnO at RT. Also, we will present the evidence for a strong interaction between the excitons and the photo-generated carriers excited by the unique light under the electric field.

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Experiment

Commercially available ZnO single crystals with (000–1) surfaces were used in this experiment. These crystals were grown by using the hydrothermal method. From the measurement of the double-crystal X-ray diffraction, the minimum value of the full width obtained at half maximum was 130 arcses. This value is larger than that of commercial GaAs wafers. The detailed structural and optical properties have been published elsewhere [20]. To apply the external electric field, we attached In electrodes to both sides of the bulk ZnO. Also, the ohmic behavior was confirmed by using current–voltage measurement. PL experiment was carried out at RT while the electric field was applied to the sample. The electric fields were varied from zero to 150 V/cm during the measurement. The surface of the sample was illuminated by 325 nm UV light emitted from He–Cd laser (Liconix, 10 mW) and the light coming from the sample was dispersed with a monochromator. The dispersed light was detected with a photomultiplier tube and then converted into a current. This converted current was recorded by a computer.

Results and discussion

Figure 1 shows the typical PL spectrum of bulk ZnO measured at RT. As shown in Fig. 1, the intense peak of 374.9 nm (3.307 eV) at UV region was observed. This strong UV peak of the NBE emission is caused by the free exciton recombination of ZnO [21]. Ordinarily, the observation of the free exciton in the semiconductor materials is very difficult because of happening easily the recombination by thermal energy (25 meV) of RT, but the exciton binding energy of ZnO is large as a 60 meV, so the free exciton emission of 3.307 eV is able to be observed at RT [22]. On the other hand, the blue emission of low intensity was observed at 431.9 nm (2.871 eV). The native defect due to oxygen vacancies (V_O) is known to produce the shallow donor level of about 0.5 eV below bottom of the conductor band [23]. As the band-gap energy of ZnO is 3.37 eV, the energy of the 2.871-eV emission is equal to the energy interval between the shallow donor level of about 0.5 eV below bottom of the conductor band and the top of the valence band. Therefore, it suggests that the 2.871-eV emission is originated from V_O. Furthermore, other emissions caused by deep levels were not observed at the long wavelength region.

Figure 2 shows the PL spectra obtained from the bulk ZnO under different electric fields. This measurement was carried out under electric fields ranging from 0 to 150 V/cm while the surface of the bulk ZnO was illuminated with 325-nm light emitted from a He–Cd laser. As shown in Fig. 2, the free exciton spectra decreased and broadened as the external electric field was increased. Also, these peaks tend to shift toward the low-energy region as the electric field is increased, and the shift energy is about 14 meV. However, the 2.871-eV emissions were independent of the

