Room-temperature stimulated emission of ZnO: Alternatives to excitonic lasing

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ZnO is a wide gap semiconductor which has possible applications in blue light emitting diodes and lasers, devices, which are currently based on GaN. One advantage of ZnO compared to GaN is the much higher exciton binding energy of 60 meV compared to 26 meV in GaN. Due to this exciton binding energy many authors ascribe stimulated emission at room temperature (RT) to excitonic processes with presumably very low thresholds. In this contribution we investigate the temperature dependence of the band gap and of the homogeneous width of the free exciton resonance. Together with new and previous calculations and experimental data, these findings cast some doubt on the above claim and we present alternative interpretations for RT stimulated emission in ZnO.

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I. INTRODUCTION

Presently, the wide band gap semiconductor ZnO sees a vivid research renaissance with more than 2000 ZnO related papers in 2005 alone.[1] One hope of the ZnO related research is to obtain with ZnO a material for a blue/UV optoelectronics or more precisely a light emitting or laser diode in addition to or even instead of GaN.[2] To reach this goal, many research groups investigate the stimulated emission including amplified spontaneous emission (ASE) under optical excitation from low temperatures up to and even beyond room-temperature (RT).[3–18] A claim found frequently is that the relatively high exciton binding energy of about 60 meV and the small excitonic Bohr radius a_B of 1.8 nm result in excitonic laser processes at RT which should have low thresholds.[4–8,10–13]

The process for RT excitonic lasing and ASE favored by many authors (e.g., Refs. 4–8 and 10–13) is inelastic exciton-exciton scattering, the so-called *P* band. In this nonlinear emission process two excitons (more precisely excitonlike polaritons) with main quantum-number $n_B=1$ interact. One is scattered onto the photonlike part of the polariton dispersion, appearing as luminescence photon while the other is scattered under energy and momentum conservation into a state with $n_B=2,3,\ldots$ or into the continuum resulting in the emission bands P_2, P_3, or P_∞, respectively.[14–18] The energy at the emission maximum is given for a hydrogenlike series of exciton states in an heuristic approach by[15]

$$\hbar\omega_{P_{n_B,f}} = E_X(n_B=1,k=0) - E_X^b\left(1-\frac{1}{n_{B,f}^2}\right) - \frac{\hbar^2}{M}\vec{k}_{i_1}\vec{k}_{i_2}, \quad (1)$$

where E_X on the right-hand side (rhs) gives the exciton ground state energy and the $\vec{k}_{i_{1,2}}$ are the wave vectors of the excitons in the initial states. The last term on the rhs can be approximated by $\delta\cdot 3k_BT$ with $0\leqslant\delta\leqslant 1$. The observation of this process is a proof for the presence of excitons alternative to the observation of the $1s\rightarrow 2p$ transition in the sense of Ref. 19. The stimulated emission based on this process can occur at the spontaneous emission peak[17] but more frequently on its low energy side[16] and it can be mapped on a four level laser scheme.[18] Strictly speaking inversion is already reached at low temperature if there are two excitons in the sample, provided that both are in the state $n_B=1$. Therefore one also speaks about thresholdless lasing or lasing without inversion. A finite loss rate of the laser cavity will of course result in a finite threshold density for the onset of lasing. The *P* bands have been observed at low temperatures and intermediate excitation conditions in many III-V, II-VI, and I-VII semiconductors.[14–18,20–22] For higher temperatures one usually finds a transition to inelastic exciton-free carrier scattering.[14,15,18] At higher pump powers an electron-hole-plasma (EHP) forms and the direct recombination from the EHP is observed.[14,18,20]

In the following we first present data for the temperature dependence of the band-gap $E_g(T)$ and of the homogeneous width $\Gamma(T)$ of the exciton resonance in ZnO. Then we present new and summarize older data on the temperature dependence of various laser processes in ZnO and their thresholds. These data will cast some doubt on excitonic RT lasing in ZnO in general and in particular on the exciton-exciton scattering process. Therefore we argue that this process is not likely to explain RT lasing in most cases and present some alternative processes for stimulated emission in ZnO at RT and above.

II. TEMPERATURE DEPENDENCE OF THE BAND GAP AND HOMOGENEOUS LINE BROADENING

In Fig. 1 we show luminescence spectra of a high quality ZnO bulk sample under low cw-excitation with a HeCd laser ($\hbar\omega_{exc}=3.81$ eV) for various temperatures. This type of sample has been grown by a gas transport technique[23] and show FWHM values in x-ray diffraction of 8.7 arcsec, close to the resolution limit,[24] measured at the Karlsruhe Synchrotron ANKA in a ω-scan for the (0002) reflex with $\lambda=0.7093$ Å. The luminescence behavior shown there is the same for epitaxial layers and partly for nanorods.[13,21] One observes the free *A* exciton luminescence around 3.37 eV and the first two LO-phonon replica around 3.30 eV and 3.23 eV, respectively. The luminescence of bound exciton complexes (BEC) shows up around 3.35 eV. The high energy shoulder of the free exciton emission seen in the spectra for 70 K and 130 K comes from the *B* exciton. At higher temperature (e.g., 230 K) *A* and *B* excitons are no longer

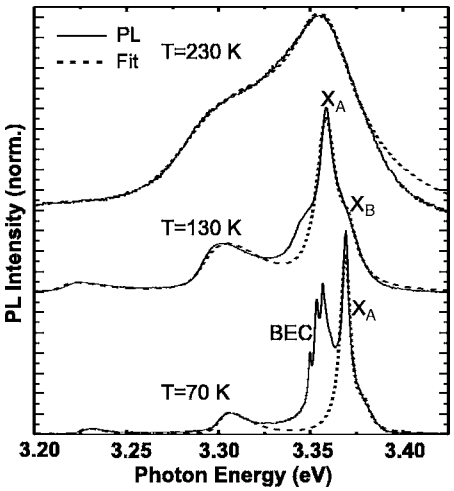

FIG. 1. Luminescence spectra of ZnO at low excitation for various temperatures with a fit to the zero phonon emission of the free A (X_A) and B (X_B) exciton and their first two LO-phonon replica.

