

Excitonic Properties of ZnO

C. Klingshirn¹, H. Priller¹, M. Decker¹, J. Brückner¹, H. Kalt¹,
R. Hauschild¹, J. Zeller¹, A. Waag², A. Bakin², H. Wehmann², K. Thonke³,
R. Sauer³, R. Kling³, F. Reuss³, and Ch. Kirchner³

¹ Institut für Angewandte Physik and Center for Functional Nanostructures der
Universität Karlsruhe, Karlsruhe, Germany

² Institut für Halbleitertechnik der Universität Braunschweig, Braunschweig,
Germany

³ Abteilung Halbleiterphysik der Universität Ulm, Ulm, Germany

Summary. In the first chapters we give some short comments on the history of ZnO research and on growth, doping, transport, and deep centers, topics which will be covered in more detail by other contributions to this symposium “ZnO-rediscovered”. Then we concentrate in a first main chapter on the band-structure, excitons, and polaritons in the regime of linear optics. The second main chapter deals with many particle effects and lasing. It is followed by a short conclusion and outlook.

1 Introduction and Historic Remarks

The research on ZnO sees presently a vital renaissance. The data collection INSPEC gives about 13500 ZnO related entries from 1969 to 2004, among which 375 fall into the three year interval from 1969 to 1971 and 3300 from 2002 to 2004.

The wide gap II-VI semiconductor ZnO has gone through various periods of active research, which are reviewed e.g. in [1, 2, 3, 4]. The emphasis of research during the last active period from roughly the seventies to the mid eighties was on bulk materials, including growth, transport, doping, band structure, and excitons, bulk and surface polaritons, high excitation or many particle effects and lasing. For data collections of bulk material and quantum structures see [5]. Examples of the optical properties entered also in [6, 7, 8].

ZnO is used presently by many hundreds of tons per year as an additive to concrete or to rubber, in smaller quantities as an additive to human or pig food, as a UV blocker in sun creams or as one component of mixed oxide varistors for voltage limiting. It was used in the electrofax copy process.

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.

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 on 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 cm³. For growth from melt or flux, see [12].

Textured or epitaxial layers and quantum wells (either ZnO or Cd_{1-y}Zn_yO wells between Zn_{1-y}Mg_yO or ZnO barriers, respectively) have been grown by a variety of techniques. For early examples of oxidation on Zn or for vapor 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] and the other contributions to this symposium. For pulsed laser deposition (PLD) see [15], for molecular beam epitaxy (MBE) [16] or for metal organic chemical vapor 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] and other contributions to this symposium. It became already possible to produce Zn_{1-y}Mg_yO/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, as mentioned above and detailed in the following contributions, n-type doping with Ga, In or Al is possible beyond $n = 10^{20}$ cm⁻³. 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]. 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 cm²/Vs [23]. It is limited by the intrinsic process of LO-phonon scattering, resulting in a relaxation time τ of 2×10^{-14} s. See also the contribution by M. Grundmann to this symposium.

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, 24]. Emission bands in the yellow range are due to deep Li or Na acceptors [25]. 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 [26]. More details on deep centers including the para- or ferromagnetic properties induced by dopants like Mn, Co, V, Fe are reviewed in the contribution by A. Hoffmann to this symposium or in [9].

3 Band Structure, Excitons, and Polaritons

ZnO has rather strong ionic binding. Consequently, the conduction band (CB) arises essentially from the Zn^{++} 4s orbitals (symmetry Γ_7) and the upper valence bands (VB) from the O^{--} 2p states with an admixture of Zn^{++} 3d levels. The VB splits due to the hexagonal crystal field Δ_{cr} and the spin orbit coupling Δ_{so} into three subbands always labeled A, B, C from higher to lower energies. The gaps are at low temperature $E_g^A = 3.437$ eV, $E_g^B = 3.442$ eV, $E_g^C = 3.481$ eV [4, 5, 6, 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 $\mathbf{E} \perp \mathbf{c}$ (Γ_5) and from the C VB for $\mathbf{E} \parallel \mathbf{c}$ (Γ_1). The other, in principle also dipole allowed transitions involve a spin flip with a drastic reduction of their oscillator strength. Group theory allows a k-linear term for Γ_7 bands for $\mathbf{k} \perp \mathbf{c}$, but not for Γ_9 ones.

