Ultrafast dynamics of hot charge carriers in an oxide semiconductor probed by femtosecond spectroscopic ellipsometry

Steffen Richter*,1,2,a, Oliver Herrfurth2,a, Shirly Espinoza1, Mateusz Rebarz1, Miroslav Kloz1, Joshua A. Leveillee3, André Schleife1,3, Stefan Zollner4,5, Marius Grundmann2, Jakob Andreasson1,6, Rüdiger Schmidt-Grund2

1 ELI Beamlines/Fyzikální ústav AV ČR, v.v.i., Za Radnicí 835, 25241 Dolní Břežany, Czech Republic
2 Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik, Linnéstr. 5, 04103 Leipzig, Germany
3 University of Illinois, Dep. of Materials Science and Engineering, 1304 W. Green St., Urbana, IL 61801, USA
4 New Mexico State University, Department of Physics, PO Box 30001, Las Cruces, NM, 88003-8001, USA
5 Fyzikální ústav AV ČR, v.v.i., Sekce optiky, Na Slovance 2, 18221 Praha, Czech Republic
6 Chalmers tekniska högskola, Institutionen för fysik, Kemigården 1, 41296 Göteborg, Sweden

*steffen.richter@eli-beams.eu †schleife@illinois.edu a These authors contributed equally.

Feb 2019

Many concurrent processes occur in highly photoexcited semiconductors, such as interband and intraband absorption, scattering of electrons and holes by the heated lattice, Pauli blocking, bandgap renormalization and formation of Mahan excitons. We disentangle their contributions and dynamics with broadband pump-probe ellipsometry, performed on a ZnO thin film. We directly obtain the real and imaginary parts of the transient dielectric function and compare them with first-principles simulations. The interband and excitonic absorption are partially blocked and screened by the hot-electron occupation of the conduction band and hole occupation of the valence band. Simultaneously, intra-valence-band transitions occur at sub-picosecond time scales after holes scatter to the edge of the Brillouin zone. Our time-resolved ellipsometry experiments with intense UV excitation pave new ways to understanding non-equilibrium charge-carrier dynamics in materials by distinguishing between changes in absorption coefficient and refractive index, thereby separating competing processes. This information will help to overcome the limitations of materials for high-power optical devices that operate in the ultrafast regime.

Many-body systems under non-equilibrium conditions, caused for instance by photo-excitation, still challenge the limits of our understanding at microscopic length and ultrashort time scales [1, 2, 3]. Accessing and controlling emergent states experimentally constitutes one of the most exciting frontiers of contemporary research in materials [4]. In addition to advancing fundamental understanding of exotic quantum states, e.g., involving large densities of free charge-carriers [5], such many-body systems can provide technological breakthroughs for novel applications including high-speed optical switching [6, 7] and computing [8, 9], fast transparent electronics [10, 11], light harvesting [12], or even new means of propulsion of space crafts [13]. The implementation of such next-generation devices requires development of techniques to probe transient states of matter and control ultrafast dynamics of excited electronic systems in solids.

Despite tremendous promises, understanding of the coupling between fundamental electronic excitations and the lattice mostly remains vague, especially directly after strong excitation. Many experimental and theoretical studies have aimed to separate fundamental electron-electron and electron-phonon effects, as well as the role of defect states in solids [14]. As illustrated schematically in Fig. 1, not only the population of charge-carrier states (as probed in luminescence experiments) matters in the highly excited regime, but also the electronic structure. Therefore, the optically accessible states change rapidly, enabling or prohibiting certain absorption channels, but also changing other material properties like the index of refraction. This is especially significant for applications of transparent semiconductors like wide-gap oxides [15].

Experimentally, angular-resolved photo-electron spectroscopy is one of the most insightful probes for the dispersion of populated electronic states [16, 17]. Beyond this, optical spectroscopy accesses a convolution of joint density of states, electron and hole populations, and transition matrix elements via the complex, frequency-dependent dielectric function (DF). For excited systems, conventional transient spectroscopy has been performed at different spectral ranges [18, 19, 20, 21]; time-resolved sum-frequency
generation can be used to probe the dynamics of electronic transitions after excitation [22]. A challenge is not only to achieve high time-resolution but to discriminate different processes triggered by the excitation [13] [24]. One must understand the entire, i.e., spectral and complex-valued, response of an excited material. This requires obtaining both, amplitude and phase information, of a sample’s DF, as encoded in its complex reflection coefficient r.

Conventional transient spectroscopy yields only amplitudes and experimental data is often explained by changes in the extinction coefficient κ, neglecting changes of the refractive index n, a challenge for excitation spectroscopy that has already been discussed in the 80’s [24]. To compensate for the lack of phase information, restrictive model assumptions are required. An alternative is to combine measurements from different angles of incidence [25] [26] [27] or p- and s-polarizations [28] [29]. Even these methods are only a work-around but cannot directly obtain phase information. On the other hand, obtaining the full dielectric response from the time domain is only possible in the THz regime but not for higher optical frequencies [30].

In ellipsometry, the angles Ψ and Δ offer relative, frequency-dependent amplitude and phase information on the physical response, \( r_p/r_s = \tan(\Psi)e^{i\Delta} \) (where indices refer to p- and s-polarizations). This provides simultaneous access to the real and imaginary part of the DF \( \varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + i\kappa)^2 \). Earlier ellipsometric pump-probe experiments suffered from experimental challenges, such as changing positions of the probe spot on the sample or stability issues with the laser, or were performed only at single wavelengths [31] [32] [33] [34] [35] [36]. Time-resolved single-wavelength ellipsometry has also been reported in imaging mode [37] [38] [39].

In this article, we present transient DF spectra of highly photo-excited ZnO with femtosecond time-resolution. These spectra yield information on the ultrafast dynamics of electron-electron and electron-phonon processes in this prototype oxide semiconductor. With its wide bandgap and excitons stable at room temperature, ZnO is an ideal testbed. Due to its strong polarity, strong electron-phonon coupling impacts the exciton dynamics. Our improved ellipsometric approach gives access the time-dependent DF of the ZnO film after excitation with about 100 fs time resolution. These results are compared to first-principles simulations. We separate Pauli blocking of absorption channels from bandgap renormalization (BGR) induced by increased screening of the electron-electron interaction by photo-excited electrons and holes. From our analysis we report direct observation of intra-valence-band (IVB) absorption in a spectral range that is normally transparent in ZnO.

### Experimental Data

The experiments were performed on a ZnO thin film, pumped by 266 nm, 35 fs laser pulses that created an electron-hole pair density of 10^{20} cm^{-3}. Supercontinuum white-light pulses were used as a probe. The transient ellipsometric angles Ψ and Δ obtained in the spectral range 2.0-3.6 eV are shown in Fig. 2. Data were recorded up to 2 ns with increasing delay steps but the strongest response occurs on time-scales shorter than 0.5 ps. The pump-induced effect on the excitonic transitions around 3.3 eV causes a sudden decrease in Ψ and an increase in Δ.

From the ellipsometric spectra, we obtain the DF of the ZnO film for every pump-probe delay Δt. Figure 3 illustrates the resulting DF \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) at selected delays. At negative Δt, the obtained DF coincides with the one obtained in standard ellipsometry. The peak around 3.35 eV comprises the excitonic transitions (X), the peak around 3.42 eV is associated with exciton-phonon complexes (EPC) [10]. There exist also further complexes at slightly higher energy.

For small positive Δt, the absorption at the band edge and above is strongly damped, as indicated by

![Figure 1: Hot charge carriers after strong excitation of ZnO with a UV pump pulse: a, b. Within a few 100 fs after excitation (violet arrows), scattering between charge carriers results in the conduction band being occupied by excited electrons (filled circles), the valence band by holes (open circles) (a). The thermal distribution (Fermi-Dirac statistics) of the excited electrons (black) and holes (red) corresponds to effective temperatures \( T_e, T_h \) of a few 1000 K (b). The quasi-Fermi-energies (dashed lines) are shifted into the bandgap due to the high temperatures. c, d. Within the first picoseconds, scattering between charge carriers and phonons as well as recombination yield cooling and reduction of the density of excited electrons and holes. Still, charge-carrier temperatures are larger than the lattice temperature \( T_l \). Black arrows in a and c mark selected optical transitions which are dynamically blocked (band-band transitions) or enabled (intra-valence-band transitions).](image)
Figure 2: Time-resolved ellipsometry data: Ellipsometric angles \( \Psi \) (amplitude ratio) and \( \Delta \) (phase difference) of the ZnO thin film after non-resonant UV pump measured at 60° angle of incidence. Increases relative to the initial spectra before excitation (black) are shown in blue, decreases in red. The sketch at the top illustrates the meaning of the ellipsometric parameters.

As Fig. 4c indicates, after an immediate redshift of the exciton by roughly 20 meV the energies increase with a linear rate of approx. 3 meV/ps during the first 4 ps (red symbols in Fig. 4c). The EPC follows the trend with even larger increase but without the initial redshift. Another later redshift of both yields an energy minimum at 100 ps. At 2 ns, the absorption edge remains redshifted by approx. 20 meV. Furthermore, it should be noted that the energetic difference between the exciton and EPC absorption peaks, which had initially increased by more than 30 meV, approaches its initial value (50 meV) monotonically until complete relaxation after several nanoseconds (Fig. 4c). Finally, our data shows that the spectral broadening of the exciton and EPC transitions is reduced as soon as the sample has been excited (\( \varepsilon_2 \) in Fig. 3). This reduced broadening remains approximately constant for at least 2 ns.

Separating Physical Processes

Charge carrier excitation by 266 nm (4.67 eV) laser pulses in ZnO involves optical transitions from the heavy-hole, light-hole and split-off valence-bands (VB) into the conduction band (CB) in the vicinity of the \( \Gamma \) point, as indicated by the violet arrows in Fig. 1a. The excited electrons carry excess energies of almost 1 eV, the excited holes almost 0.4 eV because of their larger effective mass. The initial occupation of electron and hole states due to the pump pulse is sharply peaked and non-thermal. It takes a few hundred femtoseconds until a Fermi-Dirac distribution is established as sketched in Fig. 1a and b. Estimated effective temperatures are reported in Table 1. The initial thermalization is provided mainly through carrier-carrier scattering, partially carrier-phonon scattering [14, 23, 41, 42, 43]. The immediate effect on the optical response spectra is three-fold: First, the occupation of the states leads to (partial) Pauli blocking (band filling) and hence the observed absorption bleaching of the band-to-band and excitonic transitions. The excitonic absorption enhancement is also reduced by free-carrier screening. The reduced refractive index in the visible spectral range results from the Kramers-Kronig relations. Second, due to the flatness of the valence bands, excited holes have enough excess energy to scatter towards the edge of the Brillouin zone (Fig. 1a) and thus promote IVB transitions which are observed as low-energy absorption. Third, the high density of photoexcited charge carriers yields BGR as seen by the redshift of the exciton energy. Additionally, the excited carriers screen a static electric field in the film that otherwise arises from Fermi-level pinning at the surface caused e.g. by donor-like oxygen vacancies [44]. While the steady-state broadening of the excitons is caused by the related band bending, the charge carriers reduce it. At large delay times, the vacancies are still passivated by trapped electrons at the surface thus keeping the excitonic peaks narrow. Deeply trapped holes can remain for microseconds [45].

