Carrier density driven lasing dynamics in ZnO nanowires

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Abstract
We report on the temporal lasing dynamics of high quality ZnO nanowires using the time-resolved micro-photoluminescence technique. The temperature dependence of the lasing characteristics and of the corresponding decay constants demonstrate the formation of an electron–hole plasma to be the underlying gain mechanism in the considered temperature range from 10 K to 300 K. We found that the temperature-dependent emission onset-time \( t_{on} \) strongly depends on the excitation power and becomes smallest in the lasing regime, with values below 5 ps. Furthermore, the observed red shift of the dominating lasing modes in time is qualitatively discussed in terms of the carrier density induced change of the refractive index dispersion after the excitation laser pulse. This theory is supported by extending an existing model for the calculation of the carrier density dependent complex refractive index for different temperatures. This model coincides with the experimental observations and reliably describes the evolution of the refractive index after the excitation laser pulse.

Keywords: ZnO, nanowires, laser emission, refractive index, ultrafast dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

Micro- and nanostructures are promising building blocks for the fabrication of compact integrated circuits [1], e.g. to enhance the spatial resolution of sensors and for imaging applications [2, 3]. Furthermore, they can be grown using a bottom-up approach, which avoids complicated structuring process steps but guarantees single crystal quality and optimal optical performance [4]. Semiconductor micro- and nanowires are therefore of special interest, since their electrical properties can be modified over a wide range during the growth process [5–7]. Furthermore, in the case of optical applications these structures naturally provide all necessities for a laser system: under high excitation the semiconductor material acts as an active medium and the Fabry–Pérot type resonator geometry is provided by the end facets of the nanowire. Although the optical properties of zinc oxide (ZnO) micro- and nanowires have been intensively investigated in the past years [8–10], the laser dynamics in terms of the temporal dependence of the underlying gain profile, as well as the switch-on characteristics of the nanowire itself have not yet been investigated in detail over a large temperature range. Recently it has been demonstrated, using the double-pumped time-correlated photoluminescence (PL) technique, that the switch-on time of semiconductor nanowires is below 5 ps with lowest values of around ~1 ps for ZnO [11, 12]. The aim of this work is to study the laser dynamics of highly excited ZnO nanowire emitters in a temperature range from 10 K to 300 K using a time-resolved PL technique. The emission onset-time will be studied in a wide temperature range depending on the excitation power. Furthermore, we observed, in various lasing experiments, a spectral red shift of the propagating Fabry–Pérot modes (FPM) in time after the maximal emission intensity. This effect is only accessible due to the Fabry–Pérot type morphology of nanowires and enables the investigation of the time-dependent complex refractive index in nanowires. Therefore, we extended an
existing model for the calculation of the carrier density dependent refractive index and correlated these simulations to our time-resolved measurements.

2. Experimental methods

ZnO nanowires were synthesized by a chemical vapor deposition (CVD) process using the vapor–liquid–solid (VLS) mechanism [13]. A mixture of ZnO- and carbon powder (molar ratio of 1:1) was evaporated in a horizontal tube furnace at 1050 °C and transported by a mixture of Ar and O₂ gases towards the silicon substrate, which was previously coated with a 200 nm thick ZnO seed layer. The pressure and growth time were set to 120 mbar and 30 min. Single crystalline nanowires grow with diameters in the range of (100–400) nm and lengths up to 50 μm. Single nanowires were then transferred onto a clean SiO₂/Si substrate by the dry imprint technique for subsequent μ-PL measurements. The thermally grown low refractive index SiO₂ layer (thickness of 1.5 μm) ensures strong optical mode confinement in the nanowire waveguide. Thus, leakage of the electromagnetic field and hence the energy dissipation out of the nanowire optical cavity into the substrate is avoided [14]. The nanowire sample was mounted in a liquid helium flow cryostat with integrated heating unit enabling investigations in the temperature range from 10 K to 300 K. A frequency doubled Ti:Sapphire laser ($\lambda_{\text{ex}} = 355$ nm, $t_{\text{pulse}} = 2$ ps, $\tau_{\text{rep}} = 76$ MHz) was focused by a 50× NUV microscope objective (NA = 0.4) to a spot size of around 50 μm² for the non-resonant and full-area excitation of single nanowires. A variable attenuator was used to adjust the excitation power. The luminescence light was collected by the same objective and detected by a Peltier-cooled, back-illuminated charge coupled device (CCD) camera to reach a spectral resolution of ~500 μeV. The other beam was dispersed by a spectrometer (320 mm focal length, 2400 grooves/mm grating) and detected by a Peltier-cooled, back-illuminated charge coupled device (CCD) camera to reach a spectral resolution of ~5 ps. The laser power was measured using a Si diode power meter.

