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Linköping University Post Print

N.B.: When citing this work, cite the original article.

The original publication is available at www.springerlink.com:

Shula Chen, Jan Eric Stehr, N. Koteeswara Reddy, C. W. Tu, Weimin Chen and Irina Buyanova, Efficient upconvertion of photoluminescence via two-photon-absorption in bulk and nanorod ZnO, 2012, Applied physics. B, Lasers and optics (Print), (108), 4, 919-924. <u>http://dx.doi.org/10.1007/s00340-012-5138-y</u> Copyright: Springer Verlag (Germany) <u>http://www.springerlink.com/?MUD=MP</u>

Postprint available at: Linköping University Electronic Press http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-81306

Efficient upconvertion of photoluminescence via two-photonabsorption in bulk and nanorod ZnO

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Abstract.

Efficient upconversion of photoluminescence (PL) from donor bound excitons is revealed in bulk and nanorod ZnO. Based on excitation power dependent PL measurements performed with different energies of excitation photons, two-photon-absorption (TPA) and two-step TPA (TS-TPA) processes are concluded to be responsible for the upconversion. The TS-TPA process is found to occur via a defect/impurity (or defects/impurities) with an energy level (or levels) lying within 1.14-1.56 eV from one of the band edges, without involving photon recycling. One of the possible defect candidates could be V_{Zn} . A sharp energy threshold, different from that for the corresponding one-photon absorption, is observed for the TPA process and is explained in terms of selection rules for the involved optical transitions.

PACS number(s): 78.55.Et, 71.35.Gg, 71.55.Gs

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1. Introduction

ZnO continues to attract extensive research interest as a promising material for a wide variety of device applications in e.g. transparent electronics, spintronics, solar cells, and solidstate white lighting [1-3]. Owing to a wide and direct bandgap combined with a large exciton binding energy, ZnO is also among key candidates for efficient light emitters operating in ultraviolet (UV) spectral region. Furthermore, since ZnO can be easily synthesized with superior optical quality in various nanoscale forms [4-6], it can be used in emerging nanooptoelectronic devices (e.g. in nano-lasers) to be implemented in novel photonic circuits. A lack of inversion symmetry inherent to wurtzite crystal lattice of ZnO facilitates strong nonlinear optical effects in this material such as second-harmonic generation [7-10] and twophoton-absorption (TPA) [11-15]. The latter process often leads [10] to PL upconversion, i.e. appearance of efficient near-band-edge (NBE) photoluminescence (PL) arising from recombination of non-equilibrium carriers generated due to energy upconversion via TPA under optical excitation with photon energy below the bandgap energy. Therefore, TPA is currently considered [15] as an attractive practical approach for exciting the PL emission in ZnO as it allows us to replace expensive UV pumping sources in photonic circuits by inexpensive near-infrared-laser diodes based on III-V semiconductors.

Under TPA, the non-equilibrium carriers that participate in the NBE PL are generated via simultaneous absorption of two photons through virtual-state-assisted interband transitions which leads to a quadratic dependence of the upconverted PL intensity on excitation power. Therefore, efficient TPA in ZnO is usually achieved under high pumping conditions [11, 14], often in the order of 10⁹ W/cm². Efficiency of the upconversion process, however, is known to be significantly higher if intermediate states involved in the photon absorption are not virtual but real states, e.g. impurity/defect levels. Such two-step two-photon-absorption (TS-TPA) has previously been reported in a number of semiconductor materials [16-19] and exhibits a

weaker dependence on the excitation intensity (with a power factor ≤ 2). The TS-TPA has most recently been reported in ZnO microcrystals [12], though the energy position and origin of the involved defects remain questionable. Also not certain are spectral ranges where TPA or TS-TPA dominates. The purpose of the present study is to clarify these issues by measuring excitation-power and excitation-wavelength dependences of the upconversion process, using donor bound excitons (BX) as a scaled measure of the number of the upconverted carriers in bulk and nanostructured ZnO.