Exciton series exist for all three combinations of VB and CB. The exciton binding energies E_x^b are very similar with $E_x^b = (60 \pm 1)$ meV [5, 6, 7, 8]. The lower values in [27] 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 Δ_{SO} in ZnO is not only small, but the interaction with the close lying Zn^{++} 3d states shifts one Γ_7 VB above the Γ_9 resulting in a VB-ordering A Γ_7 , B Γ_9 , C Γ_7 in contrast to the usual ordering A Γ_9 , B Γ_7 , C Γ_7 . This concept has been introduced for ZnO in [28] and later also for the cubic CuCl [29]. Theoretical justifications have been given in [30]. The unusual ordering has been questioned in [31]. Since then many experiments have confirmed the inverted VB structure e.g. in absorption [32], luminescence, \mathbf{k} -space spectroscopy, under \mathbf{B} or strain fields [33, 34, 35]. Recently the inverted assignment has been questioned again e.g. by [27, 36, 37]. Some arguments against this approach have been given already in [38].

In Fig. 1 we show reflection spectra for the $n_B = 1$ A and B Γ_5 and the C Γ_1 excitons in their respective polarizations together with fit curves. Such spectra, including also states with higher main quantum numbers $n_B > 1$ of the envelope function have been reported by many authors [4, 5, 6, 7, 27, 28, 34, 39]. The longitudinal transverse splittings are $\Delta_{LT}^A = 2$ meV,

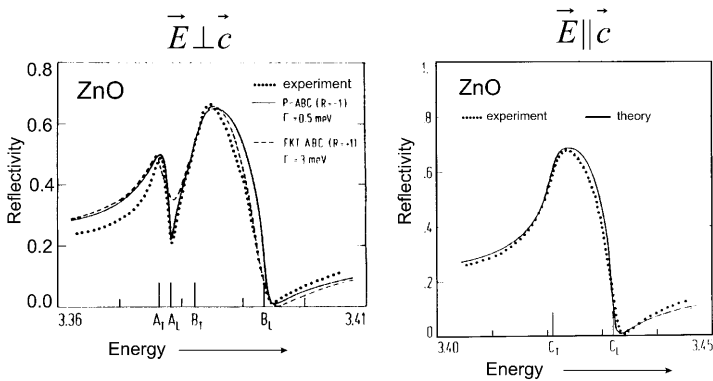


Fig. 1. Reflection spectra of the $n_B = 1$ A and B (Γ_5^L) and the C (Γ_1) exciton together with fit curves. From K. Hümmer [4]

$\Delta_{LT}^B = 10$ meV, $\Delta_{LT}^C = 12$ meV fulfilling the claim [28] that the sum of the oscillator strength of A and B excitons should equal that of the C exciton. In [37], the different values of Δ_{LT}^A and Δ_{LT}^B have been used as an argument to doubt the band structure. However, in the case of close lying resonances the value of Δ_{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 [39] and in a more didactical manner in [8]. A small reflection feature seen for $\vec{E} \parallel \vec{c}$ in [27] at the position of B Γ_5^L is attributed to a B Γ_1 state. Actually this feature is a mixed mode polariton [8, 40] resulting from the slight mismatch to $\vec{k} \perp \vec{c}$ ($< 15^\circ$). The $n_B = 1$ A or B $\Gamma_1 \oplus \Gamma_2$ or Γ_6 exciton states are 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 \vec{B} -field see e.g. [4, 5, 6, 7, 8, 33, 34, 35], and for the Landau levels and the resulting effective masses [41]. The free excitons in ZnO have been observed also in absorption. For the “forbidden” polarizations, see [32, 33]. A rather early example of the allowed transitions at RT is shown in [13], reproduced also in [2, 8]. The peak at 3.3 eV is probably the first observation of an exciton resonance in a semiconductor [8]. The Urbach-tail of the fundamental absorption edge has been investigated in [26]. The resulting variation of the gap with temperature is shown in Fig. 2.

The luminescence spectra of high quality ZnO samples are dominated at low temperature and excitation density by bound exciton complexes (BEC), especially neutral donor bound (D^0X). See e.g. [4, 8, 24, 38]. We give in Fig. 3 an example including the \vec{B} dependence. More information can be found in the contributions to this symposium.