3. Results and discussion

Figure 1(a) depicts a scanning electron microscope image of a slightly tapered ZnO nanowire with a diameter ranging from 165–190 nm and a length of $L = 7.9 \mu$m. All of the experimental results presented in this work originate from this single ZnO nanowire. Note that comparable ZnO nanowires exhibit similar optical properties.

3.1. Time-integrated lasing from 10 K to 300 K

Figure 1(b) shows the emission spectra obtained from a single facet of the ZnO nanowire for several excitation powers at 300 K. With increasing excitation power, the broad spontaneous, excitonic emission out of the entire wire volume transforms into emission spectra dominated by stimulated emission from distinct FPM, whose energy is approximated by $E_{\text{Mode}} = (\hbar c N)/(2L n)$, with $N$ being the modenumber of the FPM, $L = 7.9 \mu$m the resonator length and $n$ the carrier density dependent refractive index. At the lasing threshold, the refractive index has a value of $n \sim 2.35$. The precise correlation between the refractive index and the carrier density is discussed below in detail. Furthermore, the main PL emission exhibits an overall spectral red shift and a mode enhancement on its low energy side with increasing excitation power [15]. This is caused by the formation of an electron–hole plasma (EHP) being the underlying gain process in our nano-laser system at 300 K. The laser threshold power $P_{\text{th}} \sim 240 \text{ kW cm}^{-2}$ was obtained by modeling the excitation power dependent integrated PL intensity with a multimodal laser approach [16] (red line in figure 1(c)). The evolution of $P_{\text{th}}$ in the considered temperature range from 10 K to 300 K is shown in figure 1(d). With increasing temperature $P_{\text{th}}$ increases exponentially according to $P_{\text{th}}(T) = P_{\text{th}} (0 \text{ K}) + A \exp(T/T_0)$, with $P_{\text{th}} (0 \text{ K}) = (2 \pm 1) \text{ kW cm}^{-2}$, $A = (7.6 \pm 1.2) \text{ kW cm}^{-2}$ and a characteristic temperature $T_0 = (86 \pm 4) \text{ K}$. These values are in agreement with the literature [17]. The temperature $T_0$ is characteristic for temperature-correlated losses in the nanolaser system like the carrier redistribution in k-space due to the change of the Fermi distribution. Thus, high values of $T_0$ imply that the threshold power of the device increases less rapidly with increasing temperature and the laser device is thermally more stable. Figure 1(e) depicts temperature-dependent PL spectra at corresponding $P_{\text{th}}$, exhibiting an overall red shift of the band gap energy, a continuous broadening of the underlying gain profile [15] and a broadening of the FPM with increasing temperature. The large broadening of the dominating FPM at elevated temperatures (see especially the spectra at 250 K in figure 1(e)) is correlated to their energetic shift in the first picoseconds after the excitation pulse, as we will show below.

