

## ZnO REDISCOVERED – ONCE AGAIN!?

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In an introductory chapter we shortly review the history of ZnO research and the motivations for the present renaissance of the worldwide interest in this II-VI compound. Then we concentrate after a few comments on growth, doping, transport, and deep centers on the following topics: band structure, excitons and polaritons, luminescence dynamics, high excitation effects like biexcitons or the transition to an electron-hole plasma, and finally lasing. We finish with a short conclusion and outlook.

### 1. Introduction and Historic Remarks

ZnO is a II-VI semiconductor with a direct, dipole allowed band gap around 3.4 eV i.e. in the near UV and a relatively large exciton binding energy of about 60 meV.

ZnO has seen in the past periods of intensive research, which started gradually in the fifties of the last century [1, 2] and peaked around the end of the seventies and the beginning of the eighties [3, 4, 5, 6]. Then the interest faded away, partly because it was not possible to dope ZnO both n- and p-type, partly because the interest moved to structures of reduced dimensionality, which were at that time almost exclusively based on the III-V system GaAs/Al<sub>1-y</sub>Ga<sub>y</sub>As. The emphasis of research at that time was essentially on bulk samples covering topics like growth, doping, transport, deep centers, band-structure, excitons, bulk- and surface-polaritons, luminescence, high excitation or many particle effects and lasing. Results of the first research period are reviewed e.g. in [1, 2, 3, 4, 5, 6] and entered in data collections [7] or in textbooks on semiconductor optics [8].

The present renaissance on ZnO research started in the mid nineties and is documented by numerous conferences, workshops, and symposia and by more than 1000 ZnO-related papers per year, compared to slightly beyond 100 in 1970.

The present renaissance is based on the possibility to grow epitaxial layers, quantum wells, nano rods and related objects or quantum dots and on the hope to obtain:

- a material for blue/UV lasers and optoelectronics in addition to (or instead of) the GaN based structures
- a radiation hard material for electronic devices in a corresponding environment
- a diluted or ferromagnetic material, when doped with Co, Mn, Fe, V etc. for spintronics
- a transparent, highly conducting oxide (TCO), when doped with Ga, Al, In etc. as a cheaper alternative to ITO.

For several of the above mentioned applications a stable, high, and reproducible p-doping is obligatory, which is however still a major problem.

The emphasis of the present active period of ZnO research is essentially on the same topics as before, but including nanostructures. For first reviews of this new ZnO research period, see e.g. [9]. We shall present or cite in the following deliberately both old and new results covering six decades of ZnO research.

## 2. Growth, Doping, Transport, and Deep Centers

Bulk samples in the form of hexagonal needles or platelets can be grown by gas transport and/or oxidation of zinc. Examples are found e.g. in [10]. Hydrothermal growth under high pressure in LiOH + KOH solutions [11] may result in samples of several ten cm<sup>3</sup>. For growth from melt or flux, see [12].

Textured or epitaxial layers and quantum wells (either ZnO or Cd<sub>1-y</sub>Zn<sub>y</sub>O wells between Zn<sub>1-y</sub>Mg<sub>y</sub>O or ZnO barriers, respectively) have been grown by a variety of techniques. For early examples of oxidation of Zn or for vapour phase transport, see [13, 14]. For modern techniques we mention only a few examples out of the tremendous number of publications and refer the reader otherwise to [9]. For pulsed laser deposition (PLD) see [15], for molecular beam epitaxy (MBE) [16] or for metalorganic chemical vapour deposition (MOCVD, MOVPE) [17].

A hot topic is presently the growth of nano-rods, -combs, -brushes, -nails, -tubes, -rings, -belts, -wool, -walls, -tetrapods or -flowers by various techniques, see [9, 18]. It became already possible to produce Zn<sub>1-y</sub>Mg<sub>y</sub>O/ZnO superlattices in the nanorods [19]. Quantum dots have been prepared e.g. by sol-gel techniques or by spray combustion [20].

While p-doping is still a major problem, n-type doping with Ga, In or Al is possible beyond  $n = 10^{20}$  cm<sup>-3</sup>. Such highly doped samples look bluish, because the tail of the free carrier absorption extends into the red and the plasmon frequency approaches values close to 0.5 eV [8, 21]. In Fig. 1 we show from top to bottom the reflection spectra of a weakly and a highly doped ZnO:Ga sample, respectively, (note the different scales on the x-axis!) and the resulting energies of the transverse  $\hbar\omega_-$  and  $\hbar\omega_+$  branches of the plasmon phonon mixed states as a function of  $n^{1/2}$ , where  $n$  is the carrier density.

The diffusion constants of various dopants, including Mn and Co, have been summarized in [22]. The value of the Hall mobility of electrons at room temperature is long known and amounts about 200 cm<sup>2</sup>/Vs [23]. It is limited by the intrinsic process of LO-phonon scattering, resulting in a relaxation time  $\tau$  of  $2 \times 10^{-14}$  s.