2. Experimental

The investigated samples include commercially available bulk crystals from Cermet Inc. and Tokyo Denpa Co., as well as ZnO nanorods (NRs). The latter were synthesized by rapid thermal chemical vapor deposition on Au-coated c-plane Al₂O₃ substrates. The growth of the ZnO NRs was carried out for 10 minutes at 950 °C and pressure of 20 Torr under Ar and O₂ flow of 100 and 2 sccm, respectively. The NRs are vertically aligned, and are rather uniform in size with an average diameter of around 100 nm as revealed by scanning electron microscopy measurements.

PL measurements were performed at 5K. The 266 nm line from a continuous-wave (cw) solid state laser or second-harmonic pulses (λ_{exc} =350-360 nm) of a tunable mode-locked Ti:sapphire solid state laser, with a pulse duration of 2 ps and a repetition rate of 76 MHz, were used as one-photon excitation sources. Two-photon excitation was achieved by using: pulses with λ_{exc} =370-450 nm (740-900 nm) from a pulsed Ti:sapphire laser with (without) a frequency doubler; the 514 and 661 nm lines from cw diode lasers; photons with wavelengths of λ_{exc} =710-800 nm provided by a tunable cw-Ti:sapphire solid state laser. The incident laser beam was focused on the sample surfaces with a spot diameter of ~ 0.5 mm. Cw PL was detected by a photomultiplier tube assembled with a 0.8-m double-grating monochromator,

whereas transient PL signals were detected by a streak camera combined with a 0.5 m singlegrating monochromator. One-photon optical absorption measurements were carried out at room temperature using a halogen lamp as a light source. Optically detected magnetic resonance (ODMR) studies were performed at 3K with a microwave (MW) frequency of ~ 9 GHz. In the ODMR measurements, PL was excited by the 364 nm line of an Ar⁺ ion laser. ODMR spectra were obtained as a change of the integrated PL intensity detected by a Si detector within the visible spectral range of 420-1000 nm.

3. Results and Discussion

Representative PL spectra measured from the bulk and NR ZnO using one-photon excitation are shown by the solid lines in Figure 1 and are typical for good quality materials. In the bulk samples the spectra contain free exciton (FX) emissions from upper (FX^U) and lower (FX^L) polariton branches and a series of sharp BX lines, which are labeled as I₉, I₇, I₆, and I_{4a} following the common notations used in the literature [20]. The BX lines are somewhat broadened in the ZnO NRs where at least three excitonic emissions denoted by DX₁, DX₂ and SX can be resolved, see Figure 1. Spectral positions of DX₁ and DX₂ are very close to that of I₉ and I₇, respectively, which likely indicate the same origin of these emissions in the bulk and NR samples. The observed relative shift by about 0.5 meV of the corresponding PL peak positions between the two materials is likely due to their difference in residual strain. The broader SX line can be tentatively attributed to recombination of surface excitons [21], which are common in PL spectra of nanostructured ZnO with a large surfaceto-volume ratio. Most importantly, in all samples the BX transitions are also observed when the excitation photon energy is tuned below the BX energies. Typical spectra of this upconverted PL (UPL) are shown by the dashed lines in Figure 1 and are very similar to those measured under one-photon excitation. For the NR ZnO, a new BX line (labeled as DX₃ in Figure 1) becomes visible in the UPL spectra, likely due to suppression of the SX emission which overlaps with DX_3 . This is not surprising as light absorption under the two-photon excitation occurs over the entire volume of the sample, whereas under the one-photon excitation it takes place only within the near-surface region.

The energy upconversion process is found to occur for a wide range of excitation wavelengths of 380-735 nm, though its efficiency and dependence on the excitation power (W_{exc}) change with λ_{exc} – see Figure 2. For λ_{exc} ranging from 370 to 532 nm, the UPL emission in the bulk ZnO could be detected with W_{exc} as low as 1-5 mW, demonstrating a very high efficiency of the upconversion process. The intensity of the BX UPL emissions under these conditions is proportional to W_{exc}^n , where the power factor n is ~ 1.3-1.6 (for W_{exc} = 400 nm and 532 nm. The observed power dependence implies that the dominant energy upconversion process under these conditions is TS-TPA via real states, as shown schematically in the inset in Figure 2 (the green arrows). On the other hand, significantly stronger power dependences with n = 2.1- 2.2 are found either for high W_{ex} or when the excitation wavelength is tuned at or below 661 nm – see Figure 2 [22]. This indicates prevalence of TPA via virtual states under these conditions (shown by the red arrows in the inset of Figure 2).