3.2. Time-resolved lasing from 10 K to 300 K

Time-resolved μ-PL measurements were performed in order to investigate the temporal dynamics of the nano-laser system. Figures 2(a)–(c) show exemplary time-resolved images of the ZnO nanowire emission in false color for different excitation powers at 300 K. The broad spontaneous emission (see figure 2(a) and the black curve in figure 1(b)) exhibits an effective radiative decay time of approximately $\tau_r = (150 \pm 15) \text{ ps}$ (see figure 2(d)). This is a typical value for the average recombination lifetime of unscreened excitons in ZnO [18]. Due to the higher generation rate of electron–hole pairs at elevated excitation powers, exciton scattering becomes more favorable. This leads to lower exciton lifetimes and thus to a faster radiative decay time. At further elevated excitation powers another very fast scattering process becomes important, dominating the radiative decay above $P_{\text{th}}$, see figure 2(c). This very fast recombination process originates from the high scattering rates.
between highly screened electrons and holes in an electron–hole plasma (EHP). Overcoming the Mott density, the exciton binding energy becomes more and more reduced and a fermionic treatment of the available charge carriers is necessary. Figure 2(d) depicts the transients of the PL decay below (red), at (brown) and above (black) the laser threshold $P_{th}$ demonstrating the transition from excitonic emission with a decay constant of $\tau_1 = (150 \pm 15)$ ps to a fast decay triggered by an EHP at high excitation densities ($\tau_2 \lesssim 5$ ps). The biexponential model of the decaying PL emission at $P_{th}$ demonstrates that the very fast decay ($\tau_1 \lesssim 5$ ps) changes to a slower decay of screened excitons with a time constant of $\tau_2 = (120 \pm 7)$ ps after the first picoseconds in which the laser pulse is emitted. This demonstrates the proceeding recombination of carriers and the corresponding relaxation of the residual carrier density in time also after the coherent laser
emission. Hence, within some picoseconds the carrier density approaches the Mott density and consequently falls below it. Thus, subsequently the PL decay is characterized by excitonic recombination, see figure 2(d).

3.3. Observations from time-resolved experiments

The evaluation of a comprehensive series of time-resolved PL measurements in the temperature range from 10 K to 300 K (figure 3 shows the exemplary time-resolved PL images at 200 K and 10 K) led to three main observations.

1. The decay constants, $\gamma_1 \leq 5$ ps and $\gamma_2 = (75 - 150)$ ps do not change significantly as function of temperature, see figure 4(a). Hence, the originating gain mechanism remains over the investigated temperature range. A changing gain mechanism would be accompanied by a significant modification of the main decay time $\gamma_1$ and a change of the temperature dependence of the threshold power $P_{th}$ (figure 1(d)) would be expected. Neither was observed in our studies. Hence, carrier scattering in an EHP is shown to be the underlying gain process in the ZnO nanowires investigated in this study from 300 K to 10 K.

2. The emission onset-time, $t_{on}$ is obtained as the time difference between the built-up of the PL intensity to $1/e$ of its maximum and the temporal maximum of the impinging excitation laser beam. It exhibits a strong dependence on the excitation power as well as on the sample temperature. Figure 4(b) shows the inverse emission onset-time $t_{on}^{-1}$ as a function of the excitation power for different temperatures in a double logarithmic plot.

By increasing the excitation power, $t_{on}^{-1}$ increases for all measured temperatures. Thus, the emission sets in faster with increasing excitation power. Far below the laser threshold power ($P \lesssim 0.05 P_{th}$) no significant change of $t_{on}^{-1}$ is observable, which can be attributed to an inefficient scattering of the excited carriers into the lowest energy states. For a further increase of the excitation power an increase of $t_{on}^{-1}$ can be observed which can be described by a power law ($t_{on} \propto p^{b(T)}$). The exponent $b$ occupies two excitation regimes; within the intermediate regime ($0.05 P_{th} \lesssim P \lesssim 0.5 P_{th}$), $b$ is smaller than 1 and depends on the temperature (see figure 4(c)), following the same temperature dependence as the exciton lifetime, i.e.