Dislocations in ZnO can be decorated by various etching techniques [14, 24]. Electron transmission microscopy showed a lot of dislocations which are higher in density for epitaxial layers than for bulk samples [25]. For elastic and piezoelectric properties see [26], and for phonons [7].

As most wide gap semiconductors and insulators, ZnO shows a large variety of absorption and emission bands, situated energetically deep in the gap. Two different luminescence bands in the green are known, one is related to Cu, the other to oxygen vacancies [8, 27]. Emission bands in the yellow range are due to deep Li or Na acceptors [28]. Further emission- and/or absorption bands exist in the red or IR partly connected with iron or OH<sup>-</sup> ions. Recently a band in the orange spectral range has been

observed, which expands after the steplike onset of band-to-band excitation gradually over distances of several mm in times of several hundreds of ms [29]. More details on

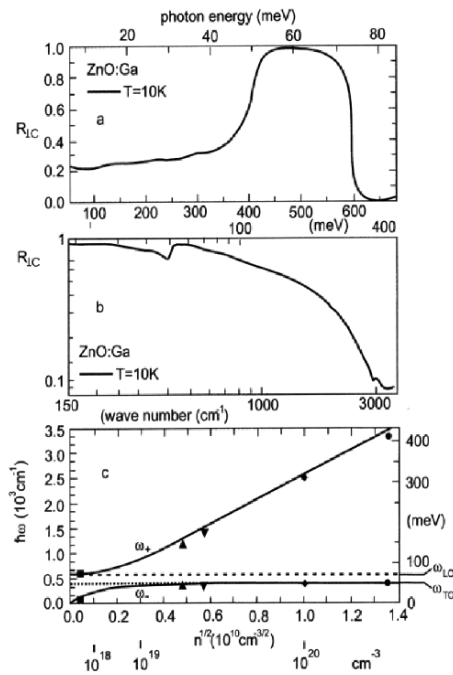


Figure 1. Reflection spectra of a weakly ( $N_{\text{Ga}} \leq 10^{17} \text{ cm}^{-3}$ ) and a highly  $N_{\text{Ga}} \leq 3 \cdot 10^{20} \text{ cm}^{-3}$  doped ZnO:Ga sample and the resulting branches of the plasmon-phonon mixed states as a function of  $n^{1/2}$ . From [21].

deep centers including the para- or ferromagnetic properties induced by dopants like Mn, Co, V, Fe are reviewed in [8, 9].

### 3. Band Structure, Excitons, Polaritons, and Dynamics

ZnO has rather strong ionic binding. Consequently, the conduction band (CB) arises essentially from the  $\text{Zn}^{++}$  4s orbitals (symmetry  $\Gamma_7$ ) and the upper valence bands (VB) from the  $\text{O}^-$  2p states with an admixture of  $\text{Zn}^{++}$  3d levels. The VB splits due to the

hexagonal crystal field  $\Delta_{cr}$  and the spin orbit coupling  $\Delta_{so}$  into three subbands always labelled A, B, C from higher to lower energies. The gaps are at low temperature approximately  $E_g^A = 3.437\text{eV}$ ,  $E_g^B = 3.442\text{eV}$ ,  $E_g^C = 3.481\text{eV}$  [4, 7]. In contrast to other wurtzite II-VI compounds  $\Delta_{cr} \gg \Delta_{so}$  due to the small nuclear charge of oxygen. This fact in turn results in selection rules such that the transitions from the A and B VB to the CB have considerable oscillator strength only for  $\mathbf{E} \perp \mathbf{c}$  ( $\Gamma_5$ ) and from the C VB for  $\mathbf{E} \parallel \mathbf{c}$  ( $\Gamma_1$ ). The other, dipole allowed transitions involve a spin flip with a drastic reduction of their oscillator strength. Group theory allows a k-linear term for  $\Gamma_7$  bands for  $\mathbf{k} \perp \mathbf{c}$ , but not for  $\mathbf{k} \parallel \mathbf{c}$  and not for  $\Gamma_9$  bands.

Exciton series exist for all three combinations of VB and CB. The exciton binding energies  $E_x^b$  are very similar with  $E_x^b = (60 \pm 1)\text{meV}$  [5, 6, 7, 8]. The lower values in [30] for B and C excitons arise from the rather unusual procedure to count from the reflection minima, i.e. from the longitudinal eigenenergies.