Analysis of the transients yields insights into individ-
in the experiment by a slightly faster rise of the cause of their lower excess energy. This is observed unal dynamics: Charge-carrier thermalization is slightly change. ε as obtained from the maxima of the exciton transition (red) and exciton-phonon complex (blue) solution of absorption amplitude (Figure 4).

Figure 3: Dielectric function at selected delay times: Real (ε₁, inset) and imaginary (ε₂, parent figure) part of the DF of the ZnO thin film at pump-probe delays from -10 ps to 2000 ps.

Figure 4: Transient changes of absorption features: Evolution of absorption amplitude (a, b) and peak energy (c) of the exciton transition (red) and exciton-phonon complex (blue) as obtained from the maxima of ε₂. Black symbols in (a, b) depict the integrated value of ε₂ in the spectral range 2.0 eV to 3.1 eV for different delay intervals. The green symbols in (c) show the spectral difference between X and EPC which is related to an effective phonon energy E_{ph}. Its equilibrium value of about 50 meV is indicated by the dotted line. Solid lines indicate exponential processes with their time constants. (d): comparison of computed (red) and experimental (black) ε₂ at maximum change.

IVB absorption compared to the exciton bleaching (cf. Fig. 4a). The subsequent fast decay of the IVB absorption is a consequence of the hole occupation far from the Γ point. Hence, its 1/e decay time of 1 ps reflects mainly the hole cooling by scattering with phonons. This process is also more effective for holes than for electrons due to their higher effective mass.

A reduction of the number of excited charge carriers (mostly Auger and defect recombination) is expressed by the vanishing BGR within the first picoseconds (cf. exciton peak energy). The transient dynamics of the absorption bleaching is, however, governed by the decrease of electron and hole temperatures. They approach each other due to cooling by scattering with optical phonons, resulting in a situation as sketched in Fig. 5. A lattice temperature is not even well defined at this state. These hot phonons slow down the electron relaxation through phonon re-absorption by the charge carriers which is also more effective for holes than for electrons due to their higher effective mass. The electron-phonon (Froehlich) interaction is generally a fast process (≈0.5 ps) and very strong in the polar ZnO. However, the excess energy of the charge carriers yields an extraordinarily large population of LO phonon states and thus immediately a non-thermal phonon distribution, as sketched in Fig. 5. A lattice temperature is not even well defined at this state. These hot phonons slow down the electron relaxation through phonon re-absorption by the charge carriers which is also more effective for holes than for electrons due to their higher effective mass.
Table 1: Statistics of the electron, hole, and lattice subsystems: Immediately after charge-carrier thermalization following a pump laser pulse with 4.67 eV to excite $10^{20} \text{cm}^{-3}$ electron-hole pairs in the ZnO thin film. The increase of $T_f$ after complete equilibration is estimated to 50 K at most. See supplementary information for details.

| Subsystem | Temperature $T$ (K) | Quasi Fermi-energy $E_{Fq}$ (meV) |
|-----------|---------------------|----------------------------------|
| Electrons | $T_e = 7000$         | $E_{Fq} - E_{CB} < -660$ meV     |
| Holes     | $T_h = 2800$         | $E_{VB} - E_{Fq} < -260$ meV     |
| Lattice   | $T_l = 300$ K        |                                   |

several optical phonons with an effective phonon energy $E_{ph}$ on the order of 30 meV resulting in about 50 meV splitting [40]. The absorption and re-emission of many optical phonons by the crystal increases the interaction probability of (high-energy) optical phonons with excitons while (low-energy) acoustic phonons are effectively suppressed, i.e., $E_{ph}$ increases.

After more than 2 ps the charge carriers have cooled down and the non-thermal phonons have disappeared (see Fig. 5). In this picosecond regime, the recovery of the exciton and EPC absorption results from the reduction of the excited carrier density, mainly by nonradiative Auger recombination [48]. Its initial time constant is 3 ps. At later times with lower carrier densities, slower radiative electron-hole recombination is dominant. The overshooting of the exciton amplitude at later time is related to the reduced exciton broadening as discussed above. Equilibration with the lattice can be estimated to be accomplished approx. 100 ps after excitation when the exciton energy reaches another minimum that indicates the highest achieved lattice temperature and thus bandgap shrinkage [40]. Assuming a deposited energy density of 100 J/cm$^2$ by the pump pulse, a maximum temperature increase of 30-50 K can be expected. If transferred entirely to the lattice, this would correspond to a bandgap decrease of approx. 25-30 meV at most. This fits the experimental observation. The following slow (approx. 2 μeV/ps) heat dissipation lasts until at least 10 ns.

Discussion

We use first-principles electronic-structure calculations to explain the different effects near the band edge: Temperatures of electrons in the conduction and holes in the valence band are taken into account via Fermi-distributed occupation numbers in the absorption spectrum for non-interacting electron-hole pairs. Many-body perturbation theory, including additional screening and Pauli blocking due to the electrons and holes at 0 K, is used to describe excitonic effects. Comparison with the experimental data in Fig. 5 shows, that the observed reduction of the exciton absorption is much less than what is expected from the calculations. An increased number of free charge carriers is known to have two opposing effects on the band-edge absorption: While the exciton is screened and should shift toward higher energies due to a reduced binding energy, the bandgap shrinks due to renormalization. Both compensate each other in a good approximation, such that the absolute exciton energy remains constant [50, 51]. However, when surpassing the so called Mott transition, excitons should cease to exist, and BGR should take over. That can explain the initially observed redshift which has been observed earlier [27, 53, 54]. Nevertheless we find that the excitonic absorption peak does not vanish entirely at any time. That reflects the difference between an equilibrated system and hot charge carriers: In the case of doping ZnO by $10^{20}$ cm$^{-3}$ excess electrons, a Burstein-Moss blueshift of the absorption edge of more than 200 meV would be expected [55]. From density-functional-theory calculation, approximately 370 meV can be estimated. It is clear that this does not apply to a hot electron-hole plasma where no strong blueshift is observed [24, 53, 54]. While BGR does generally not depend on temperature [56], it should be slightly less efficient for hot charge carriers [52] resulting in an effectively higher Mott density. Hence the Mott transition might not be passed by the widely-distributed hot carriers although their density is well beyond the classical threshold [57]. According to [58], the fraction of carriers bound to excitons is rather small, not exceeding 15%. In this respect, the non-vanishing exciton absorption peaks could indicate only partial Pauli blocking, i.e., the ground-state occupation would never exceed the Mott density. Furthermore, electron-hole coupling has indeed been observed to sustain the Mott transition albeit usually largely screened and broadened [52, 59, 60]. Narrow exciton-like peaks have even been observed well above the Mott transition in highly doped GaN [5]. The sustaining absorption peaks here are likely to be Mahan excitons [59] but in the case of excited electrons and holes.

The obvious explanation for photo-induced absorption at lower photon energies would be due to the free carrier response [62]. However, two Drude terms for electrons and holes with the known densities and reasonable effective masses and mobilities cannot describe
the large absorption in $\varepsilon_2$. Furthermore, there are indications for a maximum of $\varepsilon_2$ around 1.9 eV and 2.1 eV hinting at IVB transition at the M point. In a recent report, similar absorption features, induced by lower pump power and at much longer time scales, were attributed to defect states [55]; however, defects cannot explain the large absorption cross sections ($\varepsilon_2$) we observe. Comparison of experiment and first-principles data for $\Delta(\varepsilon_2)$ in Fig. 4d (inset) shows good agreement, in particular for energetic position and line shape of spectral features. The sub-gap energy-range between 2 and 3 eV is dominated by contributions from IVB transitions that become allowed in the presence of free holes. The computational results do not account for phonon-assisted processes, which likely explains why the computational data underestimates the experiment at these energies. Conduction-conduction band transitions do not significantly contribute in this energy range. The appearance of the low-energy absorption indicates that the spectral weight of absorption is transferred from the fundamental absorption edge to lower energies because the total number of charge carriers remains constant, which is known as sum rule [63].

Conclusion

The development of fs-time-resolved spectroscopic ellipsometry allows to study the dynamics of the complex, frequency-dependent dielectric function with sub-ps temporal resolution in a wide spectral range. Investigating a UV-pumped ZnO thin film, we were able to discriminate different processes of the nonequilibrium charge-carrier dynamics of this highly photo-degenerate semiconductor. We observe partial blocking and screening of near-band-edge and exciton absorption due to occupation of the electronic states. Non-vanishing excitonic absorption enhancement hints at the occurrence of Mahan excitons. Intra-valence-band transitions become possible when holes scatter to the edges of the Brillouin zone. Their fast response time renders them interesting for optoelectronic switching devices. Finally, there is evidence for hot-phonon effects, by both, a delayed relaxation and an increased exciton-phonon-complex energy. The described dynamics are crucially dependent on the pump energy and hence excess energy of the carriers determining their effective temperature. From our data we can also conclude that the high density of high charge carriers does not trigger the Mott transition. The survival of the excitonic absorption reflects directly the non-equilibrium distribution of the excited charge carriers. These facts stimulate demand for new theories regarding high-density exciton systems beyond the present state.

Methods

We used a c-plane oriented ZnO thin film grown by pulsed laser deposition on a fused silica substrate. The film thickness of 30 nm is sufficient to maintain bulk properties. Only a very slight excitonic enhancement due to the confinement in the thin layer is expected [52]. At the same time 30 nm is thin enough to assume a homogeneous excitation by a 266 nm pump pulse (500 μJ/cm², 35 fs pulse duration). We therefore do not need to consider the ambipolar diffusion of hot charge carriers. We estimate the excited electron-hole pair density to approx. $1 \times 10^{20}$ cm⁻². The experiment is performed at room temperature.