$$b(T) \sim (\Gamma_0 + \beta_{ph} T + \beta_{LO}(e^{E_{LO}/kBT} - 1)^{-1})$$

with $\Gamma_0$, $\beta_{ph}$, $\beta_{LO}$ and $E_{LO}$ being the inhomogeneous broadening, the exciton–phonon interaction coupling strength, the exciton–LO–phonon interaction strength and the phonon energy, respectively [19]. This relationship between the exponent $b$ and the lifetime indicates a slow relaxation of the excited hot carriers into the ground state so that the carrier relaxation time is larger than the exciton lifetime. Therefore, we can assume that the exciton–phonon scattering is the dominant process even in this intermediate excitation regime. The situation changes for excitation powers $P > 0.5 P_{th}$, when the carrier density approaches the Mott density. In this regime, the exponent $b$ changes to a fixed value of $b = 2$, which can be attributed to exciton–exciton and exciton–carrier scattering as the dominant relaxation processes in this excitation range [20], accompanied by a strong reduction of the relaxation time. This is also supported by the fact that the slope of $t_{on}^{-1}$ with increasing excitation power in this range is independent of the temperature and therefore independent of the lifetime of the excitons. The dashed vertical line in figure 4(b) marks the inverse emission onset-time at the respective threshold power being in the range of $t_{on}^{-1} \approx (0.2 – 0.8)$ ps$^{-1}$. In the laser regime, the corresponding values for $t_{on} \sim (1.3 – 5)$ ps are limited by the temporal resolution of our setup. Hence, the EHP regime, where carrier–carrier and carrier–phonon scattering are the dominating processes and even shorter onset-times are expected, could not be investigated in this study. For the spontaneous emission, we revealed emission onset-times in the range of $t_{on} = 30$ ps.

3. Mode shift. The FPMs exhibit a nonlinear spectral red shift in time, whose absolute value increases with increasing temperature from 1 meV at 10 K up to 20 meV at 300 K, see figure 4(d). This modal shift was extracted from the time-resolved PL spectra (e.g. figure 2(b)) in the first 100 ps after the excitation pulse at threshold power. Each data point in figure 4(d) represents the red shift of a FPM with a corresponding initial energy evaluated at the time $t_{on}$. In general, the mode shift is described by the temporal change of the refractive index dispersion after the optical excitation. Versteegh et al simulated the carrier density dependent dielectric function at room temperature solving the Bethe–Salpeter ladder equation with a matrix inversion method [22, 23], including a phenomenological excitonic contribution to the overall carrier density. However, the maximal excitonic fraction of $\sim 14\%$ at room temperature leads to a small absolute variation of the resulting refractive index of at most $\sim 0.3\%$. Since the treatment of the excitonic contribution in ZnO in that way is questionable and not trivially adaptable to low temperatures, we decided to disregard the excitonic contribution to the overall carrier density in our simulations, being aware that this is a rough approximation calculating the carrier density dependent refractive index. Particularly at lower temperatures, the excitonic contribution may play an important role in the intermediate excitation regime. The
correlating effects on the refractive index are not considered in this work. Our model parameters were chosen in such a way that the calculated data reproduce temperature-dependent ellipsometry data [21] in the low carrier density case (< 10^16 cm^-3). Subsequently, they were held constant for higher carrier densities. Due to a higher value of k_{max}, which is necessary for the convergence of the calculated susceptibility, our parameters differ slightly from those in [22], with k_{max} = 7 × 10^9 m^-1, d_v = 3.2 × 10^{20} cm^-3 and \chi_L = 0.8. Our simulations display a significant decrease of the Mott density n_{Mott} from around 5 × 10^{18} cm^-3 at 300 K, 3 × 10^{18} cm^-3 at 200 K to around 2 × 10^{17} cm^-3 at 25 K, which is in good agreement with the model in [24], based on the description of the electron–hole gas applying Boltzmann statistics. However, due to the disregard of the excitonic contribution to the screening process, the calculated values of n_{Mott} must be treated with caution, especially at low temperatures. Furthermore, because of the uncertainty of the excitonic contribution, we avoided temperatures lower than 200 K for the calculation of the refractive index. Compared to a nearly negligible excitonic fraction of ~14% at 300 K, it already becomes important at 200 K (~32%) and non-negligible at 100 K (~87%).

Figures 5(a) and (b) depict the simulated refractive index n as well as the extinction coefficient k at 300 K and 200 K for different carrier densities. Below the Mott density, the excitonic resonance vanishes with increasing carrier density. The extinction coefficient decreases continuously with increasing carrier density and becomes negative in a certain energy range for carrier concentrations above the Mott density indicating optical gain. The marked gray areas in figure 5 indicate the energy range where lasing modes were observed in our experiment. Although the gain profile broadens almost homogeneously, only modes on the low energy side of the gain profile are observed in the experiment. Due to the Gaussian spatial profile of the laser pulse, the nanowire is not homogeneously excited. This may lead to low excited and thus absorbing areas at the nanowire facets causing the absorption of the modes at higher energies.