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 ± 20) K.

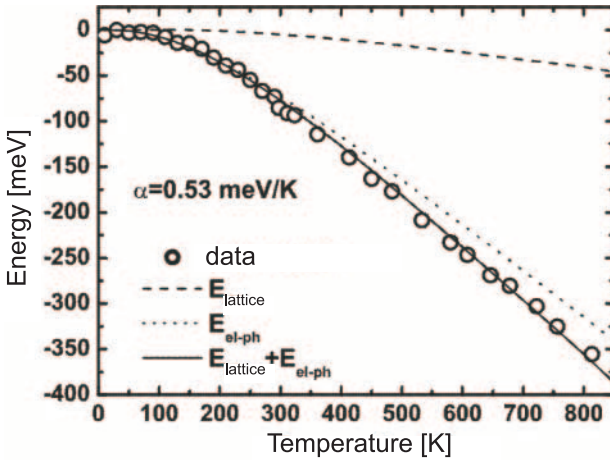


Fig. 2. The decrease of band gap with increasing temperature From [26].

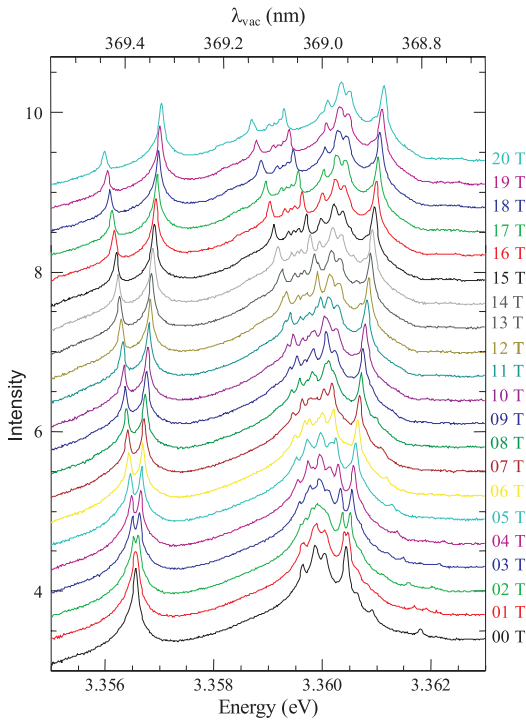


Fig. 3. Bound exciton luminescence for magnetic fields up to 20T. From G. Prinz [18] and K. Thonke [38]

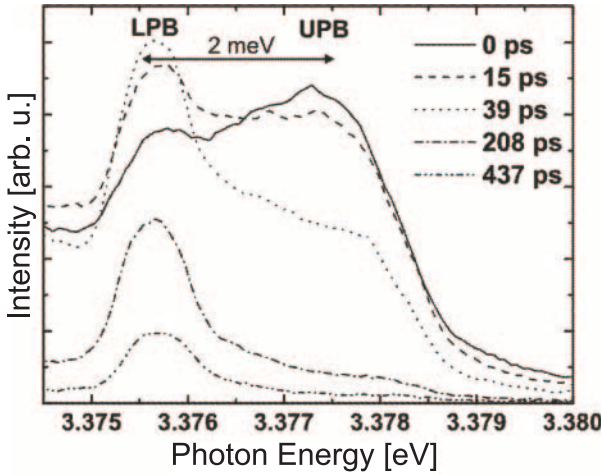


Fig. 4. Fine structure and luminescence dynamics in the exciton polariton. From [26]

The zero phonon line of the free A exciton luminescence has been investigated thoroughly in [34] and later e.g. in [26, 27, 36]. See [42]. The influence of the \mathbf{k} -linear term is nicely observed for the A Γ_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 Γ_1 is seen in $\mathbf{E} \parallel \mathbf{c}$ [34]. This emission is also reported in [27], but is used only to claim “... that the crystal is of good quality.”, but ignoring that this observation involves the presence of Γ_1 symmetry.

In Fig. 4 we show time resolved unpolarized emission spectra of the $n_B = 1$ A exciton polaritons. The features due to emission from the lower A Γ_5 polariton branch (LPB) around 3.3755 eV superimposed by the A Γ_1 exciton, from the intermediate A Γ_5 polariton branch caused by the \mathbf{k} -linear term around 3.377 eV and the upper A Γ_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 Γ_1 state. Further examples for the luminescence dynamics of excitons in ZnO can be found in [26] and references given therein.