3.1. Energy upconversion: Two-step two photon absorption.

Let us now discuss the revealed upconversion processes in more detail starting from TS-TPA via a real intermediate state, such as a defect level. This process usually involves two steps though their exact sequence depends on initial occupation of the defect level: (i) an electron is excited from the defect level to the conduction band (CB) and (ii) an electron from the valence band (VB) is excited to the defect level leaving a hole in VB - see the green arrows in the inset in Figure 2. The created free electron-hole pairs may then form bound excitons detected in UPL. Strictly speaking, a quadratic dependence of the UPL intensity on Wex may be expected for such process. However, the exact value of the power factor is known to decrease [16-19] if population of the involved intermediate state can be easily saturated due to e.g. a long lifetime of the state or a low defect density. The latter, however, is less likely in our case, as the energy upconversion is very efficient and exhibits the same power dependence even at very low W_{ex}. Since TS-TPA is observed for $\lambda_{exc} = 380-532$ nm (3.26 – 2.33 eV) but is no longer detected when λ_{exc} is tuned to 661 nm (1.88 eV), the energy position of the involved intermediate state can be estimated to lie within the range of 1.14-1.56 eV from one of the band edges. The presence of the optical absorption process via a defect/impurity level within the TS-TPA spectral range is also confirmed from one-photon absorption measurements. Results of these measurements performed on the bulk ZnO samples are shown in Figure 3. It is obvious that in addition to a sharp absorption edge at around 3.2 eV related to the onset of the band-to-band absorption, both samples exhibit a broad absorption band with a threshold energy of around 2.2 eV. (The absorption spectrum could not be measured from the ZnO NRs, unfortunately, due to strong light absorption by Au nanoparticles utilized as a catalyst for the NRs growth). The threshold energy for the onephoton absorption correlates with the threshold deduced for the TS-TPA (1.56 - 2.33 eV), which makes it possible to assume that transitions via the same defect/impurity level are monitored in both processes. This assumption is further supported by the observed correlation between the efficiency of the TS-TPA and the intensity of the one-photon absorption between the two bulk samples.

As to a possible origin of the defect/impurity level involved in the TS-TPA, it is most likely related to an intrinsic defect or a residual impurity due to contaminant, or their complex, as all investigated structures were intentionally undoped. Common trace impurities

in ZnO that introduce deep levels within the bandgap include Cu, Li, Mn and Pb [23, 23]. However, the energy positions of these levels are beyond the range determined for the observed TS-TPA process, which rules out their role in the TS-TPA. The intrinsic defects known to introduce deep levels and have reasonably low formation energies in ZnO include zinc and oxygen vacancies, V_{Zn} and V₀ [24]. Previous electron spin resonance studies [25, 26] have shown that the threshold energy of the optical excitation for the charge transition (0/+)level of V_0 is ~ 2.1 eV. A similar threshold energy of about 2.3-2.4 eV was also found for the photo-ionization process of V_{Zn} , $V_{Zn}^{2^-} + h\nu \rightarrow V_{Zn}^{-^+} + e$. Thus both defects can, in principle, provide a path for TS-TPA. We believe, however, that the participation of V_{Zn} is somewhat more likely since these defects are more abundant in as-grown ZnO, as shown by the positron annihilation spectroscopy [27], spin resonance measurements [25], as well as first-principle calculations [24]. We note that the presence of these defects in the investigated structures was directly confirmed from the performed ODMR measurements. To demonstrate this, Figure 4 shows typical ODMR spectra measured from the bulk and NR ZnO, where well-known [24, 25] signals related to V_{Zn} , a residual donor D and an exchanged-coupled pair of the donor and V_{Zn} acceptor (V_{Zn}/D) are clearly seen. The observed broadening of the ODMR lines in the ZnO NRs is likely caused by imperfect alignment of individual NRs within an ensemble, within $\sim 20^{\circ}$ based on scanning electron microscopy measurements, as all ODMR line positions are sensitive to the angle between the crystallographic axes and the direction of the external magnetic field employed in the ODMR experiments [25, 26].