Using these simulations, the experimentally observed mode shift in time after a high optical excitation can be described quite well. The upper graph in figure 5(c) depicts the decay of the carrier density over time for lasing modes at 300 K (black) and 200 K (red). The corresponding decay times (\tau_1 = 4 ps, \tau_2 = 115 ps at 300 K and \tau_1 = 8 ps, \tau_2 = 105 ps at 200 K) and amplitudes were taken from associated PL transients. We calculated the time-dependent refractive index within the nanowires by fulfilling the mode condition. Furthermore we considered that the nanowire was not excited homogeneously over its entire length because of the Gaussian spatial profile of the laser pulse. For our calculations we chose an excited length of 4 \mu m. The middle graph in figure 5(c) shows that our model (solid lines) describes the experimentally observed temporal mode shift (dashed lines) quite well for 200 K and 300 K. Our model exhibits only small deviations in the first picoseconds after excitation. In the considered time range of 100 ps the calculated refractive index exhibits a continuous increase (see lower graph in figure 5(c)), whereas the absolute increase of the refractive index at 200 K is larger compared to that at 300 K. This can be explained by our simulations quite well. At low temperatures, strong dispersion causes a strong change of the refractive index when the carrier density decreases. In this case the mode condition can only be fulfilled in a narrow spectral range resulting in a weakly pronounced mode shift. However, at room temperature the broadening of the exciton resonance causes a weaker change of the refractive index but
in a wider spectral range. Thus, the experimentally observed stronger mode shift at higher temperatures can be very well described by our model.

Furthermore, we observed at 300 K that modes closer to the exciton energy exhibit a stronger red shift in time than low energy modes, see figure 4(d). This is caused by the recovery of the strong spectral dispersion of the refractive index slightly below the exciton energy right after the laser pulse, as can be seen in figure 5(a). Considering the three dominant modes at room temperature (N = 99–101), we confirmed with our model that the change of refractive index is larger for higher mode energies (Δn100 ≈ 2.6%) than for lower mode energies (Δn99 ≈ 2.2%, not shown here). At 200 K, our model predicts a stronger change of the refractive index as well as an enhanced effect in the proximity of the exciton resonance. Considering three modes around 3.29 eV, we found Δn ≈ 6.6%–7.2%. At lower temperatures i.e. 100 K, the modal red shift is close to the systematic error of the measurement (0.03 meV ps⁻¹), hence an energy difference for different modes cannot be resolved with our streak setup.

As mentioned above, the FWHM of the FPM in time-integrated μ-PL spectra increases at elevated temperatures (see figure 1(e)), which is now agreeably explained by the time-resolved dynamics, revealing a large mode shift. At low temperatures the mode shift is negligible, hence the modes appear narrow in the time-integrated spectra. At higher temperatures the mode shift becomes stronger and the modes appear broader. Thus, an evaluation of nanowire Q-values by time-integrated spectra is revealed to be rather inaccurate.

4. Conclusion

In temperature-dependent lasing experiments on a single ZnO nanowire, the laser action was found to be stable up to room temperature, whereas the threshold power $P_\text{th}$ exhibits an exponential dependence on the system temperature with a large characteristic temperature $T_0 = (86 \pm 4)$ K. Time-resolved PL measurements revealed two characteristic decay constants $\tau_1 \approx 5$ ps and $\tau_2 \approx 75 \pm 150$ ps, caused by the decay of an electron–hole plasma during the output pulse followed by the excitonic recombination, respectively. A very fast emission onset-time in the lasing regime of $t_\text{on} \approx 1$ ps, below the resolution limit of the used system, was found over the entire temperature range. The experimentally observed temporal red shift of the resonator modes was described by the carrier density driven change of the refractive index in time. Therefore, we extended an existing model for the calculation of the carrier density dependent complex refractive index for different temperatures. By merging the decay parameters (decay constants and amplitudes) from time-resolved PL experiments with our model and fulfilling the mode condition in the nano-resonator, we calculated the time-dependent refractive index after the excitation laser pulse.
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