The temperature dependence of the near edge luminescence spectra have been observed by many groups e.g. [24, 26, 38] 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 ± 20) K BEC are thermally ionized from their centers and the free exciton luminescence, including the LO-phonon replica takes over. At RT these bands merge to an unstructured band of 100 meV FWHM, a value exceeding considerably that of many other semiconductors including GaAs and quantum structures based on this material. Furthermore it involves a homogeneous

broadening γ_h around 20 meV at RT which makes room temperature lasing on Bose-condensed exciton polaritons in a μ -cavity predicted in [43] highly improbable, since the damping exceeds the values of Δ_{LT} and the resulting T_2 time falls below the round trip time in a μ -cavity in contrast to low temperature measurements. The luminescence of a ZnO/Zn_{1-y}Mg_yO quantum well shows for low excitation emission from the ZnO buffer layer at 3.36 eV from the Zn_{1-y}Mg_yO barrier from 3.44 to 3.48 eV and two peaks from the QW at 3.40 and 3.415 eV. The higher of these two peaks is attributed to (localized) excitons the lower one to a defect state. See [26, 44]. Surface exciton polaritons have been detected by attenuated total reflection (ATR) and by nonlinear generation [45]

4 High Excitation Phenomena

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 we consider some aspects of lasing in ZnO. For some reviews of these topics in general and more specifically for ZnO, see [6, 7, 8, 46].

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 exciton like 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 labeled $P_2, P_3, \dots, P_\infty$ [6, 8, 46].

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 [6, 8, 46]. 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_{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 [6]. With further increasing excitation the epilayer shows at 3.32 eV the appearance of the P_∞ band. Surprisingly this band is absent in thin ($\approx 50nm$) but not in thick ($\approx 200nm$) nanorods [18, 26]. These rods are bulk like for excitons because both their length ($> 1\mu m$) and their diameters are large

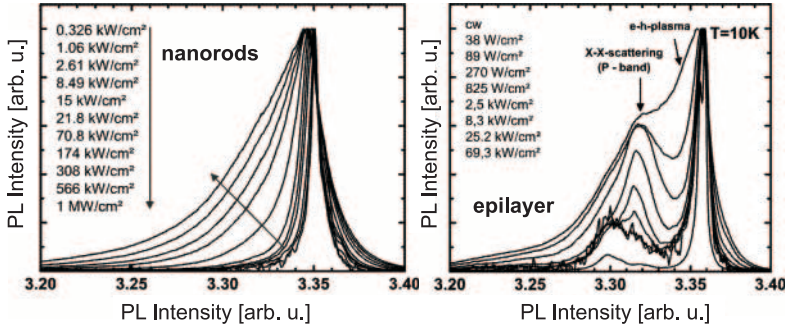


Fig. 5. The luminescence of ZnO nanorods (a) and of an epilayer (b) for increasing excitation. From [26]

compared to the excitonic Bohr radius $a_B \approx 1.8nm$. 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 or remain thermally ionized to favour this dipole-monopole interaction [6, 8, 46]. For the biexciton, values

Table 1. Biexciton energies and binding energies with respect to two A excitons and with respect to two A/B excitons. From [6, 7, 48]. The last column gives corresponding data for A/B excitons from [50], see [51]

Biexciton energy and symmetry	Binding energy with respect to two A excit.	Binding energy with respect to A / B excit.	[50]
$E_{AA\Gamma_1} = 6.7355$ eV	14.7 ± 1 meV	14.7 ± 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

of its binding energy relative to two free A Γ_1 or A Γ_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)[47]. In a joint publication [48] the binding energy of the ground-state biexciton has been found to be 15 meV and the two higher states are due to biexcitons, in which one or two holes from the A VB are replaced by B-holes. See also [49].

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 [48, 50]. The binding energies of the AA Γ_1 and AB $\Gamma_{5,6}$ biexcitons agree within experimental error. Since the data of both excitons are very similar, the deviation for the BB Γ_1 exciton claimed in [50] is difficult to understand. As mentioned in [48], FWM data may result in erroneous results. Similar arguments may hold for the claimed biexciton binding energy of a CC Γ_1 biexciton of 1.4 meV [50].

