Ultrafast biexciton dynamics in a ZnO thin film

Fang-Yi Jen, Yen-Cheng Lu, Cheng-Yen Chen, Hsiang-Chen Wang, and C. C. Yang^{a)}
Graduate Institute of Electro-Optical Engineering and Department of Electrical Engineering, National Taiwan University, 1, Roosevelt Road, Sec. 4, Taipei, Taiwan, Republic of China

Bao-ping Zhang and Yusaburo Segawa
Photodynamics Research Center, RIKEN (the Institute of Physical and Chemical Research), Sendai, Japan

(Received 11 May 2005; accepted 11 July 2005; published online 8 August 2005)

The emission lines of biexciton and donor-bound biexciton are observed in a high-quality ZnO thin-film sample with time-resolved photoluminescence (TRPL) measurement. The TRPL intensity profiles reveal the formation sequence of various types of exciton. After free excitons are first generated, part of them is trapped by neutral donors to form donor-bound excitons. The other part contributes to the generation of biexcitons through free exciton scattering. Next, a donor-bound biexciton is generated through the trapping of a biexciton or two free excitons by a neutral donor or the trapping of a free exciton by a donor-bound exciton. Except donor-bound exciton, the relaxations of all other exciton states show two decay stages. Either the increasing or decreasing trends of the calibrated decay times in increasing the excitation power are well interpreted with a four-level model. © 2005 American Institute of Physics. [DOI: 10.1063/1.2012539]

Because of its large exciton binding energy at about 60 meV, ZnO has attracted much attention in crystal growth and optical property characterization. With such a large exciton binding energy, the dominance of exciton recombination in the radiative process, even up to the room temperature, results in the high photon emission efficiency. Recently, besides the nanostructures, such as nanotubes, nanorods, and nanowalls, high-quality ZnO thin films have been grown by molecular-beam epitaxy,^{1,2} metalorganic chemical vapor deposition (MOCVD),^{3,4} and sputtering.⁵ Meanwhile, the growths of ZnO/MgZnO quantum-well structures^{6,7} and ZnSO and ZnCoO ternary compounds^{8,9} have been implemented. For device fabrication, *p*-type ZnO (Refs. 10 and 11) and ZnO grown on GaN (Ref. 12) have been the issues of interest.

Normally, in photoluminescence (PL) measurement with low excitation, the emission of donor-bound exciton (D^0X) dominates the spectrum at low temperatures (<60 K) and that of free exciton (FX) dominates at high temperatures. If the acceptor density is high in a sample, the feature of donor-acceptor pair (DAP) can be observed. In the case of high excitation, the biexciton (XX) feature can be observed in a high-quality ZnO sample.^{13,14} Although the biexciton dynamics in other materials were studied,^{15–17} that in ZnO has not been well explored. In particular, the interplay between XX , D^0X , and FX in ZnO has never been investigated.

In this letter, we study the ultrafast biexciton dynamics in a ZnO thin-film sample with time-resolved PL (TRPL) measurement. In the measurement, not only the emission line (the M line) of XX is observed, but also that (the D^0M line) of donor-bound biexciton (D^0XX) can be clearly seen. The calibrated two-stage decay times are used to build the model of ultrafast biexciton dynamics in such a ZnO sample. The ZnO thin film was grown with MOCVD on a (0001) sapphire substrate with 6 Torr in pressure at 450 °C for 90 min. The temporal resolution in the TRPL measurement is 19 ps.

The excitation photon energy is 3.444 eV (360 nm), which is higher than the FX energy level at 3.378 eV.

Figure 1 shows the time-integrated PL spectra at 10 K with several excitation powers. The focused excitation laser beam size on the sample was estimated to be 25 μm . Therefore, the average power of 9.05 mW corresponds to the average intensity of 1.93 kW/cm², which is in the same order of magnitude as those for observing biexciton in ZnO.¹³ At low excitation, a major peak at 3.37 eV (D^0X) and a minor peak at 3.306 eV (DAP) can be observed. As the excitation power increases, two more major peaks at 3.3614 and 3.353 eV can be identified. Also, the DAP peak blueshifts with increasing excitation power.¹³ Figure 2 shows the integrated PL intensities of the three major peaks as functions of excitation power in the log-log scale. The calibrated slopes of the three sets of data points at around 0.93, 1.27, and 1.53 are shown in the legend. The set with the slope of 0.93 has been identified as the feature of D^0X . The other two sets of super-linear slopes are related to the activities of biexcitons and bound-biexcitons.^{18,19} With the spectral peak position at 3.3614 eV, the central major peak corresponds to the emis-

FIG. 1. Time-integrated PL spectra at 10 K with several average excitation powers at 1.147, 3.56, 7.76, 9.05, 11.45, 15.33, 19.11, and 27.02 mW. The excitation photon energy is 3.444 eV.