The value of  $\Delta_{so}$  in ZnO is not only small, but the interaction with the close lying  $\text{Zn}^{++}$  3d states shifts one  $\Gamma_7$  VB above the  $\Gamma_9$  resulting in a VB-ordering A  $\Gamma_7$ , B  $\Gamma_9$ , C  $\Gamma_7$  in contrast to the usual ordering A  $\Gamma_9$ , B  $\Gamma_7$ , C  $\Gamma_7$  for II-VI compounds with higher nuclear anion charge like CdS(e). This concept has been introduced for ZnO in [31] and later also for the cubic CuCl [32]. Theoretical justifications have been given in [33]. The unusual ordering has been questioned in [34]. Since then many experiments have confirmed the inverted VB structure e.g. in absorption [35], luminescence,  $\mathbf{k}$ -space spectroscopy, under  $\mathbf{B}$  or strain fields [36, 37, 38]. Recently the inverted assignment has been questioned again e.g. by [30, 39, 40]. Some arguments against this approach have been given already in [41]. Others will be given below.

In Fig. 2 we show various optical spectra in the exciton region. Fig. 2a shows the room temperature absorption spectrum of a textured ZnO layer on a glass substrate produced by oxidizing an evaporated Zn layer. The experience is that such layers grow with  $\mathbf{c}$  normal to the surface. The peak at 3.3 eV corresponds to the A and B exciton absorption and is possibly the first experimental observation of an excitonic feature in a semiconductor, though the author of [13] was most probably not aware of this fact.

The low temperature absorption spectra of ZnO have been investigated by many authors, both in the allowed and forbidden orientations [35, 36, 38]. The temperature dependent absorption following the Urbach-Martienssen rule [8] was measured up to 800K and allowed to deduce the temperature dependence of the band gap. See Fig. 3. These data are in good agreement with [43].

In Fig. 2b we show reflection spectra for the  $n_B = 1$  A and B  $\Gamma_5$  and the C  $\Gamma_1$  excitons in their respective polarisations together with fit curves. A decent fit involves the problems of additional boundary conditions (abc), of spatial dispersion and possibly of an exciton free surface layer. For more information see e.g. [8, 35, 36, 37, 44] and references therein. Such spectra, including also states with higher main quantum numbers  $n_B > 1$  of the envelope function have been reported by many authors [4, 7, 30, 31, 37, 40, 44].

The longitudinal transverse splittings are approximately  $\Delta_{LT}^A = 2\text{meV}$ ,  $\Delta_{LT}^B = 10\text{meV}$ ,  $\Delta_{LT}^C = 12\text{meV}$  fulfilling the claim [31] that the sum of the oscillator strength of A and B excitons should equal that of the C exciton. In [40], the different values of  $\Delta_{LT}^A$  and  $\Delta_{LT}^B$  have been used as an argument to doubt the band structure.

However, in the case of close lying resonances the value of  $\Delta_{LT}$  of the lower one is reduced, that of the upper one increased due to their interaction as has been detailed for exciton resonances already in [44] and in a more didactical manner in [8].