In-depth information on the details of the observed TS-TPA, such as origin of the photons participating in energy upconversion, can be obtained from transient PL studies. It has previously been shown that whereas the first absorption step usually involves a photon from a laser, the photon required to complete TPA may be provided either by the laser light or via photon recycling [18, 19]. The latter can be mediated by other radiative recombination

processes such as emissions within the visible spectral range commonly observed in ZnO, which are also present, though weak, in the investigated samples. Rising of the resulting UPL emission under pulsed excitation is usually rather slow and persists even after the end of the laser pulse due to slow feeding via photon recycling. To single out importance of the photon recycling in our structures, we have studied dynamics of the BX emission under one- and two-photons excitation conditions. Representative PL transients are shown in Figure 5 taken as an example the bulk (Denpa) ZnO. Under one-photon excitation, the BX emission exhibits a rising within the first 200 ps, due to trapping of the photo-generated carriers to the BX states. This is followed by the PL decay which contains a fast (0.13 ns) and a slow (0.9 ns)component. By analogy with BX dynamics in GaN [28], the former can be tentatively attributed to lifetime of BXs generated close to the surface that is shortened due to surface recombination and scattering processes. This decay component is no longer observed under two-photon excitation. The slow component, which dominates the UPL decay, may then represent the bulk BX lifetime. Most importantly, the rising of the UPL emission is only slightly slower than that detected under one-photon excitation, which rules out significant contributions from the photon recycling. To further confirm this conclusion we have modeled the expected UPL transient if: (i) both photons are provided by the laser; (ii) the rising time of the UPL emission is the same as that under one-photon excitation and the UPL decay is solely determined by the slow component; (iii) the UPL emission is excited uniformly within the entire volume of ZnO; (iv) the emitted light is partially absorbed and also experiences a delay when propagating through ZnO media, which is determined by the dispersion of excitonpolaritons [29]. The result of this modeling is shown by the solid line in Figure 5 and is in excellent agreement with the experimental data. This provides compelling evidence that both photons participating in the TS-TPA are provided by the laser.

3.2. Energy upconversion: Two photon absorption

When excitation photon energy is insufficient to complete TS-TPA, energy upconversion may occur due to TPA via virtual states. From Figure 2, this process dominates in our structures when $\lambda_{exc} \ge 661$ nm or at high excitation power, evident from the observed quadratic dependence of the UPL intensity on W_{exc}. The TPA process is less efficient than TS-TPA and could only be detected for W_{exc} ≥ 15 mW. To determine spectral dependence of the corresponding upconversion efficiency, we performed two-photon photoluminescence excitation (PLE) measurements [10].

Figure 6 shows representative results, taking as an example spectra measured from the bulk and NR ZnO when detecting the I_7 and DX_1 emissions, respectively. All spectra exhibit several features labeled as An=2, Bn=2, and Cn=2. The spectral positions of these features are very close to that reported [30, 31, 32] for n=2 excited P states of FX related to the A-, B- and C- valence subbands, which justifies the notations. From Figure 6, we note that the UPL intensity decreases dramatically (by more than one order) when the two-photon energy is tuned below the $A_{n=2}$ peak and that transitions related to the n=1 ground state of the A- and Bexcitons are hardly visible. This is in sharp contrast with conventional one-photon PLE spectra of BX, where similar intensities of the BX emissions are usually observed [33] under excitation via either ground or excited states of FX. To further demonstrate this difference, Figure 7 compares PL spectra measured from the bulk ZnO under one- and two-photon excitation conditions with the total photon energy being above (the solid lines) and below (the dotted lines) the A_{n=2} transition. The observed difference between the thresholds for onephoton and two-photon absorption can be interpreted in terms of parity selection rules for photon absorption. Indeed, in semiconductors with s-like conduction band and p-like valence band, transitions to S-states of excitons (including the 1S states) are allowed in one-photon absorption, whereas the lowest observable states during TPA are usually 2P exciton excited states. Though these selections rules may be modified due to, e.g., strong admixture of dstates to the VB states that is the case for ZnO [34], the oscillator strength of TPA for the S excitons in bulk ZnO remains very low [32]. Our results show that the same selection rules also apply to nanostructured ZnO.