In ZnO/Zn_{1-y}Mg_yO quantum wells a new emission band appears with increasing excitation at 3.385 eV [26]. If it is due to a biexciton decay, a binding energy around 20 meV results, which would make some sense bearing in mind table 1 and the enhancement of exciton and biexciton binding energies in quantized systems [5, 8]. Further examples of ZnO QW luminescence under high excitation are found e.g. in [52].

Some selected results on two photon absorption (TPA), TPA- spectroscopy or second and third harmonic generation are found in [35, 53], the dynamics of the luminescence under high excitation has been investigated e.g. in [26, 54]. For the investigation of effects in the regime of extreme nonlinear optics, see [55]. The dephasing time T_2 and/or the homogeneous broadening have been investigated at low temperatures by an analysis of the reflection spectra [4, 33, 34, 39, 45] yielding values of the order of or slightly below 1 meV and also in beautiful time resolved FWM experiments [50] giving similar values.

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. [6, 8]. In ZnO the EHP has been observed in gain spectroscopy, e.g. in [26, 56]. Simultaneously with the appearance of EHP gain, the excitonic reflection features started to disappear. Densities exceeding 10^{18}cm^{-3} or 10^{19}cm^{-3} have been deduced in [26, 56].

The investigation of stimulated emission and lasing of ZnO started in the mid sixties. For a few early examples, see e.g. [57] and references therein and for tunable laser emission [58]. The understanding of the processes developed in parallel (see [6, 46]). It turned out, that all of the inelastic scattering and recombination processes mentioned above, including the two-electron transitions, 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 if 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_2 band is inverted if two excitons are present and none of them in the state $n_B = 2$ [6, 46]. Nowadays such processes come also with names like thresholdless lasing or lasing without inversion.

The band - to - band recombination in an EHP requires $\mu_{eh}(n_p, T_p) > E_g^n(n_p, T_p)$ for population inversion [6, 8, 56] and is therefore more like a

three level system. 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 [59]. Recent theories including this continuous transition are found e.g. in [60] 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 [26], in quantum wells obtaining partly gain up to 550 K [52, 61] and most recently in nanorods and related structures [62].

A new topic is lasing in random media i.e. here in ZnO powders, relying on weak localization of light due to enhanced backscattering [63].

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, but also long known phenomena are being reinvented. We tried to give a good mixture of both aspects. The question how long this renaissance will last, depends to a large extend on the question if a stable, high, and reproducible p-doping can be realized [64]. Since prophecy is a notoriously difficult task, especially if it concerns the future, the authors do not want to give an answer here.

Acknowledgements

The authors are grateful to the Deutsche Forschungsgemeinschaft and the Landeskompetenznetz Baden-Württemberg for financial support.

References

1. M. E. Brown (Ed.), *ZnO - Rediscovered* (The New Jersey Zinc Company, New York 1957) **275**
2. G. Heiland et al., *Solid State Physics* **8**, 191 (1959). **275, 278**
3. W. Hirschwald et al., *Current Topics in Materials Science* **7**, 143 (1981). **275**
4. R. Helbig, *Freie und gebundene Excitonen in ZnO*, Habilitation Thesis, (Erlangen 1976); K. Hümmer, *Excitonische Polaritonen in einachsigen Kristallen*, Habilitation Thesis (Erlangen 1978). **275, 277, 278, 283**
5. Landolt-Börnstein: *New Series Group III, Vols. 41 B and 34 C2*. **275, 277, 278, 283**
6. C. Klingshirn, H. Haug, *Physics Reports* **70**, 315 (1981). **275, 277, 278, 281, 282, 283**
7. B. Hönerlage et al., *Physics Reports* **124**, 161 (1985). **275, 277, 278, 281, 282**
8. C. Klingshirn, *Semiconductor Optics*, 2nd ed. (Springer, Heidelberg, Berlin, 2005). **275, 276, 277, 278, 281, 282, 283**