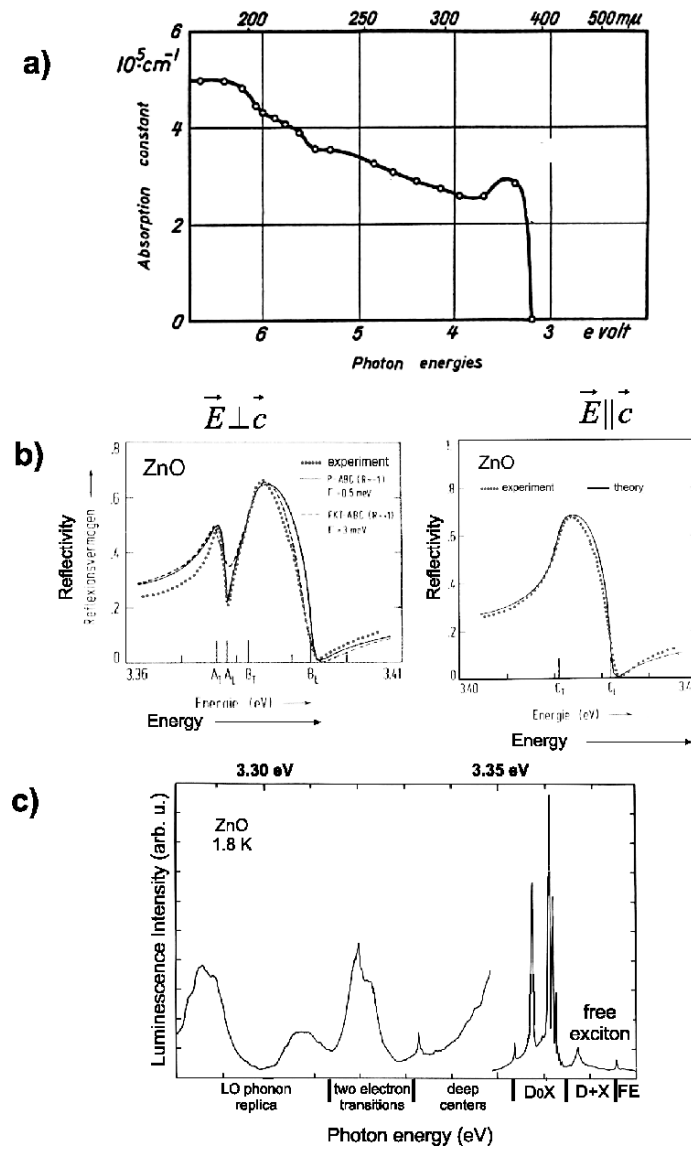


Figure 2. Room-temperature absorption spectrum of a thin, textured ZnO layer [13, 2] (a), low temperature reflection from K. Hümmer et al. [4, 37] (b) and luminescence spectra by R. Helbig et al. [4, 27] (c).

A small reflection feature seen for  $\mathbf{E} \parallel \mathbf{c}$  in [30] at the position of  $B \Gamma_5^L$  is attributed to a  $B \Gamma_1$  state. Actually this feature is a mixed mode polariton [4, 8, 45] resulting from the slight mismatch to  $\mathbf{k} \perp \mathbf{c}$  ( $<15^\circ$ ). The  $n_B=1$  A or  $B \Gamma_1 \oplus \Gamma_2$  or  $\Gamma_6$  exciton states are in ZnO spin triplets, independent of the band structure. The triplet states are always situated energetically slightly below the corresponding transverse eigenstates.

For the investigation of the exciton resonances in reflection and absorption in a  $\mathbf{B}$ -field see e.g. [4, 8, 36, 38, 41], and for the Landau levels and the resulting effective masses [46]. Though the effective masses may be anisotropic in uniaxial materials [47] like ZnO (and in fact they are e.g. for CdS or CdSe [7]), the observation of the Landau levels indicate rather isotropic values for the conduction band but also for the valence bands [46].

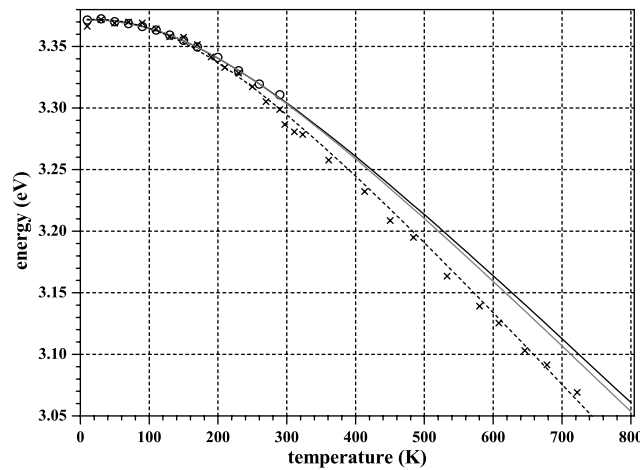


Figure 3. The temperature shift the A exciton deduced from the Urbach tail (x) and from luminescence (o) compared to a theoretical model including the thermal expansion and the electron phonon coupling. From [42].

The luminescence spectra of high quality ZnO samples are dominated at low temperature and excitation density by spectrally very narrow ( $<0.1$  meV) emission lines of bound exciton complexes (BEC), especially neutral donor bound excitons ( $D^0X$ ). See e.g. [4, 8, 27, 41]. We give in Fig. 2 an example. For photoluminescence excitation spectra (PLE) of various BEC emission lines see [51]. This technique allows to monitor excited states of BEC, e.g. ones which contain a hole from the BVB instead of the AVB.

The zero-phonon luminescence of the free excitons is at low temperatures very weak but increases relative to the BEC when the latter become thermally ionized from their defect centers in the temperature range around  $(80 \pm 20)$  K. The zero phonon line of the free A exciton luminescence has been investigated thoroughly in [37] and later e.g. in [30, 39, 42]. See [48]. The influence of the  $\mathbf{k}$ -linear term is nicely observed for the A  $\Gamma_5$  excitons in  $\mathbf{E} \perp \mathbf{c}$ , for  $\mathbf{k} \perp \mathbf{c}$  but not for  $\mathbf{k} \parallel \mathbf{c}$  as expected and the luminescence of the A  $\Gamma_1$  is seen in  $\mathbf{E} \parallel \mathbf{c}$  [37]. This emission is also reported in [30], but is used only to claim “...that the crystal is of good quality.”, but ignoring that this observation involves the presence of  $\Gamma_1$  symmetry.