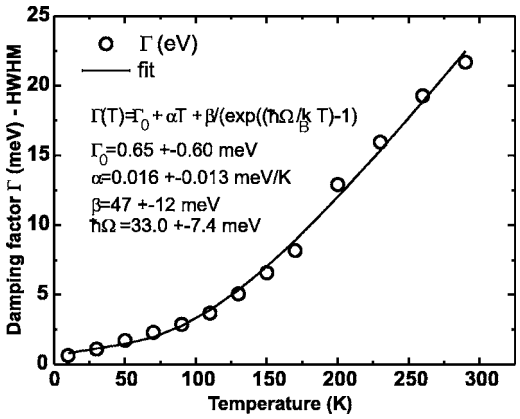

FIG. 2. The temperature dependence of the damping Γ of the A (and B) exciton resonance of ZnO.

resolved. While recombination of bound exciton complexes, including their LO-phonon replica and two electron transitions, dominate at low temperature, these features tend to disappear for $T \geqslant 70$ K due to thermal detachment of the excitons from the center (e.g., neutral donors or acceptors) and free exciton recombination including its m-LO phonon replica dominate. The disappearance of the BEC in this temperature range is consistent with binding energies of the exciton to the defect of 10 to 20 meV.[25] Neglecting the homogeneous broadening of the exciton states, the spectra of the LO-phonon replica of the free excitons can be described by the product $P_m(E_{\rm kin}, k_B T)$ of density of states, Boltzmann occupation probability and transition matrix element W_m as a function of kinetic energy of the exciton $E_{\rm kin}$,

$$P_m(E_{\rm kin}, k_B T) \propto E_{\rm kin}^{1/2} \exp\{-E_{\rm kin}/k_B T\} W_m(E_{\rm kin}) \qquad (2a)$$

for $E_{\rm kin} \geqslant 0$ and zero otherwise.[14] With

$$W_m(E_{\rm kin}) \sim E_{\rm kin}^{l_m} \quad \text{and} \quad l_1 = 1, \quad l_m = 0, \quad m \geqslant 2. \qquad (2b)$$

To obtain a fit to the luminescence spectrum $I_m^{\rm lum}$, the expression (2a) must be convoluted with a Lorentzian $L(\Gamma)$ of width Γ to account for homogeneous broadening,[26]

$$I_m^{\rm lum}(\hbar\omega) = P_m(E_{\rm kin}, k_B T) \otimes L[\Gamma(T)]. \qquad (3)$$

With $\hbar\omega = E_X(n_B = 1, k = 0) - m\hbar\omega_{\rm LO} + E_{\rm kin}$. For simplicity it is assumed that Γ depends only on temperature, not on $E_{\rm kin}$. The fit in Fig. 1 has been obtained along these lines including the zero-phonon emission from the bottleneck region[14,18] close to $\vec{k} = 0$. As can be seen in Fig. 1, the fit is accurate for low temperatures, except for the BEC transitions which have not been included in the model. At higher temperatures a discrepancy occurs on the high energy wing, which is caused by reabsorption through the temperature dependent Urbach tail. At RT the emission bands merge to an almost unstructured feature centered around 3.26 eV of 90 meV FWHM due to the increase of $\Gamma(T)$. The fit allows to deduce $\Gamma(T)$, which is shown in Fig. 2. It should be noted that the emission maximum at RT does not coincide with the free exciton energy at 3.31 eV.[5]

The damping or homogeneous broadening reaches at RT a HWHM value of 20 meV, which is already comparable to the exciton binding energy. This rather large damping is observed also in the RT absorption spectra.[12,27–29] The damping at RT is evidently determined by the intrinsic process of exciton-LO-phonon coupling.

It is much stronger than, e.g., in GaAs quantum wells, where the exciton with a binding energy of only 10 meV can still be seen at RT. Even in bulk and at RT excitons still appear weakly, though the bulk exciton binding energy is only 4.5 meV.[14,30] The damping can be approximated by

$$\Gamma(T) = \Gamma_0 + \alpha T + \beta(\exp\{\hbar\Omega/k_B T\} - 1)^{-1}, \qquad (4)$$

where Γ_0 is the low temperature value typically $\leqslant 1$ meV in agreement with data from the analysis of low temperature reflection spectra. See, e.g., Refs. 31 and 32, and references therein. The second term includes the contribution of the acoustic phonons with $\alpha = (0.016 \pm 0.013)$ meV/K and the third one summarizes the effect of all optical phonons with a coupling strength $\beta = (47 \pm 12)$ meV and an effective phonon energy $\hbar\Omega$ of (33 ± 7.5) meV which is an average of all optical phonons from 12.5 to 73.3 meV.[33] In Ref. 12 the temperature dependence of the damping has been deduced from the analysis of the absorption spectra of a 55 nm thick ZnO layer grown on $ScAlMgO_4$ in the temperature range from 10 to 150 K. The spectra coincide with those in Refs. 27, 28, and 34 and the increase of Γ with temperature in this interval is in agreement with our data. The same formula (4) has been used to fit the data. Though ZnO is known for a very strong exciton-LO-phonon coupling, the parameter β in Ref. 12 for the LO-phonon coupling strength is with values around 0.8 eV for A and B excitons unrealistically high, since it results with the given values of α at RT in a homogeneous width of around 1.7 and 0.45 eV for A and B excitons. This would prevent any observation of excitonic features at RT in contrast to experiment.[10,14,27,28] The rather high values of Γ_0 in Ref. 12 1.5 and 8 meV for the A and B Γ_5 excitons, respectively, are possibly due to a misconception. They have been deduced from the width of the absorption features. At