Time-resolved spectroscopic ellipsometry

We employ time-resolved spectroscopic ellipsometry in a pump-probe scheme. An amplified Ti:Sapphire laser (Coherent Astrella, 35 fs, 800 nm, 1 kHz repetition rate) is used to generate its third harmonic as pump and continuum white light in a CaF₂ crystal as probe beam. In a Polarizer-Sample-Compensator-Analyzer configuration, we measure the transient reflectance-difference signal ($\Delta R/R_0$) at 60° angle of incidence for a series of different azimuth angles $\alpha_z$ of the compensator. The polarizer and analyzer are kept fixed at ±45°. The probe spot had a 1 cm² diameter of 200 μm, the pump spot 400 μm (40°, s-polarized) such that lateral carrier diffusion becomes negligible. The corresponding temporal and spectral bandwidths are estimated to 10 fs and 5 nm in the UV, respectively. Spectra were captured using a prism spectrometer and a kHz-readout CCD camera (Ing.-Büro Stresing). Most critical is the fluctuating probe spectrum and amplitude due to the CaF₂ crystal movement as well as warm-up effects at the CCD camera. Both occur mostly on time scales larger than a few milliseconds. A two-chopper scheme in the pump and probe paths is employed which allows us to obtain a wavelength-dependent live-correction for the pump-probe as well as only-probe intensity spectra. The obtained reflectancedifference spectra are applied to reference spectra in order to obtain the time-resolved ellipsometric parameters. In order to minimize chirping of the probe pulse, polarization optics involve a thin, broadband wire grid-polarizer (Thorlabs) ahead of the sample. The probe beam is focused by a spherical mirror. Reflected light is analyzed by an achromatic quarter-wave plate and Glan-type prism (both B. Halle Nachfolger). We obtain transient reflectance data by scanning of the delay line at various compensator azimuth angles. The transient ellipsometric parameters are computed from the reflectance-difference spectra. The remaining chirp (few 100 fs difference between 2.0 eV and 1.6 eV - corresponding to roughly 400 μm dispersion induced by the CaF₂ as well as the support of the wire grid polarizer [88]) is removed retroactively by shifting the zero-delay in the data analysis using an even polynomial for its wavelength dependence. Further details can be found in the supplementary information.

Modeling of the ellipsometry data to obtain the material's DF is performed using a transfer matrix formalism [55] with the DF of ZnO parametrized by a Kramers-Kronig consistent B-spline function [62]. In the model, the film is assumed to be isotropic because the experimental configuration is mostly sensitive to the DF for ordinary polarization [62]. The model is fitted to the Mueller matrix elements $N, C, S$ accounting also for spectral bandwidth. The number of spline nodes was minimized in order to capture all spectral features but avoid overfitting and artificial oscillations [63].

First-principles simulations of excited electron-hole pairs at finite temperature

We use first-principles simulations based on many-body perturbation theory to study the influence of electron-hole excitations on the optical properties of ZnO. To this end, we compute Kohn-Sham states and energies within density functional theory (DFT) [78, 79] and use these to solve the Bethe-Salpeter equation (BSE) for the optical polarization function [71]. All DFT calculations are carried out using the Vienna Ab-initio Simulation Package (VASP) and the computational parameters described in Refs. [72, 73]. All BSE calculations are performed using the implementation described in Refs. [77, 78]. In order to describe excited electrons and holes, we use and modify the framework described in Refs. [76, 79, 80] and in detail in the supplementary information.

Acknowledgements

We acknowledge Peter Schlupp for growing the thin film and Michael Lorenz (both Universität Leipzig) for X-ray diffraction measurements. We gratefully acknowledge valuable discussions with Christoph Cobet, Martin Peneberg, Daniel Franta,
Kurt Hingerl, Michael Lorké, Bernd Rheinländer, Chris Sturm and Marcel Wille. Parts of this work have been funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), SFB 762 - Projektgruppe 31047526 (project B03), and FOR 1616 (SCHR2710/2). OH acknowledges the Leipzig School of Natural Sciences BuildMoNa. Experimental developments at ELI Beamlines was funded by the project “Advanced Research using high intensity laser produced photons and particles” (ADONIS), Reg. n. CZ.02.1.01/0.0/0.0/15_003/0000417, from the European Regional Development Fund, and the National Program of Sustainability II project ELI Beamlines - International Center of Excellence (ELISu), project code: LQ1606. SE was partially supported by the project Structural dynamics of biomolecular systems (ELIBIO), reg. no. CZ.02.1.01/0.0/0.0/15_003/0000417, from the European Regional Development Fund. J.A.L. and A.S. were supported by the National Science Foundation under Grant Nos. DMR-1555153 and CBET-1437230, and as part of the Blue Waters sustained-petascale computing project, which is supported by the National Science Foundation (awards OCI-0725070 and ACI-1238993) and the state of Illinois. SZ was supported by the National Science Foundation, Grant No. DMR-1505172.

Author contributions
S.R., O.H., S.E., M.R. and M.K. built the experimental setup and conducted the measurements. M.R. wrote the computer code for data collection. S.R. and O.H. wrote the computer code for the data reduction and analysis. A.S. and J.A.L. performed and interpreted first-principles simulations. J.A., R.S.G., M.G. and S.Z. supervised the work, and discussed approaches and results. S.R. and O.H. wrote the manuscript with inputs from all other authors.

Additional information
Supplementary information is provided in the online version of this publication.

Competing financial interests
The authors declare no competing financial interests.

Data availability
Measured and modeled data are available from the authors upon request.

References
[1] D. S. Chemla and J. Shah. Many-body and correlation effects in semiconductors. Nature, 414:549–557, 2001. doi:10.1038/35079000
[2] R. Huber, F. Tauser, A. Brodischm, M. Bichler, G. Abstreiter, and A. Leitenstorfer. How many-particle interactions develop after ultrafast excitation of an electron-hole plasma. Nature, 414:286–289, 2001. doi:10.1038/35104522
[3] G. R. Fleming and M. A. Ratner. Grand challenges in basic energy sciences. Phys. Today, 61(7):28–33, 2008. doi:10.1063/1.2963009
[4] E. Baldini, A. Mann, I. Benafatto, E. Cappelluti, A. Aco- dellia, V. M. Silkin, S. V. Eremeev, A. B. Kuzmenko, S. Borroni, T. Tan, X. X. Xi, F. Zerbetto, R. Merlin, and F. Carbone. Real-Time Observation of Phonon-Mediated σ−π In- terband Scattering in MgB2. Phys. Rev. Lett., 119:097002, 2017. doi:10.1103/PhysRevLett.119.097002
[5] C. Nenstiel, G. Callens, F. Nippert, T. Kure, S. Schlichting, N. Jankowski, M. P. Hoffmann, A. Dadgar, S. Fritze, A. Krost, M. R. Wagner, A. Hoffmann, and F. Bechstedt. Electronic excitations stabilized by a degenerate electron gas in semiconductors. Commun. Phys., 1(38), 2018. doi:10.1038/s42005-018-0033-4
[6] P. Colman, P. Lunemann, Y. Yu, and J. Mork. Ultrafast coherent dynamics of a photonic crystal all-optical switch. Phys. Rev. Lett., 117:233901, 2016. doi:10.1103/PhysRevLett.117.233901
[7] Z. Chai, X. Hu, F. Wang, X. Niu, J. Xie, and Q. Gong. Ultrafast alloptical switching. Adv. Opt. Mater., 5(7), 2017. doi:10.1002/adom.201600668
[8] H. Mashiko, K. Oguri, T. Yamaguchi, A. Suda, and H. Gotob. Petahertz optical drive with wide-bandgap semiconductor. Nat. Phys., 12:741–745, 2016. doi:10.1038/nphys3711
[9] R. Athale and D. Psaltis. Optical computing: Past and future. Opt. Photon. News, 27(6):32–39, 2016. doi:10.1364/OPN.27.6.00032
[10] H. Ohta and H. Hosono. Transparent oxide optoelectronics. Mater. Today, 7(4):42–51, 2004. ISSN 1369-7021. doi:10.1016/S1369-7021(04)00288-3
[11] H. Frenzel, A. Lauj, H. von Wencstern, M. Lorenz, F. Schein, Z. Zhang, and M. Grundmann. Recent progress on ZnO-based metal-semiconductor field-effect transistors and their application in transparent integrated circuits. Adv. Mater., 22(47):5332–5349, 2010. doi:10.1002/adma.201001379
[12] C. S. Ponceca Jr., P. Chábera, J. Uhlig, P. Persson, and V. Sundström. Ultrafast electron dynamics in solar energy conversion. Chem. Rev., 117(16):10940–11024, 2017. doi:10.1021/acs.chemrev.6b00807
[13] H. A. Aterwater, A. R. Davoyan, O. Ilic, D. Jariwala, M. C. Sherrer, C. M. Went, W. S. Whitney, and J. Wong. Materials challenges for the starshot lightsail. Nat. Mater., 17:861867, 2018. doi:10.1038/s41563-018-0075-8
[14] S. K. Sundaram and E. Mazur. Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses. Nat. Mat., 1:217–224, 2002. doi:10.1038/nmat767
[15] M. Lorenz, M. S. Ramachandra Rao, T. Venkatesan, E. For- tunato, P. Barquinho, R. Draaneino, D. Salgueiro, R. Mar- tins, C. Erolon, S. Liu, F. K. Shan, M. Grundmann, H. Boschler, J. Mckherjee, M. Priyadarshini, N. DasGupta, D. J. Rogers, F. H. Theherani, E. V. Sandana, P. Bove, K. Ri- etwyk, A. Zaban, A. Veziris, A. Weidenkaff, M. Muraaldhar, M. Murakami, S. Abel, J. Fompeyrine, J. Zuniga-Perez, R. Rashes, N. A. Spaldin, S. Ostanin, V. Borisov, I. Mertig, V. Lazenka, G. Srinivasan, W. Freller, M. Uhilda, M. Kawasaki, R. Pentcheva, P. Gegenwart, F. Miletto Granozio, J. Fontcuberta, and N. Pryds. The 2016 oxide electronic materials and oxide interfaces roadmap. J. Phys. D: Appl. Phys., 49(43):433001, 2016. doi:10.1088/0022-3773/49/43/433001
[16] S. Mor, M. Herzog, D. Golei, P. Werner, M. Eckstein, N. Katayama, M. Nohara, H. Takagi, T. Mizokawa, C. Mon- ney, and J. Stähler. Ultrafast electronic band gap control in an excitonic insulator. Phys. Rev. Lett., 119:086401, 2017. doi:10.1103/PhysRevLett.119.086401
[17] A. Zong, A. Kogar, Y.-Q. Bie, T. Rohwer, C. Lee, E. Bald- dini, E. Ergecen, M. B. Yilmaz, B. Freelon, E. J. Sie, H. Zhou, J. Straquadine, P. Walmsley, P. E. Dolgirev, A. V. Rozhkov, I. R. Fisher, F. Jarillo-Herrero, B. V. Fine, and N. Gedik. Evidence for topological defects in a photoin- duced phase transition. 2018.
[18] S. A. Donges, A. Sven, O. Khatib, B. T. O’Callahan, J. M. Atkin, J. H. Park, D. Colden, and M. B. Raschke. Ultrafast nanoimaging of the photoinduced phase transi- tion dynamics in VO2. Nano Lett., 16:3029–3035, 2016. doi:10.1021/acs.nanolett.5b05313
Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures. Springer Series in Solid-State Sciences 115. Springer, 2 edition, 1999. ISBN 978-3-642-08391-4, 978-3-662-03770-6.