In Fig. 5 we show time resolved unpolarized emission spectra of the  $n_B = 1$  A exciton polaritons. The features due to emission from the lower A  $\Gamma_5$  polariton branch (LPB) around 3.3755 eV (superimposed by the A  $\Gamma_1$  exciton), from the intermediate A  $\Gamma_5$  polariton branch caused by the  $\mathbf{k}$ -linear term around 3.377 eV and the upper A  $\Gamma_5$  polariton branch (UPB) around 3.378 eV are clearly visible. The luminescence dynamics shows the relaxation from the UPB and the feeding into the LPB and the A  $\Gamma_1$  state. Further examples for the luminescence dynamics of excitons in ZnO can be found in [42, 52, 53] and references given therein.

It has been found that the luminescence of the LO-phonon replica (see also below) of the free exciton polariton decays at all temperatures more slowly than the zero phonon band [42]. The explanation is the following: To the zero phonon luminescence contribute only exciton polaritons, which hit during their lifetime the surface with  $\mathbf{k}_\parallel \leq \omega/c$ . In contrast the LO phonon replica luminescence originates from excitons scattered on the photonlike polariton branch. This scattering includes all exciton like polaritons and the escape depth of the resulting photon-like polaritons is large. Therefore the LO-phonon replica monitor to a better extend the behaviour of all excitons, more precisely of exciton polaritons. For details see [8]. The temperature dependence of the near edge luminescence spectra have been observed by many groups e.g. [27, 41, 42, 52] and a consistent picture arose. At low temperature one observes depending on the sample quality more or less resolved BEC luminescence and its LO-phonon replica. Around  $(80 \pm 20)$  K BEC are thermally ionized from their centers and the free exciton luminescence, including the LO-phonon replica takes over. In Fig. 4 we show a fit of the zero phonon band and of its first two LO-phonon replica for different temperatures. The fit includes the thermal distribution of the exciton-like polaritons on their parabolic dispersion curve,  $\mathbf{k}_\parallel$  conservation in the above mentioned sense and a temperature dependent homogenous broadening  $\gamma_h(T)$  as well as the temperature dependence of the gap. See Fig. 3.

At room temperature these bands merge to an unstructured emission feature with a width of approximately 100 meV and  $\gamma_h(300\text{K}) \approx 40$  meV. This value exceeds the RT values of excitons in many other semiconductors, including GaAs and GaAs based quantum wells and micro cavities. Furthermore it exceeds  $\Delta_{LT}$  of all exciton resonances and the resulting dephasing time falls below the round trip time of most micro cavities. This high damping value is again a consequence of the strong coupling of excitons to LO-phonons. It will make room temperature lasing on Bose-condensed exciton polaritons in a micro cavity predicted in [49] highly unlikely, though micro cavities with ZnO will show at low temperatures interesting features due to the complex structure of the exciton polariton dispersion and their large oscillator strengths.

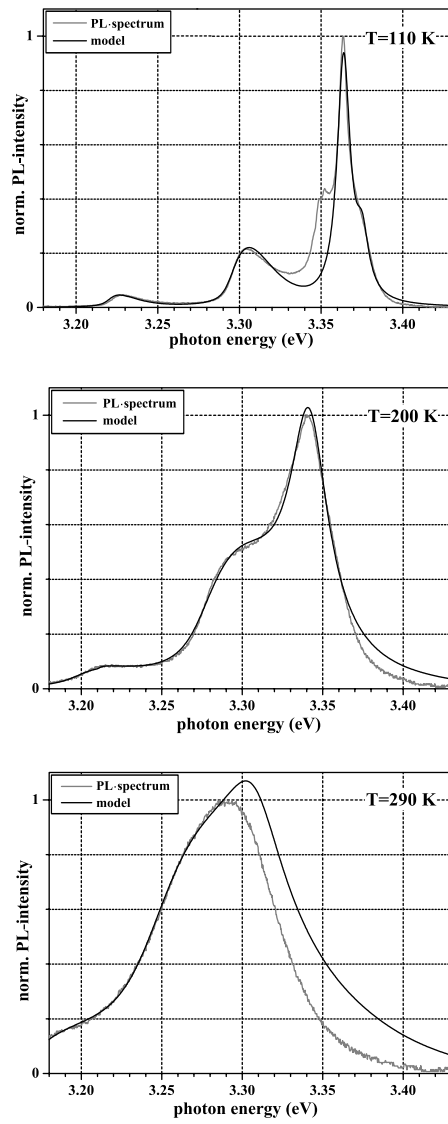


Figure 4. Luminescence spectra of ZnO for different temperatures with fit curves [42].



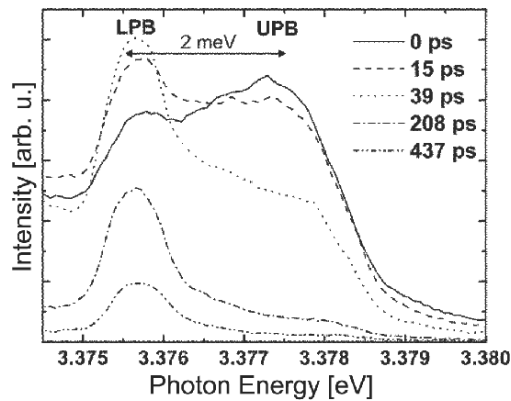


Figure 5. Fine structure and luminescence dynamics in the exciton polariton. From [42, 52].