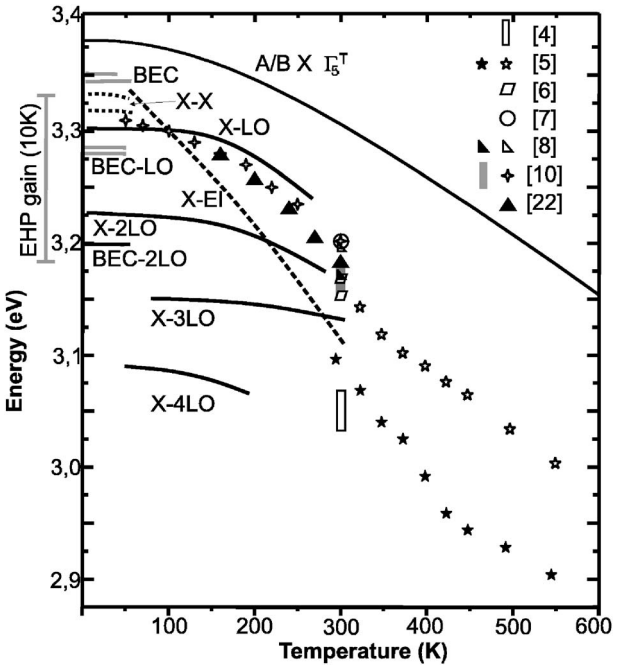

FIG. 3. Temperature dependence of the free A and B exciton resonances of ZnO together with data for various spontaneous and stimulated emission features (Refs. 4–8, 10, 15, 22, and 38).

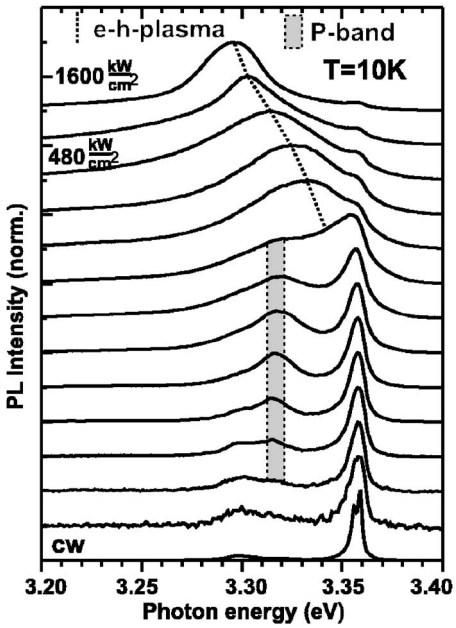

FIG. 4. The normalized luminescence spectra of a ZnO epilayer at 10 K lattice temperature for increasing excitation intensity. The m LO-phonon replica of the free exciton, which can dominate the stimulated emission for low loss and large excited volumes (Ref. 38) are of minor importance here.

low temperatures, the width of the absorption features is determined by the longitudinal transverse splitting Δ_{LT} and not by the homogeneous width Γ_{hom}. Indeed the values of Γ_0 in Ref. 12 are close to Δ_{LT} (Ref. 31) for A and B excitons, respectively. Since states with different $\vec{k}$ values contribute between $\hbar\omega_0$ and $\hbar\omega_L$ on the lower polariton branch to the absorption spectrum, this is rather an inhomogeneous broadening than a homogeneous one. Only for $\Gamma_{hom}(T) > \Delta_{LT}$ the homogeneous width may be deduced from the zero phonon absorption band. This is the case for the $A\Gamma_5$ exciton in ZnO for $T \gtrsim 100$ K (see Fig. 1 or Fig. 1 in Ref. 12). Below, Γ_{hom} can be deduced from the reflection spectra[31,32] or from the difference between the spectra of the LO-phonon replica calculated without and with damping according to (3) and (4).

The fit in Fig. 1 allows also to deduce the temperature dependence of E_g and thus of the exciton energy. However, above RT this procedure becomes increasingly difficult, therefore the band gap shift above RT has been deduced from transmission measurements by an analysis of the Urbach absorption tail. This results in the experimental curve $A/B\ X\ \Gamma_5^T$ of Fig. 3, which shows the temperature dependence of the A and B exciton resonances (which are split by 4.5 meV only), in agreement with data, e.g., in Refs. 12, 35, and 36 and of various emission features discussed below. It is well known that the empirical Varshni formula for the temperature dependent band gap shift $\Delta E_g(T)$

$$\Delta E_g(T) = E_g(T = 0\ \mathrm{K}) - E_g(T) = \frac{\gamma T^2}{T + \beta} \tag{5}$$

models the quadratic low- and the linear high-temperature behavior but fails frequently to fit both regions properly with one set of parameters. Therefore we used for the fit a numerial model including the effects of thermal expansion and the dominating one of electron-phonon interaction

$$\Delta E_g(T) = \Delta E_g^{\mathrm{lattice}}(T) + \Delta E_g^{\mathrm{el\text{-}ph}}(T) \tag{6}$$

according to Ref. 37, which gives an excellent fit from low temperatures to beyond 800 K (Ref. 26) identical to the curve $A/B\ X\ \Gamma_5^T$ shown in Fig. 3.