K. Bohnert, G. Schmieder, and C. Klinghain. Gain and reflection spectroscopy and the present understanding of the electron-hole plasma in II–VI compounds. Phys. Stat. Sol. B, 98(1):175–188, 1980. doi:10.1002/pssb.2220980117.

L. Huang, J. P. Callan, E. N. Glezer, and E. Mazur. GaAs under intense ultrafast laser excitation: Response of the dielectric function. Phys. Rev. Lett., 80:185, 1998. doi:10.1103/PhysRevLett.80.185.

C. A. D. Roesser, A. M.-T. Kim, J. P. Callan, L. Huang, E. N. Glezer, Y. Siegal, and E. Mazur. Femtosecond time-resolved dielectric function measurements by dual-angle reflectometry. Rev. Sci. Instrum., 74:3413–3422, 2003. doi:10.1063/1.1583283.

T. Shih, M. T. Winkles, T. Voss, and E. Mazur. Dielectric function dynamics during femtosecond laser excitation of bulk ZnO. Appl. Phys. A, 96(2):363–367, 2009. ISSN 0947-8396. doi:10.1007/s00339-009-0516-0.

F. Boschini, H. Hedayat, C. Piovra, C. Dallera, A. Gupta, and E. Carpano. A flexible experimental setup for femtosecond time-resolved broadband-band magneto-optics. Rev. Sci. Instrum., 86:013909, 2015. doi:10.1063/1.4906756.

E. Baldini, A. Mann, S. Borroni, C. Arrell, F. van Mourik, and F. Carbone. A versatile setup for ultrafast broadband optical spectroscopy of coherent collective modes in strongly correlated dielectric systems. Struct. Dyn., 3(6):064301, 2016. doi:10.1063/1.4971182.

C. Poellmann, P. Steinleitner, U. Leierseder, P. Nagler, G. Plechinger, M. Porer, R. Bratschitsch, C. Schüller, T. Korn, and R. Huber. Resonant internal quantum transitions and femtosecond radiative decay of excitons in monolayer WSe2. Nat. Mater., 14:889–893, 2015. doi:10.1038/nmat4356.

H. R. Choo, X. F. Hu, M. C. Downer, and V. P. Kesan. Femtosecond ellipsometric study of nonequilibrium carrier dynamics in Ge and epitaxial Si1-x-Ge0.25x. Appl. Phys. Lett., 63(11):1507–1509, 1993. doi:10.1063/1.109871.

S. Zollner, K.D. Myers, K.G. Jensen, J.M. Dolan, D.W. Bailey, and C.J. Stanton. Femtosecond interband hole scattering in Ge studied by pump-probe reflectivity. Solid State Commun., 104(1):51–55, 1997. doi:10.1016/S0038-1098(97)00068-9.

H. Yoneda, H. Morikami, K.-I. Ueda, and R. M. More. Ultrashort-pulse laser ellipsometric pump-probe experiments on gold targets. Phys. Rev. Lett., 91:075004, 2003. doi:10.1103/PhysRevLett.91.075004.

V. V. Kruglyak, R. J. Hicken, M. Ali, B. J. Hickey, A. T. G. Pym, and B. K. Tanner. Measurement of hot electron momentum relaxation times in metals by femtosecond ellipsometry. Phys. Rev. B, 71:233104, 2005. doi:10.1103/PhysRevB.71.233104.

D. Moulier, E. Morozov, P. Ruello, J.-M. Breteau, P. Picart, and V. Gusev. Detection of shear pico-second acoustic pulses by transient femtosecond polarimetry. Eur. Phys. J. ST, 153(1):243–246, 2008. doi:10.1140/epjst/e2008-00436-2.

C.-K. Min, D. G. Cahill, and S. Granick. Time-resolved ellipsometry for studies of heat transfer at liquid/solid and gas/solid interfaces. Rev. Sci. Instrum., 81(7):074902, 2010. doi:10.1063/1.3465329.

S. Rapp, M. Kaiser, M. Schmidt, and H. P. Hueber. Femtosecond pump-probe ellipsometry setup for the measurement of transient optical properties during laser ablation. Opt. Express, 24(16):17572–17592, 2016. doi:10.1364/OE.24.017572.

J. Csontos, Z. Toth, Z. Pápa, B. Gábor, M. Füle, B. Gilicze, and J.Budai. Femtosecond in-situ null-ellipsometry for studying pulsed laser - silicon surface interactions. Appl. Surf. Sci., 421:325–330, 2017. doi:10.1016/j.apsusc.2017.03.186.

T. Pflug, J. Wang, M. Olbrich, M. Frank, and A. Horn. Case study on the dynamics of ultrafast laser heating and ablation of gold thin films by ultrafast pump-probe reflectometry and ellipsometry. Appl. Phys. A, 124(2):116, 2018. doi:10.1007/s00339-018-1550-4.

S. Shokhovets, O. Ambacher, B. K. Meyer, and G. Gobsch. Anisotropy of the momentum matrix element, dichroism, and conduction-band dispersion relation of wurtzite semiconductors. Phys. Rev. B, 78:035207, 2008. doi:10.1103/PhysRevB.78.035207.

A. Othonos. Probing ultrafast carrier and phonon dynamics in semiconductors. J. Appl. Phys., 83(4), 1998. doi:10.1063/1.367411.

R. R. Gattass and E. Mazur. Femtosecond laser micromachining in transparent materials. Nat. Photon., 2:219–225, 2008. doi:10.1038/nphoton.2008.47.

S. S. Mao, F. Quéré, S. Guizard, X. Mao, R. E. Russo, G. Petitie, and P. Martin. Dynamics of femtosecond laser interactions with dielectrics. Appl. Phys. A, 79:1695–1709, 2004. doi:10.1007/s00339-004-2684-0.

M. W. Allen, C. H. Swartz, T. H. Myers, T. D. Veal, C. F. McConville, and S. M. Durbin. Bulk transport measurements in ZnO: The effect of surface electron layers. Phys. Rev. B, 81:075211, 2010. doi:10.1103/PhysRevB.81.075211.

L. Foglia, S. Vempati, B. T. Bonkano, M. Wolf, S. Sadoev, and J. Stähler. Revealing the competing contributions of charge carriers, excitons, and defects to the non-equilibrium optical properties of ZnO. 2018. URL arxiv.org/abs/1811.04499.

J. Shah. Hot electrons and phonons under high intensity photoexcitation of semiconductors. Sol. State Electron., 21:43–50, 1978. doi:10.1016/0038-1101(78)90113-2.

W. Pötz and P. Koevar. Electronic power transfer in pulsed laser excitation of polar semiconductors. Phys. Rev. B, 28:7040–7047, 1983. doi:10.1103/PhysRevB.28.7040.
C. Klingshirn and H. Haug. Optical properties of highly excited direct gap semiconductors. *Phys. Rev. B*, 4:2567–2575, 1971. doi:10.1103/PhysRevB.4.2567

C. Klingshirn and H. Haug. Optical properties of highly excited direct gap semiconductors. *Phys. Rep.*, 70:315–398, 1981. doi:10.1016/0370-1573(81)90190-3.

R. Zimmermann. Nonlinear optics and the Mott transition in semiconductors. *Phys. Stat. Sol. B*, 146:371–384, 1988. doi:10.1002/pssb.2221460140

A. Yamamoto, T. Kidoh, T. Gotoh, Y. Chen, T. Yao, and A. Kasuya. Dynamics of photoexcited carriers in ZnO epitaxial thin films. *Appl. Phys. Lett.*, 75(4):469–471, 1999. doi:10.1063/1.124411

S. Acharya, S. Chouthe, H. Graener, T. Böntgen, C. Sturm, R. Schmidt-Grund, M. Grundmann, and G. Seifert. Ultrafast dynamics of the dielectric functions of ZnO and BaTiO3 thin films after intense femtosecond laser excitation. *J. Appl. Phys.*, 115:054508, 2014. doi:10.1063/1.4864017

H. Fujimura and M. Kondo. Effects of carrier concentration on the dielectric function of ZnO:Ga and InO:Sn studied by spectroscopic ellipsometry: Analysis of free-carrier and band-edge absorption. *Phys. Rev. B*, 71:075109, 2005. doi:10.1103/PhysRevB.71.075109

C. F. Klingshirn. *Semiconductor Optics*. Springer, 2012. doi:10.1007/978-3-642-28362-8

C. Klingshirn, R. Hauschild, J. Fallert, and H. Kalt. Room-temperature stimulated emission of ZnO: Alternatives to excitonic lasing. *Phys. Rev. B*, 75:115203, 2007. doi:10.1103/PhysRevB.75.115203

M. A. M. Versteegh, T. Kuis, H. T. C. Stoof, and J. T. Dijkstra. Ultrafast screening and carrier dynamics in ZnO: theory and experiment. *Phys. Rev. B*, 84:035207, 2011. doi:10.1103/PhysRevB.84.035207

G. D. Mahan. Excitons in degenerate semiconductors. *Phys. Rev.*, 153:882–889, 1967. doi:10.1103/PhysRev.153.882

H. Haug and T. D. B. Tran. Dynamical screening of excitons by free carriers. *Phys. Stat. Sol. B*, 85(2):561–568, 1978. doi:10.1002/pssb.2220850219

M. Bachmann, M. Czerner, S. Edralati-Boostan, and C. Heiliger. Ab initio calculations of phonon transport in ZnO and ZnS. *Eur. Phys. J. B.*, 85(5):146, 2012. doi:10.1140/epjb/e2012-20503-y

E. Hendry, M. Koeeberg, and M. Bonn. Exciton and electron-hole plasma formation dynamics in ZnO. *Phys. Rev. B*, 76:045214, 2007. doi:10.1103/PhysRevB.76.045214

D. Franta, D. Nečas, and Lenka Zajčková. Application of Thomas-Reiche-Kuhn sum rule to construction of advanced dispersion models. *Thin Solid Films*, 534:432–441, 2013. doi:10.1016/j.tsf.2013.01.081