To conclude this section, a few words on the luminescence of ZnO structures of reduced dimension. In Fig. 6 we show luminescence spectra of a ZnO QW between  $Zn_{1-y}Mg_yO$  barriers. One sees for the lowest excitation emission from the ZnO buffer layer at 3.36 eV due to BEC recombination, from the barrier in the region from 3.44 to 3.48 eV and from the QW features peaking at 3.417 eV and at 3.40 eV. The higher one corresponds as usual in QW [8] to localized and defect bound excitons, the lower one is attributed in [50] to a mesoscopic crater-like defect. The new emission band appearing for higher, pulsed excitation around 3.39 eV will be discussed below.

The luminescence of nanorods looks similar to that of bulk samples apart from some (in)homogenous broadening.

It has been found in bulk materials, that surfaces  $\parallel \mathbf{c}$  are aging and deteriorating, if kept at ambient atmosphere. To obtain e.g. good reflection spectra, it was necessary to use freshly cleaved or etched surfaces. In contrast, naturally grown surfaces perpendicular to  $\mathbf{c}$  showed even after many years in ambient atmosphere perfect A and B reflection features [42]. Nanorods, which have a significant smaller ratio of volume to surface  $\parallel \mathbf{c}$  tend to show a significant deterioration of the luminescence over a few months.

#### 4. High Excitation Phenomena and Lasing

In this section we treat first so-called many particle- or high excitation phenomena in the intermediate density regime where excitons are still good quasi particles, then the transition to an electron-hole plasma at the highest density. The transition between the two regimes is not sharp but for didactic reasons this separation is useful. Finally

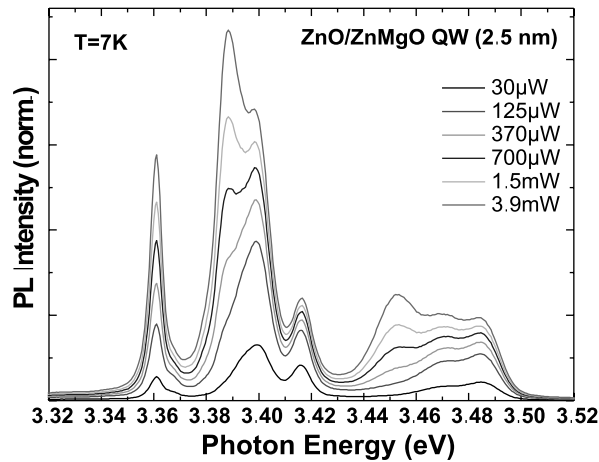


Figure 6. Luminescence spectra of a single 2.5 nm wide ZnO QW grow between  $\text{Zn}_{1-y}\text{Mg}_y\text{O}$  barriers on a ZnO buffer layer, deposited in turn on a GaN substrate [42].

we consider some aspects of lasing in ZnO. For some reviews of these topics in general and more specifically for ZnO, see [5, 6, 7, 8, 55].

Typical processes in the first regime are inelastic scattering processes and biexciton formation and decay. While elastic scattering between excitons results essentially in an excitation induced increase of homogeneous broadening, the inelastic processes give frequently rise to new emission bands. In the inelastic exciton-exciton (X-X) or more precisely polariton-polariton scattering, two excitonlike polaritons interact via their dipoles. One of them is scattered under energy and momentum conservation onto the photon-like part of the dispersion curve while the other reaches a state with higher quantum number  $n_B = 2, 3, \dots, \infty$ , resulting in new emission bands labelled  $P_2, P_3, \dots, P_\infty$  [5, 6, 7, 55].

Other inelastic scattering processes are known between free excitons and free carriers (X-e), LO-phonons (X-nLO) or between bound exciton complexes and free carriers or acoustic phonons [5, 6, 7, 55]. In Fig. 5 we show examples for the luminescence from nanorods and from an epilayer. The emission is dominated at low excitation by BEC recombination. With increasing ns excitation intensity  $I_{\text{exc}}$ , this line broadens on its low energy side due to the appearance of the so-called M-band, which may be due to biexciton decay, but also due to the process involving BEC mentioned above [5]. With further increasing excitation the epilayer shows at 3.32 eV the appearance of the  $P_\infty$  band. Surprisingly this band is absent in thin ( $\approx 50$  nm) but not in thick ( $\approx 200$  nm) nanorods (see below). These rods are bulk like for excitons because both their length