^{a)}Electronic mail: ccy@cc.ee.ntu.edu.tw

FIG. 2. Time-integrated PL intensities as functions of average excitation power at three photon energies corresponding to the emissions of D^0X , XX (M), and D^0XX (D^0M).

sion of XX , which is usually called the M line.¹³ In such an emission process, one of the electron-hole pairs of an XX recombines to release a photon and an FX . The left major peak at 3.353 eV corresponds to the emission of D^0XX , which is designated as the D^0M line.¹⁸ The relative energy levels of those exciton states are depicted in Fig. 3.²⁰ Here, we follow the convention and define the binding energies, G_M , G_{D^0M} , and G_{D^0X} , corresponding to the biexciton binding energy, donor binding energy of biexciton, and donor binding energy of exciton, respectively. In our measurement, the three binding energies are $G_M=16.6$ meV, $G_{D^0M}=16.4$ meV, and $G_{D^0X}=8$ meV. Those values are quite consistent with what reported previously.¹⁸

Figure 4 shows the TRPL intensity profiles at the spectral peaks of D^0X , M , D^0M , and FX at 10 K. The excitation power is 27.02 mW. Although the FX feature is unclear in Fig. 1 (a very minor side lobe), its energy level has been well identified (3.378 eV). In Fig. 4, the dashed fitting lines for the data curves in the log scale are plotted to demonstrate the two-stage decay characteristics of M , D^0M , and FX . It is interesting to note the large difference in decay slope between the two stages of FX . Also, the slower decay in the first stage, compared with that of the second stage, of D^0M shows the unique behavior of D^0XX . The relative time delays of the maximum intensities of FX , D^0X , M , and D^0M are 0, 14.31, 14.31, and 30.18 ps, respectively. These results indicate the generation sequence of different types of exciton. FX s are first generated after excitation. Then, part of them is trapped by neutral donors to form D^0X s. Also, an FX - FX

FIG. 3. Schematic demonstration of the relative energy levels of various exciton states.

FIG. 4. TRPL intensity profiles of four photon energies corresponding to the emissions of FX , D^0X , XX (M), and D^0XX (D^0M) at 10 K.

scattering process results in the generation of XX s. These two mechanisms have about the same time scale (14.31 ps). Next, the generation of D^0XX may have three channels. First, the trapping of an XX by a neutral donor can lead to the formation of a D^0XX . Second, the trapping of an FX by a D^0X can result in a D^0XX . Third, the trapping of two FX s by a neutral donor can also produce a D^0XX although the probability of such a process is quite low. With these processes, the formation of D^0XX is further delayed by a time scale of about 16 ps.

Figure 5 shows the calibrated decay times of the four types of exciton as functions of excitation power. Among those curves, we first notice the short first-stage decay times of FX . This fast decay (40 ps time scale) is attributed to the formations of D^0X and XX through the trapping and scattering processes, respectively. The slow down of the FX decay after the delay of about 70 ps (see Fig. 4), i.e., the slower second-stage decay (120 ps time scale), is due to the supply through the M and D^0M emissions. The recombination of one of the electron-hole pairs in an XX can lead to the generation of an FX . Therefore, one can see the increasing trend of the second-stage decay time with increasing excitation power (>10 mW in Fig. 5). On the other hand, the decreasing trend of decay time in the first stage of FX relaxation originates from the increasing XX generation as the excitation power increases. However, the weak dependence of FX decay time on excitation power, in either the first- or second-stage decay, implies that the formation of D^0X plays a significant role in FX relaxation.

The increasing trend of D^0X emission decay time with excitation power can be interpreted as the significant supply from FX (relaxed from XX) and D^0XX through their relaxations. At 10 K, D^0X is the most stable state and all the

FIG. 5. PL intensity decay times as functions of average excitation power for various exciton emissions at 10 K.

relaxations of FX , XX , and D^0XX end up with the supply to D^0X . The decay times of both the faster first-stage and the slower second-stage decays of XX (the M line) decrease with excitation power. The faster first-stage decay is due to the relaxation of XX into the D^0XX state. The slowdown of the second-stage XX relaxation can be attributed to the saturation of D^0XX formation. It is noted that the major supply to the XX population through the FX - FX scattering occurs only in the very early stage (<70 ps), which is earlier than the temporal range for the decay time calibration of the M line. The decreasing trends of the M -line intensity with excitation power originate from the higher radiative recombination rate of XX than that of FX .^{16,17,21} In a case of high excitation power, a higher fraction of total carriers exists in the form of XX such that in the XX - FX cycling process, the effective decay rate of the total carrier density becomes higher, when compared with that of a lower excitation case. Such a higher decay rate is observed as the shorter decay times of the M -line intensity. The behavior of D^0XX is quite different. First, the first-stage decay time of the D^0M line is longer than that of the second stage. Second, the decay time of the first stage increases with excitation power although that of the second stage shows the opposite trend. The slower first-stage decay can be attributed to the significant supply from XX and D^0X . The increasing decay time with excitation power in this stage is simply due to the more supply as the excited carrier density (and hence the XX density) is increased. After this supply process (the first stage of the M line) is slowed down, the decay time in the second stage is expected to decrease with excitation power, like the case of the M line.