D. Pal, J. Singhal, A. Mathur, A. Singh, S. Dutta, S. Zoller, and S. Chattopadhyay. Effect of substrates and thickness on optical properties in atomic layer deposition grown ZnO thin films. *Appl. Surf. Sci.*, 421:341, 2017. doi:10.1016/j.apsusc.2016.10.130

M. Schubert. Polarization-dependent optical parameters of arbitrarily anisotropic homogeneous layered systems. *Phys. Rev. B*, 53:4265–4274, 1996. doi:10.1103/PhysRevB.53.4265

B. Jhoo and J. S. Hale. Dielectric function representation by B-splines. *Phys. Stat. Sol. A*, 205:715–719, 2008. doi:10.1002/pssa.200777754

S. Shokhovets, L. Spieß, and G. Gobsch. Spectroscopic ellipsometry of wurtzite ZnO and GaN: examination of a special case. *J. Appl. Phys.*, 107(2):023509, 2010. doi:10.1063/1.3285485

D. V. Likhachev. Selecting the right number of knots for B-spline parameterization of the dielectric functions in spectroscopic ellipsometry data analysis. *Thin Solid Films*, 636:519–526, 2017. doi:10.1016/j.tsf.2017.06.056

P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:864–871, 1964. doi:10.1103/PhysRev.136.B864

W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133–A1138, 1965. doi:10.1103/PhysRev.140.A1133

G. Onida, L. Reining, and A. Rubio. Electronic excitations: density-functional versus many-body Greens-function approaches. *Rev. Mod. Phys.*, 74:601, 2002. doi:10.1103/RevModPhys.74.601

M. Gajdös, K. Humer, G. Kresse, J. Furthmüller, and F. Bechstedt. Linear optical properties in the projector-augmented wave method. *Phys. Rev. B*, 73:045112, 2006. doi:10.1103/PhysRevB.73.045112

G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54:11169–11186, 1996. doi:10.1103/PhysRevB.54.11169

A. Schleife, C. Rölö, F. Fuchs, J. Furthmüller, and F. Bechstedt. Optical and energy-loss spectra of MgO, ZnO, and CdO from ab initio many-body calculations. *Phys. Rev. B*, 80:035112, 2009. doi:10.1103/PhysRevB.80.035112

A. Schleife, C. Rölö, F. Fuchs, K. Hannewald, and F. Bechstedt. Optical absorption in degenerately doped semiconductors: Mott transition or Mahan excitons? *Phys. Rev. Lett.*, 107:236405, 2011. doi:10.1103/PhysRevLett.107.236405

C. Rölö, F. Fuchs, J. Furthmüller, and F. Bechstedt. Ab initio theory of excitons and optical properties for spin-polarized systems: Application to antiferromagnetic MnO. *Phys. Rev. B*, 77:184408, 2008. doi:10.1103/PhysRevB.77.184408

F. Fuchs, C. Rölö, A. Schleife, and F. Bechstedt. Efficient $O(N^2)$ approach to solve the Bethe-Salpeter equation for excitonic bound states. *Phys. Rev. B*, 78:085103, 2008. doi:10.1103/PhysRevB.78.085103

A. Schleife. Electronic and optical properties of MgO, ZnO, and CdO. *Südwestdeutscher Verlag für Hochschulschriften*, 2011. ISBN 3838127668.

A. Schleife. Electronic and optical properties of MgO, ZnO, and CdO. *Comput. Mater. Sci.*, 160:207–216, 2019. doi:10.1016/j.commatsci.2019.01.004
I. Experimental setup

A schematic of the setup for femtosecond time-resolved spectroscopic ellipsometry is shown in figure S1. The fundamental mode of the titanium sapphire laser Ti:Sa is used for third harmonic generation THG (266 nm), employed as pump beam and guided through the chopper wheel C1 ($f_1 = 250$ Hz) to the delay line DL and focussed (lens L) onto the sample. 1% of the laser power is used for supercontinuum white-light generation SCG in CaF$_2$ employed as probe beam which passes through the chopper wheel C2 ($f_2 = 500$ Hz) and is focussed onto the sample S by a spherical mirror through the polarizer P. The reflected light is collimated (lens L) and guided via compensator C and analyzer A to the prism spectrometer with CCD detector. We refer also to reference [S1].

![Figure S1: Schematic of the femtosecond time-resolved spectroscopic ellipsometry setup. See also [S1].](image-url)
II. Measurement scheme and data reduction

In contrast to sapphire, calcium fluoride-based white light generation offers more UV intensity up to 3.6 eV, but the crystal needs to be moved during creation of continuum white light in order to protect the crystal from heat damage. This movement and CCD warm-up yield fluctuating intensity spectra. The situation is very different from any other ellipsometer where the light source is stable at least over the time of a complete revolution of the rotating element. We circumvent the problem by applying a two-chopper scheme as depicted in Fig. S2. Repeatedly, four different intensity signals, "pump & probe" (S1), "pump only" (S2), "probe only" (S3), and "dark" (S4) are measured. Hence, at any time, background- or even luminescence-corrected "pump & probe" ($R_p(E) \equiv I_{S1} - I_{S2}$) as well as "probe only" ($R_0(E) \equiv I_{S3} - I_{S4}$) spectra are obtained for each compensator angle $\alpha_j$. However, they are still subject to intensity fluctuations as can be seen in Fig. S3.

![Figure S2: a Visualization of the two-chopper scheme. b Example of a set of measured intensity spectra at $\Delta t = 400$ fs and compensator azimuth angle 100°.](image)

![Figure S3: Spectra of the ellipsometric parameters $\Psi$, $\Delta$ obtained from "probe only" (S3) reflectance measurements. The green line indicates the average and the red line shows reference spectra obtained with a commercial ellipsometer. Note that these spectra are only shown as a benchmark. They are prone to offsets and modulations arising from long-term changes in the white-light spectra or intensities. The oscillations originate from the quarterwave plate. For the time-resolved ellipsometry, the reflectance difference signal is evaluated instead. These are robust against long-term changes.](image)

Evaluating only the reflectance-difference spectra ($\Delta R(E)/R(E) = (R_p(E) - R_0(E))/R_0(E) \equiv (I_{S1} - I_{S2})/(I_{S3} - I_{S4}) - 1$) is comparable to a multi-channel lock-in system and allows comparison of spectra measured a long time after each other. Furthermore, it minimizes systematic errors from polarization uncertainties.

In order to compute the ellipsometric angles we utilize Moore-Penrose pseudo-inversion (ordinary least-squares regression) in a Müller matrix formalism for each photon energy and delay time [S2]: The Müller matrix of the sample in isotropic or pseudo-isotropic configuration is given as...
\[ M_{\text{sample}} = \begin{pmatrix} M_{11} & M_{12} & 0 & 0 \\ M_{12} & M_{11} & 0 & 0 \\ 0 & 0 & M_{33} & M_{34} \\ 0 & 0 & -M_{34} & M_{33} \end{pmatrix} \] (S1)

For each compensator angle \( \alpha_j \), the Müller matrix \( M_{\text{det},j} \) shall represent a respectively oriented compensator followed by an analyzer (as in the experiment). Likewise, \( M_{\text{prep}} \) shall represent the Müller matrix of a polarizer at the angle of the analyzer in the experiment. Having measured \( N \) different configurations (compensator angles) \( j = 1 \ldots N \), we can introduce a \( 4 \times N \) setup coefficient matrix \( \hat{M}_{\text{setup}} \). Its \( j \)th column can be written as

\[ \hat{M}_{\text{setup}}^j = \begin{pmatrix} M_{11}^{\text{det},j} M_{11}^{\text{prep}} + M_{12}^{\text{det},j} M_{21}^{\text{prep}} \\ -M_{11}^{\text{det},j} M_{11}^{\text{prep}} - M_{12}^{\text{det},j} M_{21}^{\text{prep}} \\ M_{13}^{\text{det},j} M_{13}^{\text{prep}} + M_{14}^{\text{det},j} M_{23}^{\text{prep}} \\ M_{13}^{\text{det},j} M_{14}^{\text{prep}} - M_{14}^{\text{det},j} M_{24}^{\text{prep}} \end{pmatrix} \] (S2)

With the row vector \( \hat{R} \) containing the \( N \) intensity values \( R_j \) for each compensator angle \( \alpha_j \), it holds

\[ M_{11}(1,N,C,S) = \hat{R} \hat{M}_{\text{setup}}^T (\hat{M}_{\text{setup}} \hat{M}_{\text{setup}}^T)^{-1} \]. (S3)

Instead of using the "pump & probe" intensity spectra \( R_j^0(E) \), the reflectance difference signal \( (\Delta R(E)/R(E))_j \) is applied to ideal (theoretical) intensity spectra of the unexcited sample \( R_j^{00}(E) \) as computed from reference spectra: \( R_j = R_j^{00}(1 + (\Delta R/R_j)) \).

In a final step, the Müller matrix elements can be transferred to ellipsometric angles and the degree of polarization (DOP):

\[ \Psi = \frac{1}{2} \tan^{-1} \left( \frac{\sqrt{C^2 + S^2}}{N} \right) , \] (S4)

\[ \Delta = \tan^{-1} \left( \frac{S}{C} \right) , \] (S5)

\[ \text{DOP} = \sqrt{N^2 + C^2 + S^2} , \] (S6)

requiring \( \Psi \in [0^\circ, 90^\circ] \) and \( \Delta \in (90^\circ, 270^\circ) \) if \( C < 0 \), \( \Delta \in (0^\circ, 90^\circ) \cup (270^\circ, 360^\circ) \) if \( C > 0 \). It should be noted that \( \Psi \) and \( \Delta \) are to first order unaffected by depolarization, i.e., the above equations intrinsically involve only the non-depolarizing part of the Müller matrix. Depolarization results in \( M_{22} \neq M_{11} = 1 \) in contrast to Eq. S1. However, as in the experimental configuration the input polarization was chosen to be linear at azimuth angle \( \pm 45^\circ \), \( M_{22} \) is not probed and thus depolarization does not affect the data reduction. The non-depolarizing Mueller matrix is obtained by replacing \( (N,C,S) \) by \( (N,C,S)/\text{DOP} \).

The ellipsometric parameters \( \Psi \) and \( \Delta \) are defined by the ellipsometric ratio

\[ \rho = \frac{r_p}{r_s} = \tan \Psi e^{i \Delta} , \] (S7)

where \( r_{s,p} \) are the complex reflection coefficients for s/p-polarized light.

In the experiments, the compensator was rotated in 10 steps of 50\(^\circ\). The polarizer was set at \(-45^\circ\), the analyzer at \(+45^\circ\). Each spectrum was averaged over 500 pulses.