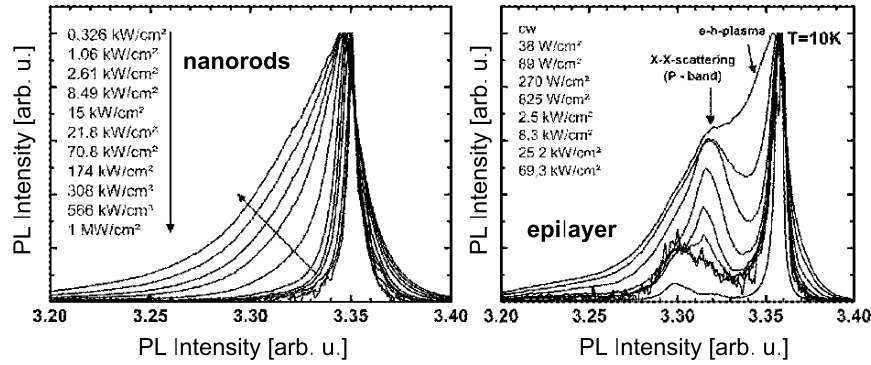


Figure 7. The luminescence of ZnO nanorods (a) and of an epilayer (b) for increasing excitation. From [42].

(>1 $\mu$ m) and their diameters are large compared to the excitonic Bohr radius  $a_B \approx 1.8$  nm. But for photon-like polaritons the thin rods act as one dimensional wave-guides.

This reduction of the phase-space in one of the outgoing channels in the X-X process may quench this process. Further work is necessary to verify or falsify this hypothesis. With increasing temperature, the X-X process goes over to the X-e process, if a sufficient number of excitons are thermally ionized to favour this dipole-monopole interaction [5, 8, 55].

In Fig. 8 we show the emission of thick nanorods after excitation with frequency tripled 100 fs pulses from a TiSa laser. The rather broad emission band around 3.32 eV could be due to either the P-bands mentioned above or to the beginning formation of an EHP discussed below. The narrow spikes appearing at 3.34 eV indicate the onset of stimulated emission. Their spectral position is not fully compatible with X-X scattering and needs further investigation.

For the biexciton various contradicting values of its binding energy relative to two free  $A \Gamma_1$  or  $A \Gamma_5^T$  excitons between 10 and 20 meV have been deduced from luminescence or ns four wave mixing (FWM) experiments. The solution came, when two groups observed in samples from different sources independently three biexciton levels in a modified two photon absorption experiment namely luminescence assisted two photon spectroscopy (LATS) [57]. In a joint publication [58] the binding energy of the ground-state biexciton has been found to be 15 meV and two higher states were observed, which are due to biexcitons, in which one or two holes from the A VB are replaced by B-holes. See also [59].

In table 1 we give a listing of the respective biexciton energies and of the binding relative to two A excitons or to the involved A and / or B excitons from [58, 60]. The binding energies of the AA  $\Gamma_1$  and AB  $\Gamma_{5,6}$  biexcitons agree within experimental error [61]. Since the data of both excitons are very similar, the deviation for the BB  $\Gamma_1$  exciton claimed in [60] is difficult to understand. As mentioned in [58], FWM data may

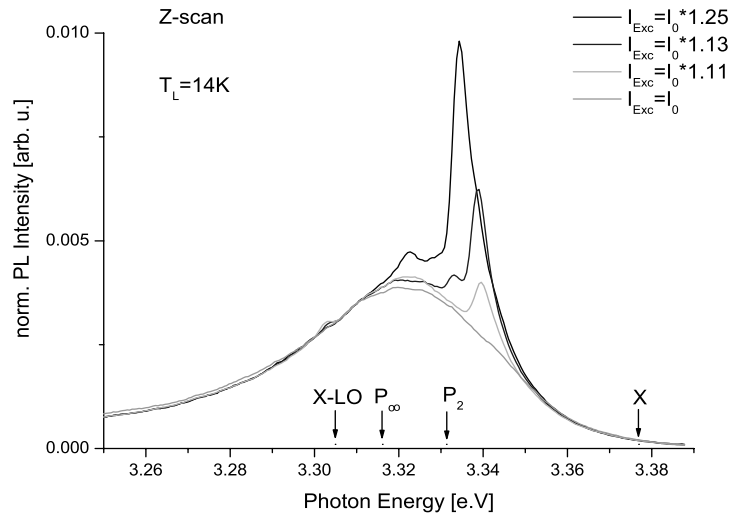


Figure 8. luminescence of thick nanorods under band-to-band excitation with 100 fs pulses for increasing fluence [56].

result in erroneous results. Similar arguments may hold for the claimed biexciton binding energy of a CC  $\Gamma_1$  biexciton of only 1.4 meV [60].