III. HIGH EXCITATION LUMINESCENCE AND STIMULATED EMISSION

In Fig. 4 we show the luminescence of a high quality ZnO epitaxial layer at low temperature and for increasing optical excitation with 15 ns pulses from a XeCl excimer laser ($\hbar\omega_{exc}$=4.02 eV). The layer has a thickness of about 0.4 μm. It has been grown by MOVPE on Al_2O_3 (111) with a GaN buffer layer. The bound exciton lines are partly resolved and have at low temperatures a FWHM around (2.5±0.5) meV as shown in the lowest trace of Fig. 4, which has been excited with a cw HeCd laser and shows the dominance of BEC emission lines mentioned already above. The evolution of the spectra confirms nicely the scenario developed in Refs. 14 and 18. One observes the M band around 3.36 eV, which can be due to radiative decay of biexcitons, but also due to excitonic processes involving the spectrally close lying BEC.[18] With further increasing pump power the P band mentioned above is seen around 3.32 eV with its various components not being resolved. At the highest pump powers (possibly stimulated) emission from a degenerate EHP takes over in the range from 3.28 eV to 3.34 eV, shifting with increasing excitation intensities to lower energies due to in-

creasing band gap renormalization (BGR).[20,31,32] Stimulated emission or at least ASE is evidenced, e.g., by a decreasing half-width with increasing excitation intensity I_{exc}, though the spontaneous emission spectrum would get broader with increasing electron-hole pair density n_p. This notation implies that the real part of the density dependent self-energy can be identified with renormalization of the band gap, while the imaginary part gives the damping.[18] The density at which the transition to an EHP occurs in ZnO will be discussed in more detail below. Here we note that this density is only weakly temperature dependent and in the range of the Mott density

$$n_M^{\mathrm{ZnO}} \approx 0.5 \times 10^{18}\ \mathrm{cm}^{-3}. \tag{7}$$

See the discussion in Appendix A.

In Fig. 3 we show as a function of temperature the range of BEC emission and of its m LO-phonon replica, which tend to disappear above $\approx$70 K as mentioned already. The m LO-phonon replica of the free A and B excitons are influenced in the cases of both spontaneous and stimulated emission at higher temperature by reabsorption and losses, depending on the thickness of the excited volume.[15,38] Furthermore the positions of the P_2 and P_∞ bands are given, which tend to cross the inelastic X-el scattering for $T \approx 100$ K. Indeed the P bands have never been observed in bulk ZnO samples for temperatures above approximately 100 K (Refs. 14, 15, and 18) for the following reasons.

The $n_B > 1$ states become increasingly populated with increasing temperature causing reabsorption of the P_2 emission and the excitons become increasingly ionized favoring the monopole-dipole scattering of the remaining excitons with free carriers over the dipole-dipole interaction between free excitons.[16] A characteristic feature of the X-el recombination is its faster shift to lower energies with increasing temperature compared to the band gap. This is due to a term involving the ratio of exciton and electron masses

$$\hbar\omega_{X\text{-el}} \approx E_X(n_B = 1, K = 0) - \frac{3}{2}k_B T\left(\frac{m_X}{m_e} - 1 + 2\delta'\sqrt{\frac{m_X}{m_e}}\right) \tag{8}$$

with δ' of the order of unity, resulting again from an heuristic approach involving energy and momentum conservation.[15] A theoretical modelling supports this heuristic approach.[39] The inelastic X-el scattering has also been observed in different III-V, II-VI, and I-VII semiconductors in the intermediate density and temperature regime.[14,18,22,39] In Fig. 3 we also show RT data of high excitation emission bands or lasing from various authors. Open symbols represent an attribution (made by the respective authors) to inelastic X-X scattering (sometimes specified as P_2 or P_∞ bands) and full symbols represent emission attributed to EHP. In Refs. 4 and 5 two high excitation emission bands, possibly stimulated emission or ASE, could be followed up to 550 K which are claimed to be due to the inelastic X-X scattering and recombination in an electron-hole plasma, respectively.

It is obvious that the spread of the claimed P-band energies tends to surpass the interval given by Eq. (1). Furthermore it must be noted that the only argument for the P-band interpretation at RT is the fact that an extrapolation of the experimental data for $0 \leqslant T \lesssim 100$ K to RT may end roughly in this interval. This is, however, also true for other processes like the m LO-phonon replica or the exciton-electron process shown in Fig. 3. At this point it must be also noted that the transition from one process (e.g., X-X scattering) to another one (e.g., X-el scattering) with increasing temperature often occurs around 100 K without a discontinuous spectral jump.

IV. DISCUSSION

The separation of the emission processes in excitonic ones at intermediate densities and recombination in an electron-hole plasma at the highest densities is didactically very valuable and both aspects have their right and give a correct description of the experimental findings in certain parameter ranges of density and temperature.[40]

It is known, however, that the transition from an exciton gas to an EHP is a continuous one in direct gap semiconductors due to the short lifetime of carrier pairs, which prevent the evolution of the phase separation below a critical temperature predicted by quasiequilibrium thermodynamics.[14,32] Furthermore it has been shown recently by advanced many particle models that an emission peak at the exciton energy does not necessarily mean that there are excitons in the system, but such a peak can result also from a plasma recombination process due to a resonance or enhancement of the oscillator strength at the exciton energy.[19] Though the theory has been applied mainly to GaAs and GaAs based quantum structures, which have a small exciton binding energy compared to ZnO, it must be anticipated that such results will hold also for ZnO at least at higher densities (approaching or exceeding 10^{17} cm^{-3}) and elevated temperatures where the homogeneous width of the exciton becomes comparable to its binding energy. In these advanced theoretical models it becomes even difficult to identify or separate strictly the band gap renormalization from other phenomena.[41,42] This is one of the aspects to doubt the P-band interpretation of RT stimulated emission in ZnO. Some others are the following:

As already stated above, in bulk samples the P bands are not observed in ZnO up to RT, see Refs. 14, 15, and 18, and references therein. The explanation can be found in Fig. 1 from Ref. 16, which is reproduced here as Fig. 5 and which gives the calculated temperature dependence of electron-hole pair density at the laser threshold for a realistic loss rate. The calculation is for CdS, but can be translated to ZnO by scaling the temperature axis by a factor 2, because both the exciton binding and the relevant LO-phonon energy are in ZnO roughly a factor 2 bigger than in CdS. The relative positions of the thresholds of the linear X-LO and the quadratic X-X and X-el scattering processes depend on the loss rate.

The calculations in Fig. 5 are confirmed by experimental data.[14,16] The increase of the threshold for the P_2 band with temperature comes essentially from two effects namely from the increase of the population of the $n_B = 2$ state with temperature, resulting in reabsorption and at higher temperatures additionally from thermal ionization of the excitons which favors at RT the monopole-dipole interaction of X-el scattering over the dipole-dipole interaction of X-X scattering, as already mentioned above.

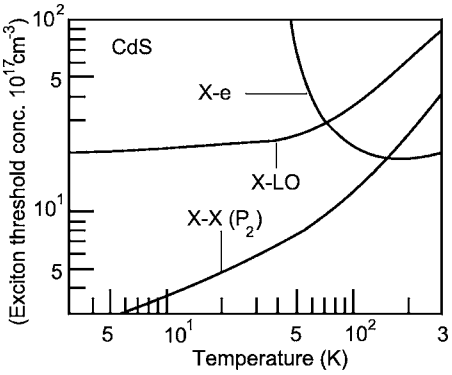

FIG. 5. The calculated temperature dependence of the electron-hole pair density at laser threshold for various excitonic processes in CdS (Ref. 16).

The absolute values in Fig. 5 or the experimental data, e.g., in Fig. 22.2 of Ref. 14 show that the densities at laser threshold at room temperature come close to or partly exceed the values of the Mott density of ZnO, which is at RT around 0.5×10^{18} cm^{-3} [see (7) and Appendix A]. This statement holds also for recent results of various groups,[4–8] where typically values of the pump intensity I_{exc} around or above 0.5 $MW\,\mathrm{cm}^{-2}$ are used. The density of electron-hole pairs n_p at laser threshold or at the appearance of new emission bands is evidently a crucial quantity to distinguish various excitonic processes from the formation of or even the stimulated emission from an EHP. Before we proceed with the discussion of various results, we develop a rule of thumb, which allows to calculate n_p for various excitation conditions. Assuming that every absorbed photon creates one electron hole pair we can write

$$n_p = \frac{I_{exc}\tau}{\hbar\omega_{exc} l}, \tag{9a}$$

where I_{exc} and $\hbar\omega_{exc}$ are the energy flux density (or intensity) of the exciting pump light and $\hbar\omega_{exc}$ its photon energy. The characteristic time τ and length l have different meanings, according to the excitation conditions. The time constant τ is given by the lifetime of the excited exciton-hole pairs T_1 of typically 300 ps (Refs. 13 and 38) for excitation pulses of duration T_{exc} longer than T_1, typically a few ns, i.e., under quasistationary conditions

$$\tau = T_1 \quad \text{for } T_{exc} > T_1. \tag{9b}$$

For pulses shorter than T_1 the total deposited energy determines n_p, i.e.,

$$\tau = T_{exc} \quad \text{for } T_{exc} < T_1. \tag{9c}$$

This condition (9c) is typically fulfilled for (sub-) ps lasers. For thick samples (thickness d), the characteristic length l is given by either the penetration depth of the pump-light $l_{exc}=\alpha_{exc}^{-1}$ or by the diffusion length l_D of the excited carriers over which they expand (diffusively or even ballistically) during T_1. For one-photon absorption in the band-to-band transition region one has $\alpha_{exc}\gtrsim 2\times10^5$ cm^{-3} (Refs. 11, 14, 27, and 28) or $l_{exc}\approx 0.05$ μm. In contrast one finds frequently values of l_D of 1 $\mu\mathrm{m}\lesssim l_D\lesssim 3$ μm in wide, direct gap semiconductors[14,43] resulting in

$$l = l_D \quad \text{for } d > l_D, \tag{9d}$$

$$l = d \quad \text{for } l_{exc} < d < l_D \tag{9e}$$

if we neglect fast surface recombination. For very thin samples with $d\lesssim l_{exc}$ the fraction $I_{exc}[1-\exp(-\alpha_{exc}d)]$ of the light absorbed in such a thin film must be considered resulting in

$$l^{-1} = \frac{1-\exp(-1)}{d} \quad \text{for } \alpha_{exc}d \approx 1 \tag{9f}$$

and

$$l^{-1} = \alpha_{exc} \quad \text{for } \alpha_{exc}d < 1. \tag{9g}$$

If Eqs. (9a)–(9g) tell us that n_p is considerably below the value given by (7) and if we are at low lattice temperatures T_L well below RT, we can safely assume that excitonic processes dominate. If the densities are still low, but T_L approaches RT or is even above, we must anticipate that a substantial number of excitons are thermally split into its constituents, in a similar way as BEC tend to disappear around $T_L\gtrsim 70$ K. If n_p falls in the region given by (7) we must anticipate that we reached the transition region from an exciton gas to an EHP, independent from T_L since the screening and band-gap renormalization are essentially temperature independent.[14] For even higher values of n_p an EHP is formed. However, this does not imply automatically stimulated emission from the direct recombination of electron-hole pairs in an EHP. This gain process occurs only if the EHP is degenerate or more precisely if the chemical potential of the electron-hole pair system $\mu(n_p,T)$, i.e., the energetic distance between the quasi-Fermi levels of electrons and holes is larger than the reduced band gap $E_g'(n_p,T)$, i.e.,