Finally, the obtained data reveal an imprinted chirp of the white light, i.e. propagation through the CaF\(_2\) window and the support of the wiregrid polarizers caused light of longer wavelength to arrive earlier at the sample than light of shorter wavelength. This is illustrated in Fig. S4. An even polynomial function is used to describe this chirp and adjust the zero delay for each photon energy. Data is interpolated accordingly.
III. General sample characterization

Time-resolved photoluminescence (PL) spectroscopy conducted with a streak camera reveals information on the temporal evolution of the occupation of electronic states. The sample was optically excited with 4.67 eV pulses of a frequency-tripled Ti:Sapphire laser (3 MHz, 150 fs, 1 nJ). Figure S5 a shows the transient photoluminescence at the absorption edge of ZnO (3.28 eV), which is much less intense compared to the defect luminescence centered at 2.4 eV. This hints at the defect-rich crystal growth induced by the amorphous SiO$_2$ substrate. The ratio of near-band-edge to defect-related luminescence is not constant over the sample surface.

We model the transient UV-PL (Fig. S5 b, c) with onset $\tau_o$ and decay time $\tau_d$ of roughly 4 ps, which we expect to be limited by the time resolution of our streak camera. The preferred radiative recombination channel appears to be related to defect states having an order of magnitude higher onset $\tau_o = 60$ ps as well as decay times $\tau_{d,1} = 80$ ps and $\tau_{d,2} = 415$ ps. These time constants match the late absorption recovery that is observed in the time-resolved ellipsometry experiment. The excited electron population seems to be not yet fully recombined after 2 ns, corresponding to the time scale for vanished band bending observed in the time-resolved spectroscopic ellipsometry data.

The X-ray data (Fig. S6) confirm c-plane orientation of the thin film and show the response of the amorphous substrate. The FWHM of the ZnO (002) rocking curve is larger compared to other PLD-grown ZnO thin films [S3]. The grain size is estimated to be on the order of the film thickness using the Scherrer formula.
Figure S5: a) Time-resolved photoluminescence measured by a streak camera. The dashed lines indicate the transients shown in panel b, c. Blue (red) lines indicate an exponential model fit to obtain characteristic onset (decay) times.

Figure S6: 2θ-ω scan of the 30 nm thick ZnO film on an SiO$_2$ substrate. The inset shows the rocking curve of the ZnO (002) peak.

IV. Optical transitions in ZnO

With the symmetry assignments of the bands according to [S4], the dipole-allowed transitions for the electric field oriented perpendicular to the optic axis ($\mathcal{E} \perp c$) in wurtzite ZnO (space group 186) are listed in table IV; cf. also [S5, 6]. Only relevant bands at high-symmetry points of the Brillouin zone are considered and Koster notation of the irreducible representations is used. Transitions for $\mathcal{E} || c$ are only allowed between states of the same symmetry representation.

| direction | point group symmetry | dipole operator representation | allowed transitions for $\mathcal{E} \perp c$ |
|-----------|---------------------|-------------------------------|------------------------------------------|
| Γ, Δ, A   | 6mm ($C_{6v}$)      | $\Gamma_5$                    | $\Gamma_1 \leftrightarrow \Gamma_5$, $\Gamma_2 \leftrightarrow \Gamma_5$, $\Gamma_3 \leftrightarrow \Gamma_6$, $\Gamma_5 \leftrightarrow \Gamma_6$ |
| P, K, H   | 3mm ($C_{3v}$)      | $\Gamma_3$                    | $\Gamma_1 \leftrightarrow \Gamma_3$, $\Gamma_2 \leftrightarrow \Gamma_3$, $\Gamma_3 \leftrightarrow \Gamma_3$ |
| U, M, L   | 2mm ($C_{2v}$)      | $\Gamma_3$                    | $\Gamma_1 \leftrightarrow \Gamma_3$, $\Gamma_2 \leftrightarrow \Gamma_4$ |

For the reciprocal-space directions corresponding to monoclinic $C_s/C_{1h}$ symmetry (R, Σ as ..m, and S, T...
where the \( c \)-direction of the crystal is parallel to the respective mirror planes, the assignment of band symmetries and transitions is generally more complex. The dipole operator would transform generally like \( \Gamma_1 \), in some cases like \( \Gamma_3 \).

V. Charge carrier density

Assuming linear absorption, the density \( N \) of photo-excited electron-hole pairs in the film can be estimated as

\[
N \approx \frac{E_{\text{pulse}} \lambda_{\text{pump}}}{\hbar c_0} (1 - R) \left[ 1 - \exp \left( - \frac{\alpha_{\text{film}} d_{\text{film}}}{\cos(\theta_{\text{film}})} \right) \right] \left[ \frac{\cos(\theta_{\text{pump}}) \cos(\theta_{\text{film}})}{(d_{\text{pump}}/2)^2 \pi \, d_{\text{film}}} \right]
\]

with

| quantity     | meaning                                      |
|--------------|----------------------------------------------|
| \( E_{\text{pulse}} \) = 1 \( \mu \text{J} \) | pump pulse energy                            |
| \( \lambda_{\text{pump}} \) = 266 nm       | pump photon wavelength                        |
| \( d_{\text{pump}} \) = 400 \( \mu \text{m} \) | pump spot diameter                           |
| \( \theta_{\text{pump}} \) = 40°           | pump incidence angle                         |
| \( \theta_{\text{film}} \) = 19°          | pump angle in the film (with refr. index \( n \approx 2 \)) |
| \( d_{\text{film}} \) = 30 nm             | ZnO film thickness                           |
| \( \alpha_{\text{film}} \) = (50 nm\(^{-1} \)) | ZnO absorption coefficient                   |
| \( R = 0.2 \)                             | surface reflectance                          |

This formula accounts for reflectance losses and an effectively enlarged pump spot as well as film thickness at oblique incidence. It does not account for reflectance from the film-substrate interface which increases the absorption (in fact, here it would increase the intensity available for absorption by about 1%). With the experimental parameters above, the effective energy density of the pump was about 500 \( \mu \text{J}/\text{cm}^2 \), already taking into account 20% reflection losses. With a penetration depth of 50 nm in ZnO, roughly 45% of the pump power is absorbed in the film. The substrate is transparent for light of 266 nm wavelength. Furthermore, only about 87% of the entire pulse energy are contained within the 1\( \mu \)area which defines \( d_{\text{pump}} \). However, the latter is compensated by the non-even beam profile as we probe only the central 200\( \mu \)m of the 400\( \mu \)m diameter of the excited area. With the numbers above given, one arrives at \( N \approx 9.75 \times 10^{19} \text{ cm}^{-3} \).

It should be noted that we assume linear absorption. In fact, absorption bleaching of the material can also take place at the laser energy if the corresponding initial and final states are already empty or filled, respectively. This effect can only matter if the excitation pulse is sufficiently short so that carrier scattering cannot compensate for the bleaching during the time of the excitation pulse. In other words, there is a limit for the highest achievable density of excited electron-hole pairs for ultrashort laser pulses. Even with higher pump power, parts of that laser pulse would not be absorbed. This could be an explanation why the excitonic absorption peaks do not completely vanish, meaning the excitation density is overestimated. However, the estimated number of excited electron-hole pairs in the experiment here seems to be consistent with other works, using different pulsed laser sources. Finally, there are preliminary indications that shorter laser pulses in the order of 20 fs instead of 35 fs induce less IVB absorption. This hints at absorption bleaching.

VI. Charge carrier statistics

Upon optical pumping with a 266 nm \( (E_{\text{pump}} = 4.66 \text{ eV}) \) laser pulse, the excited electrons and holes obtain different amounts of excess energy, related to their effective masses (parabolic band approximation) \[S7\]:

\[
\Delta E_e = \frac{E_{\text{pump}} - E_{\text{gap}}}{1 + m_e/m_h}
\]

\[
\Delta E_h = \frac{E_{\text{pump}} - E_{\text{gap}}}{1 + m_h/m_e}
\]

With a bandgap energy of \( E_{\text{gap}} \approx 3.4 \text{ eV} \), electron effective mass \( m_e = 0.24 m_0 \) \[S8\] and hole effective mass \( m_h = 0.59 m_0 \) \[S9\] (\( m_0 \) being the free electron mass), it follows \( \Delta E_e \approx 0.90 \text{ eV} \) and \( \Delta E_h \approx 0.36 \text{ eV} \).

Assuming the free-electron/hole gas as an ideal gas, an average kinetic energy corresponding to the excess energy \( \Delta E_{e/h} \) is related to an effective temperature \( T_{e/h} \) by

\[
\Delta E_{e/h} = \frac{3}{2} k_B T_{e/h}
\]

with Boltzmann factor \( k_B \). From this, we can estimate initial effective temperatures for the charge carriers as \( T_e \approx 7000 \text{ K} \) and \( T_h \approx 2800 \text{ K} \).
While the effective charge-carrier temperatures express directly the average excess energy of excited electrons and holes, their density $N_e = N_h$ is given as [S10]:

$$N_e = N_C \frac{2 \pi}{2} \left( \frac{E_F - E_C}{k_B T_e} \right)$$

$$N_h = N_V \frac{2 \pi}{2} \left( \frac{E_V - E_h^F}{k_B T_h} \right)$$

with the Fermi-Dirac integral $F_{1/2}$. $E_{C/V}$ are the energies of the conduction-band minimum and valence-band maximum, respectively. The effective densities of states (DOS) at the conduction band minimum and valence band maximum are, respectively

$$N_C = 2 \left( \frac{m_e k_B T_e}{2 \pi \hbar^2} \right)^{3/2}$$

$$N_V = 2 \left( \frac{m_h k_B T_h}{2 \pi \hbar^2} \right)^{3/2}$$

It can be estimated that $N_C(T_e \approx 7000 \text{K}) \approx 3.3 \cdot 10^{20} \text{cm}^{-3}$ and $N_V(T_h \approx 2800 \text{K}) \approx 3.2 \cdot 10^{20} \text{cm}^{-3}$ for the estimated carrier temperatures. However, it should be noted that the temperature dependence of those effective DOS’s results only from a substitution of the integrating variable from $E$ to $E/k_BT_{e/h}$ when expressing $N_{e/h} = \int \text{DOS}(E)/(1 + e^{(E-E_{F}^{e/h})/k_BT_{e/h}}) dE$ through $F_{1/2}$ as above. When estimating quasi Fermi-energies for the hot charge carriers, it is important to understand both, their dependence on carrier density and temperature. Zero-temperature approximations do not hold. At a given temperature, a higher carrier density will clearly shift the quasi Fermi-energies towards/into the respective bands, i.e. $E_F^{e/h}$ increases and $E_{F}^{h}$ decreases. However, the effect of high temperatures at a given carrier density is more sophisticated: Evaluating the Fermi-Dirac integral with constant prefactors $N_{C/V}$ shows that the quasi Fermi-energies would shift further towards/into the bands if the effective temperatures are higher. On the other hand the temperature dependence of $N_{C/V}$ yields exactly the opposite and is even more dominant. Thus, in total, despite the high density of charge carriers, the quasi Fermi-energies are pushed into the bandgap due to the high carrier temperatures. Fitting the Fermi-Dirac integral to the initial density $N_{e/h} \approx 10^{20} \text{cm}^{-3}$ results in estimates on the order of $E_{F}^{e} - E_{C}^{e} \approx -660 \text{meV}$ and $E_{V}^{e} - E_{F}^{h} \approx -260 \text{meV}$ for the above-obtained effective temperatures. This means that both quasi Fermi-energies are within the bandgap, which is consistent with the numerical first-principles computations, see

\[1\] At room temperature, $N_C \approx 3 \cdot 10^{18} \text{cm}^{-3}$ and $N_V \approx 1 \cdot 10^{19} \text{cm}^{-3}$

\[2\] The term Fermi energy or Fermi level is used in consistency with most literature on semiconductors. However, precisely spoken, we refer actually to the chemical potential and note that Fermi energy is the limit of the chemical potential at zero temperature.