In ZnO/Zn<sub>1-y</sub>Mg<sub>y</sub>O quantum wells a new emission band appears with increasing excitation at 3.385 eV (see Fig. 6). If it is due to a biexciton decay, a binding energy around 20 meV results since the biexcitonic M-band luminescence has ideally the shape of an inverted Boltzmann distribution [8], so that the binding energy can be deduced from the distance between the exciton energy and the high energy slope of the M-band. This value would make some sense bearing in mind table 1 and the enhancement of exciton and biexciton binding energies in quantized systems [8]. Further examples of ZnO QW, nanorod and nanodot luminescence under high excitation are found e.g. in [62].

Some selected results on two photon absorption (TPA), TPA-spectroscopy or second and third harmonic generation are found in [38, 63], the dynamics of the luminescence under high excitation has been investigated e.g. in [42, 52, 53, 64]. For the investigation of effects in the regime of extreme nonlinear optics, see [65].

The dephasing time  $T_2$  and/or the homogeneous broadening have been investigated at low temperatures by an analysis of the reflection spectra [4, 36, 37, 44, 54] yielding values of the order of 1 meV and also in time resolved FWM experiments [60] with comparable results.

TABLE 1. Biexciton energies and binding energies with respect to two A excitons and with respect to two A/B excitons. The last column gives corresponding data for A/B excitons from [60], see [61].

Biexciton energy and symmetry [58]	Binding energy with respect to two A excit [58]	Binding energy with respect to A/B excit. [58]	[60]
$E_{AA\Gamma_1} = 6.7355$ eV	$14.7 \pm 1$ meV	$14.7 \pm 1$ meV	15.6 meV
$E_{AB\Gamma_{5,6}} = 6.7407$ eV	9.5 "	14.7 "	16.6 meV
$E_{BB\Gamma_1} = 6.7469$ eV	3.3 "	13.7 "	4.7 meV

If the generation rate is increased to sufficiently high values, excitons cease to exist as individual quasi-particles and a new collective phase is formed, the electron-hole plasma (EHP). For details of this transition, see e.g. [5, 8]. In ZnO the EHP has been observed in gain spectroscopy, e.g. in [52, 66]. Simultaneously with the appearance of EHP gain, the excitonic reflection features start to disappear. Densities exceeding  $10^{19}$  cm<sup>-3</sup> have been deduced. For more information on the EHP, including its dynamics and structures of reduced dimensionality, see [42, 52, 67] and references therein.

The investigation of stimulated emission and lasing of ZnO started in the mid sixties. For a few early examples, see e.g. [68] and references therein and for tunable laser emission [69]. The understanding of the processes developed in parallel (see [5, 55]). It turned out, that all of the inelastic scattering and recombination processes mentioned above, including the two-electron transitions [41], may result in stimulated emission. Most of them can be mapped on a four level laser system, with correspondingly low thresholds for inversion. The X-LO emission process is inverted when one exciton is created and no LO-phonon present i.e. at  $\hbar\omega_{LO} \gg k_B T$ . Similarly the X-X processes, e.g. the P<sub>2</sub> band is inverted if two excitons are present and none of them in the state  $n_B=2$  [5, 55]. Nowadays such processes come also with names like thresholdless lasing or lasing without inversion.

The band - to - band recombination in an EHP requires  $\mu_{eh}(n_p, T_p) > E_g(n_p, T_p)$  for population inversion [5, 8, 66, 67] and is therefore more like a three level system. The quantities  $\mu_{eh}(n_p, T_p)$  and  $E_g(n_p, T_p)$  stand for the chemical potential of the electron-hole pair system and the reduced or normalized band-gap depending both on the plasma density and temperature  $n_p$  and  $T_p$ , respectively. However, inelastic scattering processes between carriers or the emission of phonons or plasmons may lead to thresholds below that given above. Generally it has to be stated that the transition from excitons to the EHP is continuous in direct gap semiconductors [70]. Recent theories including this continuous transition are found e.g. in [71] and references given therein.

In the present phase of ZnO activity, stimulated emission and gain are generally attributed to the processes known already in bulk, but now for epitaxial layers [42, 52, 62], in quantum wells obtaining partly gain up to 550 K [62, 72] and most recently in nanorods and related structures [73] and Fig. 8.

A new topic is lasing in random media i.e. here in ZnO powders, relying on weak localization of light due to enhanced backscattering [74].

## 5. Conclusion and Outlook

Evidently ZnO sees a very vital renaissance of basic and applied research. As is usual in such situations, beautiful new effects are found, old mistakes are straightened out, new ones are made and also long known phenomena are being reinvented. We tried to give a good mixture of all these aspects. The question how long this renaissance will last, depends to a large extent on the question if a stable, high, and reproducible p-doping can be realized. Since prophecy is a notoriously difficult task, especially if it concerns the future, the authors do not want to give an answer here.

### Note Added in Proof

A group in Sendai reported in May 2005 on a first blue/UV ZnO based LED.

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