9. Ü. Özgür et al., *J. Appl. Phys. Rev.* (2005) (in press); C. Klingshirn et al.: *Physik Journal* (2005) (in press). 276, 277
10. E. Scharowski, *Z. Physik* **135**, 318 (1953); E. M. Dodson, J. A. Savage, *J. Mat. Sci.* **3**, 19 (1968); R. Helbig: *J. Crystal Growth* **15**, 25 (1972). 276
11. R. A. Laudise, A. A. Ballmann, *J. Phys. Chem.* **64**, 688 (1960); E. Ohshima et al., *J. Crystal Growth* **260**, 166 (2004). 276
12. J. W. Nielsen, E. F. Dearborn, *J. Phys. Chem.* **64**, 1762 (1960); D. C. Reynolds et al., *J. Appl. Phys.* **95**, 4802 (2004). 276
13. E. Mollwo, *Reichsber. Physik* **1**, 1 (1943), 276, 278
14. H. Schneck, R. Helbig, *Thin Solid Films* **27**, 101 (1975). 276
15. M. Lorenz et al., *Annalen der Physik* **13**, 59 (2004). 276
16. T. Yao et al., *J. Vac. Sci. Technol. B* **18**, 2313 (2000); *J. Crystal Growth* **209**, 816 (2000). 276
17. W. I. Park et al., *Appl. Phys. Lett.* **79**, 2022 (2001); Th. Gruber et al., *Phys. Stat. Sol. a* **192**, 166 (2002) and *Appl. Phys. Lett.* **84**, 5359 (2004); D. Gerthsen et al., *Appl. Phys. Lett.* **81**, 3972 (2002); T. Riemann et al., *Phys. Stat. Sol. b* (to be published). 276
18. Z. W. Pan et al., *Science* **291**, 1947 (2001); H. Yan et al., *Adv. Mater.* **15**, 402 (2003); D. Banerjee et al., *Appl. Phys. Lett.* **83**, 2061 (2003); X. Y. Kong et al., *Science* **303**, 1348 (2004); R. Kling et al., *Nanotechno.* **15**, 1043 (2004); G. Prinz et al., to be published, R. Hauschild et al., to be published. 276, 279, 281
19. W. I. Park et al., *Adv. Mater.* **15**, 526 (2003). 276
20. L. Spanhel et al., *J. Am. Chem. Soc.* **113**, 2826 (1991) and *J. Sol-Gel Sci. and Technol.* **26**, 499 (2003); L. Mädler et al., *J. Appl. Phys.* **92**, 6537 (2002). 276
21. M. Göppert et al., *J. Luminesc.* **72-74**, 430 (1997); C. Klingshirn and E. Mollwo, *Z. Physik* **254**, 437 (1972). 276
22. F. W. Kleinlein, R. Helbig, *Z. Physik* **266**, 201 (1974). 276
23. A. R. Hutson, *Phys. Rev.* **108**, 222 (1957); H. Rupprecht, *J. Phys. Chem. Sol.* **6**, 144 (1958); M. A. Seitz, D. H. Whitmore, *J. Phys. Chem. Sol.* **29**, 1033 (1968); J. A. Savage, E. M. Dodson, *J. Mat. Sci.* **4**, 809 (1968); P. Wagner, R. Helbig, *J. Phys. Chem. Sol.* **35**, 327 (1974) 276
24. Chr. Solbrig, *Z. Physik* **211**, 429 (1968); R. Dingle, *Phys. Rev. Lett.* **23**, 579 (1969); D. C. Reynolds et al., *Phys. Rev.* **140**, A1726 (1965) and *Phys. Rev.* **185**, 1099 (1969); E. Tomzig, R. Helbig, *J. Luminesc.* **14**, 403 (1976); R. Kuhnert, R. Helbig, *J. Luminesc.* **26**, 203 (1981); K. A. Vanheusden et al., *Appl. Phys. Lett.* **68**, 403 (1996). 277, 278, 280
25. D. Zwingel, F. Gärtner, *Sol. State Commun.* **14**, 45 (1974). 277
26. H. Priller, Ph.D Thesis, Karlsruhe (2005), partly published in H. Priller et al., *Phys. Stat. Sol. b* **241**, 587 (2004) and *Appl. Phys. Lett.* **86**, 111909 (2005); *Proc. ICPS, Flagstaff 2004* (in press); *Proc. EXCON, Krakau 2004 J. Luminesc.* **112**, 173 (2005). 277, 278, 279, 280, 281, 282, 283, 284
27. S. F. Chichibu et al., *J. Appl. Phys.* **93**, 756 (2003). 277, 278, 280
28. D. G. Thomas, *J. Phys. Chem. Sol.* **15**, 86 (1960); J. J. Hopfield, *J. Phys. Chem. Sol.* **15**, 97 (1960), 277, 278
29. M. Cardona, *Phys. Rev.* **129**, 69 (1963) and *J. Phys. Chem. Sol.* **24**, 1543 (1963). 277
30. K. Shindo et al., *J. Phys. Soc. Japan* **20**, 2054 (1965); B. Segall, *Phys. Rev.* **163**, 769 (1967); U. Rössler, *Phys. Rev.* **184**, 733 (1969). 277