---

**Figure S7:** Quasi Fermi-energies and distributions at high charge-carrier temperature: a) quasi Fermi-energies for electrons (black) and holes (red) depending on the carrier temperature for a fixed carrier density of $10^{20} \text{cm}^{-3}$ and temperature. Zero-temperature approximations do not hold. At a given temperature, a higher carrier density will clearly shift the quasi Fermi-energies towards/into the respective bands, i.e. $E_F^{e/h}$ increases and $E_F^{h}$ decreases. However, the effect of high temperatures at a given carrier density is more sophisticated: Evaluating the Fermi-Dirac integral with constant prefactors $N_{C/V}$ shows that the quasi Fermi-energies would shift further towards/into the bands if the effective temperatures are higher. On the other hand the temperature dependence of $N_{C/V}$ yields exactly the opposite and is even more dominant. Thus, in total, despite the high density of charge carriers, the quasi Fermi-energies are pushed into the bandgap due to the high carrier temperatures. Fitting the Fermi-Dirac integral to the initial density $N_{e/h} \approx 10^{20} \text{cm}^{-3}$ results in estimates on the order of $E_{F}^{e} - E_{C}^{e} \approx -660 \text{meV}$ and $E_{V}^{e} - E_{F}^{h} \approx -260 \text{meV}$ for the above-obtained effective temperatures. This means that both quasi Fermi-energies are within the bandgap, which is consistent with the numerical first-principles computations, see

\[1\] At room temperature, $N_C \approx 3 \cdot 10^{18} \text{cm}^{-3}$ and $N_V \approx 1 \cdot 10^{19} \text{cm}^{-3}$

\[2\] The term Fermi energy or Fermi level is used in consistency with most literature on semiconductors. However, precisely spoken, we refer actually to the chemical potential and note that Fermi energy is the limit of the chemical potential at zero temperature.
Fig. S7. Compared with the intrinsic Fermi energy $E_F$ which is typically close the conduction-band minimum due to intrinsic free electrons, $E_F^0$ is shifted even further into the bandgap.

It should be noted that those estimates rely on parabolic approximations. The non-parabolicity of the bands yields another strong increase of the DOS through increasing effective masses for energies far from the minimum of the conduction and maximum of the valence band. A doubled effective mass causes the distances of the quasi Fermi-levels to the valence/conduction band maximum/minimum to increase to roughly twice the calculated values. For the conduction band with the obtained carrier temperature $T_e$ we can estimate from a non-parabolicity parameter on the order of 0.4 eV$^{-1}$ [S11] that $E_F^0-E_C$ should be in the order of 1 eV below the conduction band minimum [S12]. Assuming a similar non-parabolicity for the valence band results consequently in $E_V-E_F^0 \approx -300$ meV.

VII. First-principles simulations of excited electron-hole pairs at finite temperature

In order to describe excited electrons and holes, we use the framework described in detail in Refs. [S13, 14, 15]. In the following, we explain how this accounts for the effects of Pauli blocking, bandgap renormalization (BGR), and additional free-carrier screening on exciton binding energies and the spectral shape of the dielectric function.

We first focus on optically excited states at zero temperature. In this case, the lowest conduction-band states are occupied with free electrons of the density $N_e$ and the highest valence states with holes of the same density $N_h = N_e$. Hence, transitions between these states are excluded. This is described in our framework via occupation numbers of otherwise unchanged single-particle Kohn-Sham states. To account for Pauli blocking, we adjust these occupation numbers according to $N_h = N_e$ when computing the independent-particle dielectric function from the single-particle electronic structure and also when computing the BSE Hamiltonian.

The effect of BGR due to free carriers in the optically excited state is a many-body effect and here we use the model given by Berggren and Sernelius [S16, 17] for doped systems to describe it as an effective bandgap shrinkage. For a charge-carrier density of $10^{20}$ cm$^{-1}$, 311 meV shrinkage is assumed [S18].

Finally, our framework accounts for electronic interband screening of the electron-hole interaction in the BSE Hamiltonian, using the static dielectric constant obtained in independent-particle approximation, $\varepsilon_{\text{eff}} = 4.4$. In addition, as discussed earlier for doped ZnO [S13], excited carriers modify the electron-hole interaction by contributing intraband screening. In our framework, we approximate this contribution using the small-wave-vector limit of a static, wave-vector ($q$) dependent Lindhard dielectric function, which, in the presence of free electrons and holes becomes [S13, 14, 15]

$$\varepsilon_{\text{intra}}(q) \approx 1 + \frac{q^2 \varepsilon_{\text{TF}}}{q^2} + \frac{q^2 \varepsilon_{\text{TF},h}}{q^2},$$

(S8)

with the Thomas-Fermi (TF) wave vectors

$$q_{\text{TF},e/h} = \sqrt{\frac{3N_{e/h}e^2}{2\varepsilon_0\varepsilon_{\text{eff}}\tilde{E}_{\text{F}}^e/h}}.$$  

(S9)

The relative Fermi energies of electrons and holes, $\tilde{E}_{\text{F}}^e/h$, 

$$\tilde{E}_{\text{F}}^e/h = \frac{\hbar^2}{2m_{e/h}} \left(3\pi^2N_{e/h}\right)^{2/3},$$

(S10)

refer to the conduction-band minimum and valence-band maximum, $\tilde{E}_{\text{F}} = E_F^0 - E_{\text{CB}}$ and $\tilde{E}_{\text{F}}^h = E_{\text{VB}} - E_F^0$, respectively. Eq. (S8) then becomes

$$\varepsilon_{\text{intra}}(q) = 1 + \frac{3e^2}{\varepsilon_0\varepsilon_{\text{eff}}h^2q^2} \left(\frac{m_eN_e}{(3\pi^2N_e)^{2/3}} + \frac{m_hN_h}{(3\pi^2N_h)^{2/3}}\right).$$

(S11)

For equal excited electron and hole concentrations $N_h = N_e \equiv N$, this corresponds to

$$\varepsilon_{\text{intra}}(q) = 1 + \frac{1}{q^2} \frac{3Ne^2}{2\varepsilon_0\varepsilon_{\text{eff}}} \left(2\frac{(m_e + m_h)}{h^2} \frac{1}{(3\pi^2N)^{2/3}}\right).$$

(S12)

The term in parentheses in Eq. (S12) resembles Eq. (S10) and is, thus, a modified expression for the Fermi energy that accounts for excited electrons and holes in the screening expression. Effective electron and hole masses are parametrized using parabolic fits to our first-principles band-structure data, leading to $m_e = 0.3m_0$. For the hole
effective mass in Eq. (S12) we use the geometric average of the masses of the three degenerate uppermost valence bands, i.e. $m_h = 0.62 m_0$. This approach is valid for zero temperature of the free carriers and its implementation in our BSE code [S13] allows us to compute the dielectric function, including excitonic effects, as a function of free-carrier concentration $N$. We refer to this quantity as $\varepsilon_{\text{BSE}(N)}(E)$ in the following. In contrast, we use $\varepsilon_{\text{DFT}(N)}(E)$ to label the corresponding independent-particle dielectric-function that still accounts for Pauli blocking at zero temperature and BGR, but neglects excitonic effects. The difference between these two is $\Delta \varepsilon_{\text{exc}}(N, E)$:

$$\Delta \varepsilon_{\text{exc}}(N, E) = \varepsilon_{\text{BSE}(N)}(E) - \varepsilon_{\text{DFT}(N)}(E)$$  \hspace{1cm} (S13)

In order to account for the high carrier temperatures seen in the experiment, we use Fermi-distributed occupation numbers of electrons and holes. This turns the eigenvalue problem for the excitonic Hamiltonian into a generalized eigenvalue problem [S19]. Here we avoid this increase in computational cost and, instead, neglect the influence of temperature on excitonic effects; we only use Fermi-distributed occupation numbers when computing independent-particle spectra.

We then compute independent-particle dielectric functions for valence-conduction-band transitions ($\varepsilon_{\text{DFT}(N,T)}^{\text{VBCB}}(E)$), intra-valence-band transitions ($\varepsilon_{\text{DFT}(N,T)}^{\text{IVB}}(E)$), and intra-conduction-band transitions ($\varepsilon_{\text{DFT}(N,T)}^{\text{ICB}}(E)$). The latter two occur in the presence of holes in the valence and electrons in the conduction band, respectively. While this describes Pauli blocking, we use the same zero-temperature values for BGR to shift the bandgaps. Finally, we compute the temperature-dependent dielectric function as the sum of these three temperature-dependent independent-particle contributions and account for the influence of excitonic effects by approximating those with the zero temperature difference $\Delta \varepsilon_{\text{exc}}(N, E)$:

$$\varepsilon(N, T, E) \approx \varepsilon_{\text{DFT}(N,T)}^{\text{VBCB}}(E) + \varepsilon_{\text{DFT}(N,T)}^{\text{IVB}}(E) + \varepsilon_{\text{DFT}(N,T)}^{\text{ICB}}(E) + \Delta \varepsilon_{\text{exc}}(N, E)$$  \hspace{1cm} (S14)

Finally, to compare with experimental pump-probe data, we compute and visualize the difference

$$\Delta \varepsilon = \varepsilon(N, T, E) - \varepsilon_{\text{BSE}(N=0)}(T = 0 \text{ K}, E).$$  \hspace{1cm} (S15)

Figure S8 shows such a visualization along with experimentally obtained data.