In summary, we have performed the TRPL measurement on a high-quality ZnO thin-film sample and observed the emission lines of XX and D^0XX . The TRPL intensity profiles indicated the formation sequence of different types of exciton. After FX s were first generated, part of them was trapped by neutral donors to form D^0X s. The other part became XX s through FX - FX scattering. Next, a D^0XX could be generated through the trapping of an XX or two FX s by a neutral donor or the trapping of an FX by a D^0X . Except D^0X , all other exciton states showed two decay stages in their relaxations. Either the increasing or decreasing trends of the calibrated

decay times in increasing the excitation power were well interpreted with a four-level model.

This research was supported by National Science Council of Taiwan, The Republic of China, under Grant Nos. NSC 93-2210-M-002-006 and 94-2215-E-002-015, and by U.S. Air Force under Contract Nos. AOARD-04-4026 and AOARD-05-4085.

- ¹Y. Chen, D. Bagnall, and T. Yao, *Mater. Sci. Eng., B* **77**, 190 (2000).
- ²D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).
- ³K. Haga, T. Suzuki, Y. Kashiwaba, H. Watanabe, B. P. Zhang, and Y. Segawa, *Thin Solid Films* **433**, 131 (2003).
- ⁴T. Gruber, C. Kirchner, K. Thonke, R. Sauer, and A. Waag, *Phys. Status Solidi A* **192**, 166 (2002).
- ⁵S. F. Chichibu, T. Yoshida, T. Onuma, and H. Nakanishi, *J. Appl. Phys.* **91**, 874 (2002).
- ⁶B. P. Zhang, N. T. Binh, K. Wakatsuki, C. Y. Liu, Y. Segawa, and N. Usami, *Appl. Phys. Lett.* **86**, 032105 (2005).
- ⁷T. Makino, C. H. Chia, N. T. Tuan, H. D. Sun, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *Appl. Phys. Lett.* **77**, 975 (2000).
- ⁸B. K. Meyer, A. Polity, B. Farangis, Y. He, D. Hasselkamp, T. Krämer, C. Wang, U. Haboeck, and A. Hoffmann, *Phys. Status Solidi C* **1**, 694 (2004).
- ⁹Y. Zheng, J. C. Boulliard, A. Soyer, and J. F. PeËtrot, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **A60**, 339 (2004).
- ¹⁰L. G. Wang and A. Zunger, *Phys. Rev. Lett.* **90**, 256401 (2003).
- ¹¹Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong, and H. W. White, *J. Cryst. Growth* **216**, 330 (2000).
- ¹²T. Gruber, C. Kirchner, R. Kling, F. Reuss, and A. Waag, *Appl. Phys. Lett.* **84**, 5359 (2004).
- ¹³B. P. Zhang, N. T. Binh, K. Wakatsuki, Y. Segawa, Y. Kashiwaba, and K. Haga, *Nanotechnology* **15**, S382 (2004).
- ¹⁴K. Hazu, T. Sota, K. Suzuki, S. Adachi, S. F. Chichibu, G. Cantwell, D. B. Eason, D. C. Reynolds, and C. W. Litton, *Phys. Rev. B* **68**, 033205 (2003).
- ¹⁵M. Ikezawa and Y. Masumoto, *Phys. Rev. B* **53**, 13694 (1996).
- ¹⁶G. Bacher, R. Weigand, J. Seufert, V. D. Kulakovskii, N. A. Gippius, A. Forchel, K. Leonardi, and D. Hommel, *Phys. Rev. Lett.* **83**, 4417 (1999).
- ¹⁷K. Kyhm, R. A. Taylor, J. F. Ryan, T. Aoki, M. Kuwata-Gonokami, B. Beaumont, and P. Gibart, *Phys. Status Solidi B* **228**, 475 (2001).
- ¹⁸A. Yamamoto, K. Miyajima, T. Goto, H. J. Ko, and T. Yao, *Phys. Status Solidi B* **229**, 871 (2002).
- ¹⁹H. J. Ko, Y. F. Chen, T. Yao, K. Miyajima, A. Yamamoto, and T. Goto, *Appl. Phys. Lett.* **77**, 537 (2000).
- ²⁰M. Nakayama, H. Ichida, and H. Nishimura, *J. Phys. C* **11**, 7653 (1999).
- ²¹J. C. Kim, D. R. Wake, and J. P. Wolfe, *Phys. Rev. B* **50**, 15099 (1994).