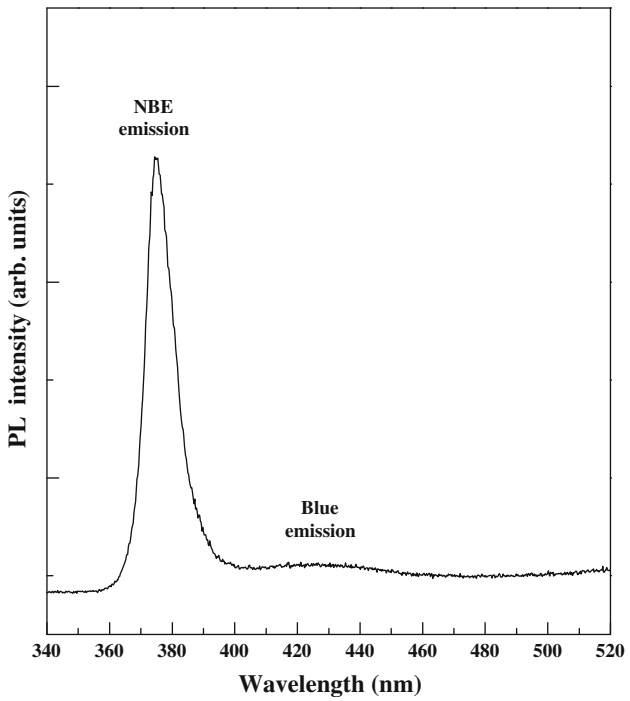

Fig. 1 Typical PL spectrum of bulk ZnO measured at RT

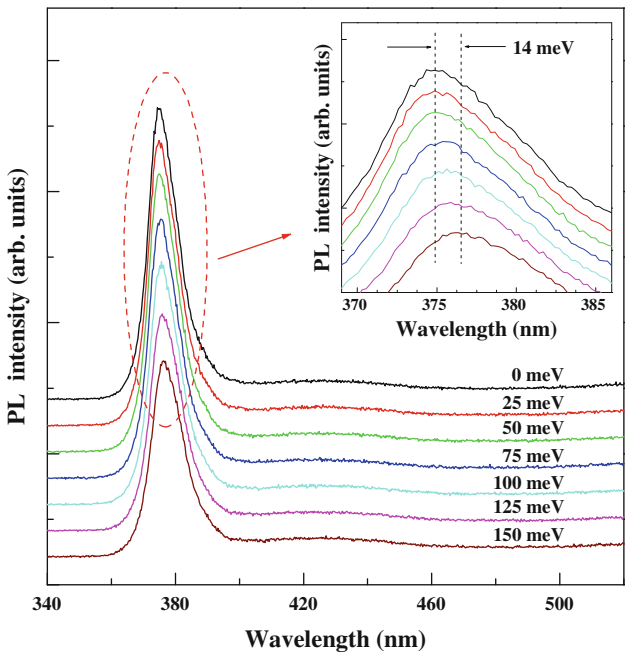

Fig. 2 PL spectra obtained from the bulk ZnO in the electric field range from 0 to 150 V/cm in a step of 25 V/cm

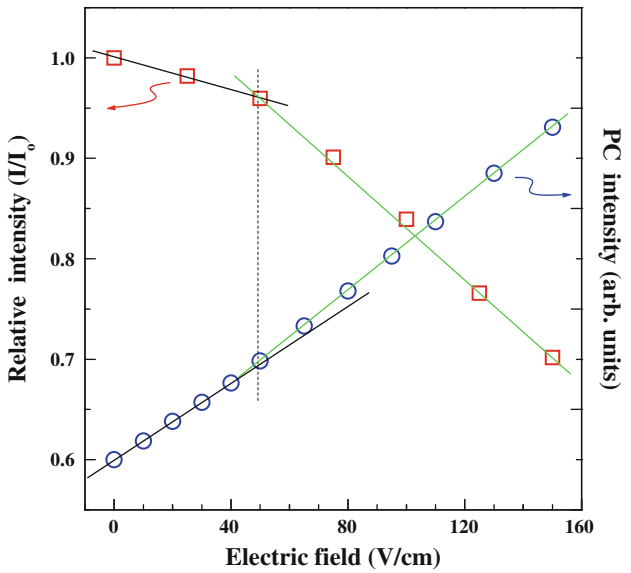

Fig. 3 Relative intensities of the free exciton emissions and PC-intensity variance in an applied electric field. Here, I and I_o mean the intensity of the free exciton emission with and without the applied electric field, respectively. Also, the PC is measured under illumination with unique light of 325 nm

variation of the external electric field. This clearly indicates that the intensity of the free exciton emission was strongly dependent on the applied electric field. To better comprehend the electric-field-induced quenching phenomena of PL, the photocurrent (PC) measurement was conducted. Figure 3 plots the relative intensities of the free exciton emissions and the PC-intensity variance in an applied electric field. Here, I and I_o mean the intensity of the free exciton emission with and without the applied electric field, respectively. As Fig. 3 shows, the relative intensities of the free exciton emission decreased with an increasing electric field. Furthermore, the relative intensities are steeply quenching at the electric field over 50 V/cm while these show the gentle slope below electric fields of 50 V/cm. This indicates that there exists a strong correlation at the electric field over 50 V/cm. On the other hand, the PC experiment was carried out under illumination with unique light of 325 nm at various electric fields. As shown in Fig. 3, the gradient of the PC intensity is gentle at below electric fields of 50 V/cm, but the PC intensity has a steep gradient at the electric field over 50 V/cm. Generally, when photons with energies greater than the band-gap energy of a semiconductor are incident upon a photoconductive material, electrons and holes are created in the conduction and the valence bands, respectively. The created electrons and holes are immediately guided to the electrodes on both sides. The PC signal detected is the current resulting from these photo-created electrons and holes. Therefore, the quenching effect of the free exciton emissions is closely tied to the mechanism generating the electrons and holes. The intensity of the free exciton emissions decreases steeply at electric fields over 50 V/cm while the PC intensity increases rapidly. The PL and the PC experiments were carried out simultaneously with the same electric field and excited light. The free excitons are transited by PL excitation to the conduction band. Moreover, the PC carriers of the free electron and hole created by the absorption of light with energy greater than the band-gap energy affect the conduction and the valence bands, respectively, and the PC carriers are gradually accelerated as the external electric field is increased. Therefore, the generated and accelerated PC carriers should readily interact with the free excitons transited by the excitation source of PL, disturbing the direct recombination and reducing the lifetime of the free excitons. Consequently, the PL-intensity quenching is related to a decrease in the recombination of the free exciton. Also, these results led us to conclude that the quenching mechanism in the free exciton emission was strongly related to the electric field.