$$\mu(n_p,T) = E_e^F(n_p,T) - E_h^F(n_p,T) \geqslant E_g'(n_p,T). \tag{10}$$

The onset of a degenerate population is given by the effective density of states which reads for a twofold spin degenerate, parabolic band with effective mass m^*,

$$n_{\mathrm{eff}} = 2\left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2}. \tag{11}$$

This results for ZnO at RT with $m_e=0.28m_0$ and $m_h=0.59m_0$ (Ref. 33) in $n_{\mathrm{eff}}=5\times10^{18}$ cm^3 and $p_{\mathrm{eff}}=1.1\times10^{19}$ cm^{-3} Equation (10) will be fulfilled for $n_p\approx10^{19}$ cm^{-3}. This means one has in ZnO at RT at the laser threshold frequently densities of the order of n_M but too small to fulfill the condition (10).

In the following we develop two models which can describe ASE and lasing at RT and above. This is followed by a discussion that these models can explain most of experimental data.

What is the origin of stimulated emission observed at RT under high excitation densities? A pure excitonic model can be ruled out because (see also arguments above).

(i) At RT even at low excitation densities the homoge-

neous width of the exciton is comparable with its binding energy as shown in Sec. II. Since higher excitation densities lead to an additional excitation induced broadening and to a reduction of the exciton binding energy it is doubtful that the exciton concept is applicable under these conditions.

(ii) The density is around the Mott density. This means that the band gap renormalization is comparable to the exciton binding energy and the exciton binding energy consequently tends to zero, see Appendix A for further details.

We propose in the following two processes to explain RT lasing in ZnO:

(i) Recombination of an electron-hole pair under emission of one or more plasmon-phonon mixed state quanta. Since the term plasmon-phonon is less commonly known, we give a short explanation. For vanishing damping the longitudinal and transverse eigenenergies of this state follow from the zero points and singularities of the dielectric function $\varepsilon(\omega)$,[14]

$$\varepsilon(\omega) = \varepsilon_b + \frac{f}{\omega_{\mathrm{TO}}^2 - \omega^2} + \frac{\omega_{pl}^{0^2}}{-\omega^2}, \tag{12}$$

where ε_b is the background dielectric constant for frequencies well above the transverse phonon frequency ω_{TO} and the (screened) plasma frequency ω_{pl}^0 given by

$$\omega_{pl}^0 = \left(\frac{e^2 n_p}{\mu \varepsilon_0 \varepsilon_b}\right)^{1/2}, \quad n = p = n_p \tag{13}$$

with the reduced mass $\mu = \frac{m_e m_h}{m_e + m_h}$. This dielectric function is just a linear superposition of the contributions from the optical phonons and the plasmons. The transverse and longitudinal energies of the resulting quasiparticles are just given by the singularities and zeros of $\epsilon(\omega)$. In the density range around $n_p \simeq 2.7 \times 10^{18}$ cm^{-3} $\hbar\omega_{pl}^0$ and $\hbar\omega_{\mathrm{TO}}$ are equal, therefore the interacting system of optical phonons and plasmons results in a new quasiparticle, the plasmon-phonon mixed state. For more details see Ref. 14, and references therein.

This emission process has a certain analogy to the exciton-*m* LO process discussed in Sec. II with the differences that the carrier pair is not necessarily bound in an exciton and that the band gap is reduced to the spectral region of the exciton resonance at low densities. Presumably the coupling strength to plasmon-phonon mixed states is higher than to LO phonons only, because of the larger transversal-longitudinal splitting of the plasmons.

(ii) Recombination of an electron-hole pair under inelastic scattering of a free carrier, presumably an electron. This process has obviously a similarity to the inelastic exciton-electron scattering process again with the differences that the carrier pair is not necessarily bound and that the band gap is reduced as mentioned already above.