31. D. C. Reynolds, C. W. Litton, T. C. Collins, Phys. Rev. **140**, A1726 (1965). [277](#)
32. J. J. Hopfield, D. G. Thomas, Phys. Rev. Lett. **15**, 22 (1965). [277](#), [278](#)
33. G. Blattner et al., Phys. Rev. B **25**, 7413 (1982). [277](#), [278](#), [283](#)
34. K. Hümmer, R. Helbig, M. Baumgärtner, Phys. Stat. Sol. b **86**, 527 (1978); R. Kuhnert, R. Helbig, K. Hümmer, Phys. Stat. Sol. b **107**, 83 (1981). [277](#), [278](#), [280](#), [283](#)
35. M. Fiebig et al., Phys. Stat. Sol. b **177**, 187 (1993); J. Wrzesinski, D. Fröhlich, Phys. Rev. B **56**, 13087 (1997); Sol. State Commun. **105**, 301 (1998). [277](#), [278](#), [283](#)
36. D. C. Reynolds et al., Phys. Rev. B **60**, 2340 (1999). [277](#), [280](#)
37. B. Gil, Phys. Rev. B **64**, 201310 R (2001). [277](#), [278](#)
38. W. R. L. Lambrecht et al., Phys. Rev. B **65**, 075207 (2002); B. K. Meyer et al., Phys. Stat. Sol. b **241**, 231 (2004); A. V. Rodina et al., Phys. Rev. B **69**, 125206 (2004); R. Sauer, K. Thonke in *Optics of Semiconductors and Their Nanostructures*, H. Kalt and M. Hetterich (Eds.), Springer Series in Solid State Sciences **146**, 73 (2004), [277](#), [278](#), [279](#), [280](#)
39. J. Lagois, K. Hümmer, Phys. Stat. Sol. b **72**, 393 (1975); J. Lagois: Phys. Rev. B **16**, 1699 (1977). [277](#), [278](#), [283](#)
40. R. I. Weiher, W. C. Tait, Phys. Rev. **185**, 1114 (1969) and Phys. Rev. **B5**, 623 (1972); K. Hümmer, P. Gebhardt, Phys. Stat. Sol. b **85**, 271 (1978). [278](#)
41. K. Hümmer, Phys. Stat. Sol. b **56**, 249 (1973). [278](#)
42. The references [34] show , that the claim in [36] to observe “...free exciton emission... for the first time” is clearly unjustified. [280](#)
43. A. Kakovin, M. Zamfirescu et al., Phys. Stat. Sol. a **192**, 212 (2002) and Phys. Rev. B **65**, 161205 R (2002). [281](#)
44. T. Makino et al., Appl. Phys. Lett. **77**, 975 (2000); H. D. Sun et al., Appl. Phys. Lett. **78**, 2464 (2001); S. Giemsch et al., to be published. [281](#)
45. J. Lagois, B. Fischer, Phys. Rev. Lett. **36**, 680 (1976); J. Lagois, Phys. Rev. B **23**, 5511 (1981); I. Hirabayashi et al., J. Phys. Soc. Japan **51**, 2934 (1982); M. Fukui et al., J. Phys. Soc. Japan **53**, 1185 (1984); F. DeMartini et al., Phys. Rev. Lett. **38**, 1223 (1977); M. Fukui et al., Phys. Rev. B **22**, 1010 (1980), [281](#), [283](#)
46. C. Klingshirn, Phys. Stat. Sol. b **71**, 547 (1975); J. M. Hvam, Sol. State Commun. **12**, 95 (1973); Phys. Stat. Sol. b **63**, 511 (1974); S. W. Koch et al., Phys. Stat. Sol. b **89**, 431 (1978). [281](#), [282](#), [283](#)
47. H. Schrey, V. Lyssenko, C. Klingshirn, Sol. State. Commun. **32**, 897 (1979). [282](#)
48. J. M. Hvam et al., Phys. Stat. Sol. b **118**, 179 (1983). [282](#), [283](#)
49. H. J. Ko, Y. F. Chen, T. Yao, Appl. Phys. Lett. **77**, 537 (2000). [282](#)
50. K. Hazu et al., Phys. Rev. B **68**, 332051 (2003); J. Appl. Phys. **95**, 5498 (2004); J. Appl. Phys. **96**, 1270 (2004). [282](#), [283](#)
51. The absolute values of the exciton and biexciton energies differ e.g. in [4-7,32-34,48,50] and other papers by one or two meV. This is no serious discrepancy. If spectrometers are not frequently calibrated with low pressure spectral lamps, they may easily show deviations of the order of 1 meV. [282](#)
52. H. D. Sun et al., Appl. Phys. Lett. **77**, 4250 (2000). [283](#), [284](#)
53. E. Mollwo, G. Pensl, Z. Physik **228**, 193 (1969); R. Dinges et al., Phys. Rev. Lett. **25**, 922 (1970); C. Klingshirn, Z. Physik **248**, 433 (1971); W. Kaule, Sol.