4. Conclusions

In conclusion, we have observed efficient upconvertion in the bulk and NR ZnO by monitoring the BX emission. Based on the excitation power dependence with different energies of excitation photons, the processes responsible for the upconversion are assigned to TPA via virtual states and TS-TPA via real states. It is concluded that the TS-TPA process does not involve photon recycling and occurs via a defect/impurity (or defects/impurities) with an energy level (levels) lying within 1.14-1.56 eV from one of the band edges. Likely candidates of such defects/impurities are intrinsic defects and residual impurities, with V_{Zn} as a possibility. The presence of these defects in the investigated samples is confirmed by the ODMR measurements. Optical transitions via defect/impurity levels within the TS-TPA spectral range were also detected in the one-photon absorption spectra of the bulk ZnO. The TPA process is shown to dominate when $\lambda_{exc} \ge 661$ nm or at high excitation power. The observed different threshold energy for TPA as compared with that for the one-photon absorption is explained in terms of the selection rules for the concerned optical transitions. The obtained results could provide a useful guideline for designing efficient non-linear optical devices based on bulk and nanostructured ZnO.

Acknowledgements

Financial support by the Swedish Research Council (grant # 621-2010-3971) is greatly appreciated.

References

- For a review, see e.g. Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan,
 V. Avrutin, S. J. Cho and H. J. Morkoc: Appl. Phys. 98, 041301 (2005)
- 2. C. Klingshirn: Phys. Stat. Sol. (a) 244, 3027 (2007).
- S.J. Pearton, D.P. Norton, M.P. Ivill, A.F. Hebard, J.M. Zavada, W.M. Chen and I.A. Buyanova, IEEE Transations on Electron Devices 54, 1040 (2007).
- 4. A. B. Djurisic and Y. H. Leung, Small: 2, 944 (2006)
- 5. Y. C. Zhong, A. B. Djurišić, U. F. Hsu, K. S. Wong, G. Brauer, C. C. Ling, and W. K. Chan: J. Phys. Chem. C 112, 16286 (2008).
- 6. S. K. Lee, S. L. Chen, D. Hongxing, L. Sun, Z. Chen, W.M. Chen and I.A. Buyanova: Appl. Phys. Lett. 96, 083104 (2010).
- 7. R. Prasanth, L.K. van Vugt, D. A. M. Vanmaekelbergh, and H. C. Gerritsen: Appl. Phys. Lett. 88, 181 501 (2006).
- S.W. Chan, R. Barille, J.M. Nunzi, K.H. Tam, Y.H. Leung, W.K. Chan and A.B. Djurišić: Appl. Phys. B 84, 351 (2006).
- 9. D. C. Dai, S. J. Xu, S. L. Shi, M. H. Xie, and C. M. Chen: IEEE Photonics Techn. Lett. 18, 1533 (2006).
- 10. Y.C. Zhong, K.S.Wong, A.B. Djurišic, Y.F. Hsu: Appl. Phys. B 97, 125 (2009)
- C. F. Zhang, Z. W. Dong, G. J. You, R. Y. Zhu, and S. X. Qian: Appl. Phys. Lett. 89, 042117 (2006)
- 12. W. Cao, W. Du, F. Su, and G. Li: Appl. Phys. Lett. 89, 031902 (2006)
- 13. S. Mani, J. I. Jang, and J. B. Ketterson: Appl. Phys. Lett. 93, 041902 (2008)

14. S. K. Das, M. Biswas, D. Byrne, M. Bock, E. McGlynn, M. Breusing, and R. Grunwald: J. Appl. Phys. 108, 043107 (2010).

15. C. Zhang, F.Zhang, T.Xia, N. Kumar, J. Hahm, J. Liu, Z. L. Wang, and J. Xu, Opt. Express: 17, 7803 (2009)

16. B. Clerjaud, F. Gendron, and C. Porte: Appl. Phys. Lett. 38, 212 (1981)

17. P. P. Paskov, P. O. Holtz, and B. Monemar, J. M. Garcia, W. V. Schoenfeld, and P. M.Petroff: Appl. Phys. Lett. 77, 812 (2000)

R. Hellmann, A. Euteneuer, S. G. Hense, J. Feldmann, P. Thomas, E. O. Göbel, D. R.
 Yakovlev, A. Wagg, and G. Landwehr: Phys. Rev. B 51,18053 (1995).