Now we discuss some selected experimental results with respect to the above ideas. Using Eqs. (9a)–(9g) for the evaluation of n_p for ns (Refs. 5, 6, 9, 13, 16, and 22) and ps (Refs. 7 and 8) excitation we find frequently that the densities reached at RT with values in the range from 4×10^{17} cm^{-3} to 2×10^{18} cm^{-3} are beyond the Mott density (7) but below the density for an inverted EHP according to (10). So neither an interpretation of stimulated emission or gain by simple *X*-*X* scattering is likely nor from direct recombination in an EHP. However, the two processes introduced above can explain the findings and even the scattering of the emission energies in Fig. 3 over a certain spectral range, because the energy of the plasmon and of the plasmon-phonon mixed state depend on n_p (12) and (13) as well as the position of the reduced gap. Due to lack of space we cannot discuss all results in detail and address only a few ones. The lower energy emission peak in Ref. 5 extrapolates beautifully the exciton-electron scattering from lower temperatures to 550 K. Due to the high temperature and densities we attribute it to the recombination of an electron-hole pair under inelastic scattering with a free electron. The interpretation put forward in Ref. 5 in terms of EHP recombination has in addition to the fact, that the EHP is not inverted, the problem that the reduced band gap must be below the emission maximum irrespective if the peak is due to stimulated emission, ASE or simply spontaneous recombination. As discussed in Appendix B this implies densities of the order of 3×10^{20} cm^{-3} which are far above the damage threshold for ns excitation. The higher energy peak in Ref. 5 cannot be attributed the *X*-*X* scattering because the exciton does no longer exist as a good quasiparticle in an EHP. It falls however in the range where an electron-hole pair in an EHP can emit a photon under simultaneous emission of one or two plasmon phonon mixed state quanta. The data in Refs. 10 and 11 deserve a special consideration because the densities deduced with (9) fall with values of 8×10^{16} cm^{-3} for $I_{\mathrm{exc}} = 24$ kW/cm^2 below the Mott density. Therefore one could still imagine an inelastic *X*-*X* scattering process, however, between substantially broadened exciton resonances. In contrast the stimulated emission from an EHP is unlikely at RT because inversion is not reached for $I_{\mathrm{exc}} = 60$ kW/cm^2. The stimulated emission in nanorods[13] is strongly influenced by the transverse and longitudinal mode patterns of the rods.[21,44] The stimulation peaks in Ref. 13 emerge at the peak of the spontaneous emission, again in the range around 3.22 eV (Fig. 3). The densities deduced with (9) are with 2×10^{17} cm^{-3} only slightly below the value of (7). Together with the large damping, excitonic processes claimed in Ref. 13 seem again to be less likely. We do not want to extend the discussion to ZnO QW in general, because there localization effects, an enhancement of the exciton binding energy and modification of the density of states and of the screening behavior come into play.[14] The data in Ref. 22 result, with similar arguments as in (9), in densities around 2×10^{19} cm^{-3} or 4×10^{12} cm^{-2} in each QW. Therefore EHP gain is possible up to RT. However, the band labelled EHP in Ref. 22 shifts with a temperature increase from 200 K to 300 K by 100 meV to the red, a value, which coincides perfectly with the data for inelastic scattering in Fig. 3.

We want to conclude the discussion with the two following aspects: The excitonic processes *X*-LO, *X*-*X* scattering and *X*-el scattering tend to coincide spectrally around 100 K (see Fig. 3 of Ref. 15). Consequently, even when one follows a peak from 5 K up to RT one cannot be completely sure

which band reappears above 100 K. Only the inelastic scattering with a free carrier that clearly falls below the range around 3.2 eV already at and even more beyond RT can be identified with high confidence. In the range around 3.2 eV, where some authors observe stimulated emission or ASE at RT, it is not possible to distinguish the various stimulation processes from their spectral position alone. Calculations of the density, of the BGR or of the chemical potential μ (11) and (12) are necessary for a clear identification. The other aspect concerns the question to what extend the experimental data may depend on the excitation conditions or on the "sample quality." The increasing damping of the exciton resonance, the screening of the exciton binding energy, and the band-gap renormalization are intrinsic processes which do not leave much room for the influence of excitation conditions and sample quality. The latter aspect may come into play for quantum wells, alloys or otherwise disordered samples, because in these conditions localized tail states appear, which show strongly reduced many particle effects[14] and since screening depends on the quasidimensionality of the system. Therefore we excluded quantum wells and dots from our discussion. For nanorods the above statements remain essentially true, because the typical diameters of the rods (30 to 300 μm) do not involve any lateral quantization effects, but the phase space for the emitted luminescence or more precisely for the photonlike exciton polaritons in the outgoing channel is significantly reduced by the transverse and longitudinal mode pattern of the waveguidelike nanorods.[21,44]

V. CONCLUSION AND OUTLOOK

The excitonic (and biexcitonic) recombination processes and the stimulated emission based on them in analogy to a four level laser system are good candidates to explain lasing in ZnO preferentially at temperatures below RT (up to about 200 K) and moderate densities well below n_M. The stimulated direct recombination in an EHP works only at densities above the effective density of states, where inversion is reached. In between process have to be considered in which electron-hole pairs recombine, which are still Coulomb correlated and which scatter with either a free carrier in the recombination process or emit one or more plasmon-phonon mixed state quanta. This interpretation based on simple formula and intuitive arguments for ZnO is considered as a challenge for theory to verify or falsify these ideas using advanced many-particle theories e.g. along the lines given in Refs. 41 and 42.

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APPENDIX A

The transition from an exciton gas to an electron-hole plasma occurs, according to the ideas developed in the 1970s and 1980s[14,18] of the last century, in the following way. With increasing electron-hole pair density n_p the band-gap decreases monotonously due to exchange and correlation effects. Simultaneously the Coulomb interaction between a single electron and hole, which is responsible for the formation of an exciton is screened, resulting in a decrease of the exciton binding energy $E_X^b(n_p,T)$. Both effects tend to compensate each other, so that the absolute energy position of the exciton is hardly influenced by the increasing carrier density, only its damping increases. This allows to formulate the criterion for the Mott density as

$$E_g(n_p=0,T) - E_g'(n_M,T) = E_X^b(n_p=0). \tag{A1}$$

According to the above arguments this condition is equivalent to

$$E_X^b(n_M,T) = 0. \tag{A2}$$

This condition is fulfilled in three dimensions if the inverse screening length l_s of the screened electron-hole Coulomb potential

$$V(r_{eh}) = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{-e^2}{|\vec{r}_e-\vec{r}_h|}e^{-|\vec{r}_e-\vec{r}_h|/l_s} \tag{A3}$$

fulfills the condition

$$a_B l_S^{-1} = 1.19. \tag{A4}$$

Though this approach looks rather straightforward, there are many different formulas available in the literature, which give very different values of n_M. We give here a short review and values for ZnO and arrive at the end of this appendix at, what we believe, reliable data. Equation (A5) is frequently used as a rule of thumb,[14,45]

$$n_M a_B^3 = 1. \tag{A5}$$

Actually, it strongly overestimates n_M, i.e., it gives too high values. For ZnO with a_B=1.8 nm (Ref. 33) it results in

$$n_M^{\mathrm{ZnO}} = \frac{1}{(a_B^{\mathrm{ZnO}})^3} = 1.7\times 10^{20}\ \mathrm{cm}^{-3},$$

a value about two orders of magnitude too high. Using (A5) for Si would result with a_B^{Si}=4.3 nm in n_M^{Si}=1.25 $\times 10^{19}$ cm^{-3} in contrast to clear phase diagrams (e.g., in Ref. 14) of an electron-hole liquid already at 3×10^{18} cm^{-3}.