- State Commun. **9**, 17 (1971); G. Pensl, Sol. State Commun. **11**, 1277 (1972); G. Koren, Phys. Rev. B **11**, 802 (1975); G. Wang et al., Appl. Optics **40**, 5436 (2001); C. Y. Liu et al., Optics Com. **237**, 65 (2004); Appl. Phys. B **79**, 83 (2004); U. Neumann et al., Appl. Phys. Lett. **84**, 170 (2004). **283**
54. J. Collet, T. Amand, Phys. Rev. B **33**, 4129 (1986); J. Gutowski, A. Hoffmann, Adv. Mat. Opt. and Electr. **3**, 15 (1994). **283**
55. O. D. Mücke, T. Tritschler, M. Wegener, Opt. Lett. **27**, 2127 (2002). **283**
56. K. Bohnert, G. Schmieder, C. Klingshirn, Phys. Stat. Sol. b **98**, 175 (1980). **283**
57. F. H. Nicoll, Appl. Phys. Lett. **9**, 13 (1966); J. R. Packard et al., J. Appl. Phys. **38**, 5255 (1967); S. Irwai, S. Namba, Appl. Phys. Lett. **16**, 354 (1970); J. M. Hvam: Phys. Rev. B **4**, 4459 (1971); W. D. Johnston jr., J. Appl. Phys. **42**, 2731 (1971); C. Klingshirn, Sol. State Commun. **13**, 297 (1973), **283**
58. W. Wünnstel, C. Klingshirn, Optics Commun. **32**, 269 (1980). **283**
59. K. Bohnert et al., Z. Physik B **42**, 1 (1981). **284**
60. M. F. Pereira, K Henneberger, Phys. Stat. Sol. b **202**, 751 (1997); Phys. Stat. Sol. b **206**, 477 (1998); T. J. Inagaki, M. Aihara, Phys. Rev. B **65**, 205204 (2002) and references therein. **284**
61. G. Tobin et al., Physica B **340-342**, 245 (2003); D. M. Bagnall et al., Appl. Phys. Lett. **73**, 1038 (1998); P. Yu, J. Crystal Growth **184/185**, 601 (1998) and references therein. **284**
62. M. H. Huang et al., Science **292**, 1897 (2001); J. C. Johnson et al., J. Phys. Chem. B **105**, 11387 (2001) and Nano Letters **4**, 197 (2004); Y. G. Wang et al., Chem. Phys. Lett. **377**, 329 (2003); Th. Nobis et al., Phys. Rev. Lett. **93**, 103903 (2004). **284**
63. H. Cao, Waves Random Media **13**, R 1 (2003); G. Hackenbroich, Physik Journal **3** (7), 25 (2004). **284**
64. D. C. Look et al., Phys. Stat. Sol. a **201**, 2203 (2004) and Semicond. Science and Technol. **20**, S55 (2005); A. Dadgar et al., E-MRS Meeting, Strasbourg (2005), Superl. and Microstr., in press. **284**