Figure 4 shows the energy variances of the free exciton emissions in ZnO with increasing electric field. As shown in Fig. 4, their peak energies tend to shift toward the lower energy region with increasing electric field. In particular, these energies stay nearly constant below electric fields of 50 V/cm, but they are steeply quenching at electric fields above 50 V/cm. This phenomenon is due to the PC effect. With increasing electric field, the PC carriers screen the PL emissions. Thereby, the PL emissions involve a spatially indirect recombination. Naturally the number of carriers

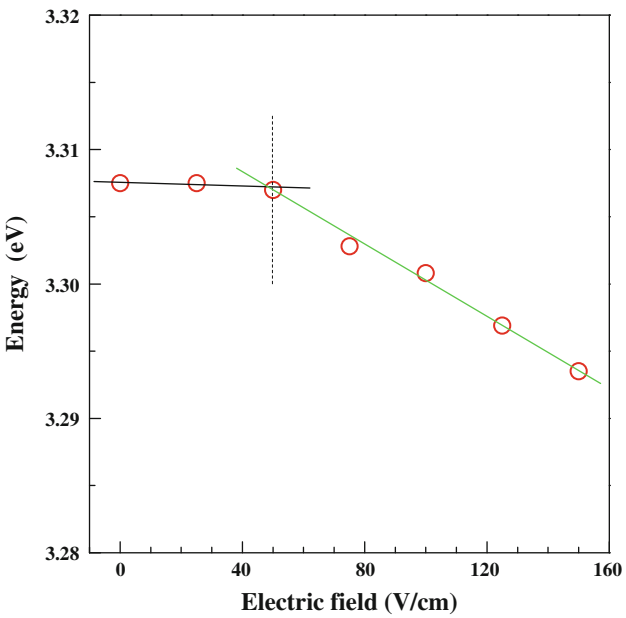

Fig. 4 Energy variances of the free exciton emissions in ZnO with increasing electric field

participating in recombination will be reduced. Such recombination should yield a linear red Stark shift, which relates to a change in the atomic energy on application of an electric field [24]. The peak energy of the free exciton decreases linearly with a slope of 0.135 meV/(V/cm) at electric fields over 50 V/cm. This is the first-order Stark effect due to a low electric field. Therefore, this phenomenon suggests that this strong interaction between the free excitons and photo-generated PC carriers leads to a displacement or widening of the spectrum. Moreover, it naturally follows that this interaction causes intensity quenching and a peak shift of the exciton spectra.

Conclusion

The effect of an external electric field on the NBE emission of bulk ZnO was studied by using PL and PC experiments. The free exciton spectra decreased and broadened as the external electric field was increased. Also, with increasing electric field, these peaks tend to shift toward the low-energy region, and the shift energy is about 14 meV. The behavior of the free exciton emissions was found to depend strongly on the electric field applied. The combined results of PL and PC measurements suggest that the free excitons readily interact with the PC carriers of the photo-created electrons and holes. This interaction disturbs the direct recombination of the free excitons. Consequently, the PL-intensity quenching is related to a decrease in the recombination of the free exciton. Moreover, these PL emissions involve a spatially indirect recombination. Therefore, the number of carriers participating in recombination should be naturally reduced. Such recombination should yield a linear red Stark shift, which relates to a change in the atomic energy on application of an electric field. As a result, we have found that these phenomena are caused to the exciton–electron scattering due to a strong interaction between the excitons and the photo-generated electron carriers with increasing the applied electric field.

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