In the Debye-Hückel screening approach, which is valid for distinguishable particles following Boltzmann statistics one finds[14]

$$n_M^{\mathrm{DH}} = (1.19)^2\frac{k_B T}{2a_B^3 E_X^b}. \tag{A6}$$

The numerial prefactor changes slightly from author to author but is always slightly larger than unity. For ZnO at RT this yields

$$n_M^{\mathrm{ZnO}} \approx 5.5 \times 10^{19}\ \mathrm{cm}^{-3}. \tag{A7}$$

Such a value has been used as an argument for excitonic lasing.[6] Unfortunately electron and hole in an EHP do not fulfill the assumption for (A6). Furthermore this equation gives both in the high and in the low temperature limits nonphysical results:

$$\lim_{T\to 0} n_M^{\mathrm{DH}} = 0 \quad \text{and} \quad \lim_{T\to\infty} n_M^{DH} = \infty, \tag{A8}$$

so it is not obvious why the formula should hold at RT. The formula using the Thomas-Fermi screening length results in[14]

$$n_M^{\mathrm{ThF}} = (1.19)^6 a_B^{-6} (3\pi^2)^2 \left(\frac{\varepsilon\varepsilon_0 \hbar^2}{3e^2} \frac{1}{m_e + m_h} \right)^3. \tag{A9}$$

Sometimes a factor 4π appears in the denominator. This formula gives for ZnO,

$$n_M^{\mathrm{ThF}} = 9.3 \times 10^{16}\ \mathrm{cm}^{-3}. \tag{A10}$$

Now clearly underestimating the true value since this density leads to an average distance between excitons

$$d = (n_M^{\mathrm{ThF}})^{-1/3} = 22\ \mathrm{nm} \tag{A11}$$

which is much larger than a_B, so that there should be not too much of interaction except for scattering processes treated in Sec. III. A relatively reliable formula for the band gap reduction $\Delta E_g(n_p, T)$,

$$\Delta E_g(n_p, T) = E_g(n_p = 0, T) - E_g'(n_p, T) \tag{A12}$$

has been introduced in Ref. 46 and refined in Ref. 47 resulting in a weak temperature dependence. It has been verified for the more covalent group IV and III-V compounds experimentally.[14] The more ionic II-VI compounds tend to show slightly larger values of ΔE_g, see Fig. 21.2 in Ref. 14. In these calculations the density n_p is expressed or normalized via

$$r_s = \left(\frac{4\pi a_B^3}{3} n_p \right)^{-1/3}. \tag{A13}$$

The criteria (A1) and (A2) and the inspection of Fig. 21.2 in Ref. 14 results in

$$r_s = \left(\frac{4\pi a_B^3}{3} n_M \right)^{-1/3} \approx 5. \tag{A14}$$

This yields for ZnO

$$n_M^{\mathrm{ZnO}} \approx 3 \times 10^{17}\ \mathrm{cm}^{-3}. \tag{A15}$$

This is a realistic value. A similar value has been obtained for ZnO by Ref. 48 using the Saha equation. In Ref. 31 values of the EHP densities in ZnO have been deduced from experimental gain spectra starting from $6 \times 10^{17}\ \mathrm{cm}^{-3}$ though using in a line shape fit the recombination without $\vec{k}$ conservation, which was the standard model at that time. Using $\vec{k}$ conservation and final state damping or Fermi-sea shake up[14] would result in slightly smaller but similar values.

APPENDIX B

At low temperatures one has observed[31] in ZnO values of $\Delta E_g(n_p, T \approx 0)$ from about 85 meV corresponding to $1.4E_X^b$ at $n_p = 5 \times 10^{17}\ \mathrm{cm}^{-3}$ up to 210 meV corresponding to $3.5E_X^b$ for $n_p \approx 10^{19}\ \mathrm{cm}^{-3}$.[21,31] In Ref. 5 stimulated emission due to recombination in an EHP at 550 K is claimed at 2.9 eV (see Fig. 3 above). Even if it was just ASE or spontaneous emission the reduced gap must be situated at even lower energies. A conservative guess gives $E_g'(n_p, 550\ \mathrm{K}) \approx 2.85$ eV or approximately $6.8E_X^b$ below the gap. With Fig. 21.2 of Ref. 14 this would result in $r_s \lesssim 0.5$ or $n_p = 3 \times 10^{20}\ \mathrm{cm}^{-3}$. It is impossible that stimulated emission due to excitonic processes can coexist at this value, because the density is orders of magnitude higher than the Mott density. An excitation intensity I_{exc} necessary to reach such high values of n_p is beyond the damage threshold for ns pulses. On the other hand, a degenerate EHP at 550 K would result with (11) in $n_p = 2.5 \times 10^{19}\ \mathrm{cm}^{-3}$. This value is experimentally feasible but not compatible with the band-gap renormalization of about 400 meV.

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