 M. Izadifard, J. P. Bergman, W.M. Chen, I.A. Buyanova, Y. G. Hong, C. W. Tu, J. Appl. Phys. 99: 073515 (2006)

20. B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen,A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck and A. V. Rodina : Phys. Stat. Sol. (b)241, 231 (2004).

21. V. V. Travnikov, A. Freiberg, S. F. Savikhin: J. Luminescsence 47, 107 (1990).

22. Due to a limited output power from a 661 nm diode laser, the UPL emission under this excitation could only be detected from the Cermet ZnO, i.e. in the sample which exhibits the highest PL intensity under one-photon excitation.

23. V. A. Nikitenko: J. Appl. Spectrosc. 56, 783 (1994).

24. For a recent review, see e.g. A. Janotti and C. G Van de Walle: Rep. Prog. Phys. 72, 126501 (2009)

25. X J Wang, L S Vlasenko, S J Pearton3, W M Chen and I A Buyanova: J. Phys. D: Appl. Phys. 42, 175411 (2009).

26. R. Laiho, L. S. Vlasenko and M. P. Vlasenko: J. Appl. Phys. 103, 123709 (2008)

- 27. F. Tuomisto, V. Ranki, K. Saarinen and D. C. Look: Phys. Rev. Lett. 91, 205502 (2003).
- 28. B. Monemar, P. P. Paskov, J. P. Bergman, G. Pozina, A. A. Toropov and T. V. Shubina, T. Malinauskas, and A. Usui: Phys. Rev. B 82, 235202 (2010).
- 29. S. L. Chen, W. M. Chen and I. A. Buyanova: Phys. Rev. B 83, 245212 (2011)
- 30. R. Dingles, D. Fröhkich, B. Staginnus, and W. Staude: Phys. Rev. Lett, 25, 922 (1970).
- 31. W. Kaule: Solid State Commun. 9, 17 (1971)
- 32. A. Mang, K. Reimann, and St. Rubenacke: Solid State Commun. 94, 251 (1995).
- 33. B. K. Meyer, J. Sann, S. Eisermann, S. Lautenschlaeger, M. R. Wagner, M. Kaiser, G.
- Callsen, J. S. Reparaz, and A. Hoffmann: Phys. Rev. B 82, 115207 (2010)
- 34. W. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall and B. K. Meyer: Phys. Rev. B 65, 075207 (2002).

Figure captions

Figure 1. (Color online) Representative PL spectra measured from the bulk (Denpa) and NR ZnO under one-photon (the solid lines) and two-photon (the dashed lines) excitation. The spectra are displayed in the semi-logarithmic scale and are offset vertically, for clarity.

Figure 2. (Color online) Excitation power dependence of the UPL intensity measured from the Cermet (dots), Denpa (triangles) and NR (open squares) ZnO at the specified excitation photon wavelengths. The data are offset vertically, for clarity. The detection energies were set at the peak of the dominant I_6 (DX₁) transition for the bulk (NR) ZnO. The dotted lines represent the best fit of the data by the power functions as specified in the text. The same power dependence were observed for all BX transitions. The inset shows a schematic diagram of the upconversion processes. The thin (red) vertical arrows denote the TPA-induced transitions through a virtual intermediate state (VS), whereas the TS-TPA process via a defect level (DL) is visualized by the thick (green) arrows.

Figure 3. (Color online). One-photon absorption spectra measured at room temperature from the bulk ZnO samples.

Figure 4. (Color online). Typical ODMR spectra measured at 3K from the bulk and NR ZnO. The spectra were obtained with an applied magnetic field B oriented at 50° off the direction of the crystallographic c-axis.

Figure 5 (Color online) Decays of the BX emissions measured from the bulk (Denpa) ZnO under one-photon (the blue symbols) and two-photon (the red symbols) excitation. The solid line is a modeled PL decay curve.

Figure 6. (Color online) Characteristic PLE spectra of the UPL emission via the two-photon absorption from the bulk and NR ZnO samples.

Figure 7. (Color online) PL spectra recorded from the bulk (Denpa) ZnO under one-photon and two-photon excitation with the specified excitation photon energies



Fig.1



Fig.2



Fig.3



Fig.4



Fig.5



Fig. 6



Fig.7