Figure S8: Obtained versus computed $\varepsilon_2$ for high carrier excitation: a: Difference of the imaginary part $\varepsilon_2$ of the DF for excited and non-excited ZnO. Symbols represent experimental data at 200 fs, lines the computed DF assuming $10^{20} \text{ cm}^{-3}$ excited charge carriers with effective temperatures of 2800 K for holes and 7000 K for electrons. The inset shows a zoom into the IVB absorption range. b: Related $\varepsilon_2$ spectra.
VIII. Comparison of the dielectric function with existing models for highly excited ZnO and conventional transient spectroscopy

Figure S9: Obtained DF vs. DF model and conventional spectroscopy: a: DF of highly excited ZnO. Symbols represent the spectra obtained in this work at three different delays after photo-excitation. Lines show the expected spectra according to the model of Wille et al. for three different charge-carrier densities. b: Computed transient reflectance and c: transmittance difference spectra at normal incidence for a 30 nm thin ZnO film on fused silica substrate according to the DF’s in a. Note that although IVB absorption sets in, transmittance at lower energies increases upon pumping while reflectance decreases. This is caused by the lowered refractive index.

In comparison to ellipsometry, conventional reflectance and transmittance measurements lack any phase information of the electromagnetic waves interacting with the sample. This is usually compensated for by before-hand assumptions on the physical processes that, however, can lead to incorrect conclusions. Reflectance and transmittance spectra can be reconstructed from the knowledge of the DF. We generate reflectance spectra based on the DF obtained by time-resolved spectroscopic ellipsometry and compare them to theoretical values of Versteegh et al. [S20] which were refined by Wille et al. [S21]. The underlying DF of Wille et al. allows to explain gain and lasing mechanisms in ZnO micro- and nanowires [S22]. Both theoretical approaches are based on a solution of the Bethe-Salpeter equation [S23] for a simplified ZnO-like bulk system. The reflectance spectra are exemplary for various different pump-probe reflectance studies on ZnO [S24, 25, 26, 27]. Symbols in Fig. S9 show the DF as obtained in this work at selected pump-probe time delays; lines represent theoretical curves according to Wille et al. for various carrier densities. Both studies find a decrease in the real and the imaginary part of the DF with increasing carrier density. The model of Wille et al. is about 100 meV blueshifted and predicts $\varepsilon_2 < 0$ which can lead to optical gain and lasing. This is not observed in our experiment due to the reflection geometry. Optical gain can only occur due stimulated emission which produces photons of equal wavevector (magnitude and direction). So-called gain spectroscopy was only reported in transmission geometry. Furthermore, it is seen that the theoretical curve of Wille et al. is not able to explain the features related to exciton-phonon complexes at 3.4 eV since electron-phonon interaction is neglected in the model. In the spectral range far below the band gap which is not covered by Wille et al., we find increased absorption which is related to the IVB absorption.

The relative difference spectra of transmittance (panel b in Fig. S9) and reflectance (panel c) are computed for
a structure consisting of 30 nm c-plane oriented ZnO on a fused SiO\textsubscript{2} substrate which is equivalent to the sample studied in this work. Reflection from the substrate backside is ignored. Changes around the absorption edge of ZnO are on the same order of magnitude for both, using the DF from theoretical model (lines) and applying the DF obtained in this work. Surprisingly, in the spectral range of the IVB absorption the transmittance is increased although absorption appears. It is clear that the increased transmittance is related to decreased reflectance caused by the decrease in $\varepsilon_1$ and hence refractive index. This is in accordance with the Kramers-Kronig relations and is related to both, the occurring IVB absorption as well as the absorption bleaching at the absorption edge. We would like to emphasize here that interpretation of the conventional reflectance or transmittance changes can lead to erroneous conclusions about their physical origin because effects caused by changes in the real and imaginary part of the DF cannot be separated. Assuming a non-varying refractive index is insufficient and retrieval by exploiting the Kramers-Kronig relations is usually hampered by the limited spectral range.

References

[S1] M. Rębarz, M. Kloz, S. J. Espinoza Herrera, and C. D. Brooks. UV-VIS-NIR femtosekundový elipsoidometrický systém, užitný vzor 30838, Česká republika, úrad prumyslového vlastnictví, 2017. URL http://spiny.upv.cz/UtilityModels/FullDocuments/FDUM0030/uv030838.pdf.

[S2] R. A. Chipman. Polarimetry, in Handbook of Optics, chapter 22. McGraw-Hill, 1995. ISBN 9780070477407.

[S3] M. Lorenz. Pulsed Laser Deposition of ZnO-Based Thin Films, pages 303–357. Springer Berlin Heidelberg, Berlin, Heidelberg, 2008. ISBN 978-3-540-73612-7. doi:10.1007/978-3-540-73612-7.

[S4] U. Rössler. Energy bands of hexagonal II-VI semiconductors. Phys. Rev., 184:733–738, 1969. doi:10.1103/PhysRev.184.733.

[S5] R. C. Casella. Symmetry of wurtzite. Phys. Rev., 114:1514–1518, 1959. doi:10.1103/PhysRev.114.1514.

[S6] H. W. Streitwolf. Selection rules for the space group $c\bar{4}6v$ (wurtzite). Phys. Stat. Sol. B, 33:225–233, 1969. doi:10.1002/pssb.19690330120.

[S7] J. Shah. Hot electrons and phonons under high intensity photoexcitation of semiconductors. Sol. State Electron., 21:43–50, 1978. doi:10.1016/0038-1101(78)90113-2.

[S8] W. S. Baer. Faraday rotation in ZnO: Determination of the electron effective mass. Phys. Rev., 154:785–789, 1967. doi:10.1103/PhysRev.154.785.

[S9] K. Hümmer. Interband magnetoreflection of ZnO. Phys. Stat. Sol. B, 56:249–260, 1973. doi:10.1002/pssb.2220560124.

[S10] M. Grundmann. The Physics of Semiconductors: An Introduction Including Nanophysics and Applications. Springer, third edition edition, 2016.

[S11] W. A. Hadi, S. K, O’Leary, M. S. Shur, and L. F. Eastman. The sensitivity of the steady-state electron transport within bulk wurtzite zinc oxide to variations in the non-parabolicity coefficient. Solid State Commun., 151(12):874–878, 2011. doi:10.1016/j.ssc.2011.04.004.

[S12] R. Beresford. Statistical properties of an ideal nonparabolic Fermi gas. J. Appl. Phys., 70(11):6834–6841, 1991. doi:10.1063/1.349831.

[S13] A. Schleife, C. Rödl, F. Fuchs, K. Hannewald, and F. Bechstedt. Optical absorption in degenerately doped semiconductors: Mott transition or Mahan excitons? Phys. Rev. Lett., 107:236405, 2011. doi:10.1103/PhysRevLett.107.236405.

[S14] A. Schleife. Electronic and optical properties of MgO, ZnO, and CdO. Südwestdeutscher Verlag für Hochschulschriften, 2011. ISBN 3838127668.

[S15] K. Kang, A. Kononov, C.-W. Lee, J. A. Leveillee, E. P. Shapera, X. Zhang, and A. Schleife. Pushing the frontiers of modeling excited electronic states and dynamics to accelerate materials engineering and design. Comput. Mater. Sci., 160:207–216, 2019. doi:10.1016/j.commatsci.2019.01.004.

[S16] K.-F. Berggren and B. E. Sernelius. Band-gap narrowing in heavily doped many-valley semiconductors. Phys. Rev. B, 24(4):1971–1986, 1981. doi:10.1103/PhysRevB.24.1971.
[S17] J. Wu, W. Walukiewicz, W. Shan, K. M. Yu, J. W. Ager, E. E. Haller, H. Lu, and W. J. Schaff. Effects of the narrow band gap on the properties of InN. *Phys. Rev. B*, 66(20):201403, 2002. doi:10.1103/PhysRevB.66.201403.

[S18] A. Kronenberger, A. Polity, D. M. Hofmann, B. K. Meyer, A. Schleife, and F. Bechstedt. Structural, electrical, and optical properties of hydrogen-doped ZnO films. *Phys. Rev. B*, 86:115334, 2012. doi:10.1103/PhysRevB.86.115334.

[S19] F. Bechstedt. *Electron-Hole Problem*, pages 439–457. Springer Berlin Heidelberg, 2015. ISBN 978-3-662-44593-8. doi:10.1007/978-3-662-44593-8_19.

[S20] M. A. M. Versteegh, T. Kuis, H. T. C. Stoof, and J. T. Dijkhuis. Ultrafast screening and carrier dynamics in ZnO: theory and experiment. *Phys. Rev. B*, 84:035207, 2011. doi:10.1103/PhysRevB.84.035207.

[S21] M. Wille, C. Sturm, T. Michalsky, R. Röder, C. Ronning, R. Schmidt-Grund, and M. Grundmann. Carrier density driven lasing dynamics in ZnO nanowires. *Nanotechnology*, 27:225702, 2016. doi:10.1088/0957-4484/27/22/225702.

[S22] M. Wille, T. Michalsky, E. Krüger, M. Grundmann, and R. Schmidt-Grund. Absorptive lasing mode suppression in ZnO nano- and microwires. *Appl. Phys. Lett.*, 109(6):061102, 2016. doi:10.1063/1.4960660.

[S23] H. Haug and S. W. Koch. *Quantum Theory of the Optical and Electronic Properties of Semiconductors*. World Scientific, 1990. doi:10.1142/0936.

[S24] T. Shih, E. Mazur, J.-P. Richters, J. Gutowski, and T. Voss. Ultrafast exciton dynamics in ZnO: excitonic versus electron-hole plasma lasing. *J. Appl. Phys.*, 109(4):043504, 2011. doi:10.1063/1.3549614.

[S25] T. Shih, M. T. Winkler, T. Voss, and E. Mazur. Dielectric function dynamics during femtosecond laser excitation of bulk ZnO. *Appl. Phys. A*, 96(2):363–367, 2009. ISSN 0947-8396. doi:10.1007/s00339-009-5196-0.

[S26] P. C. Ou, J. H. Lin, and W. F. Hsieh. Spectral dependence of transient reflectance in a ZnO epitaxial film at room temperature. *Appl. Phys. B*, 106:399–404, 2012. doi:10.1007/s00340-011-4706-x.

[S27] C. J. Cook, S. Khan, G. D. Sanders, X. Wang, D. H. Reitze, Y. D. Jho, Y.-W. Heo, J.-M. Erie, D. P. Norton, and C. J. Stanton. Ultrafast carrier relaxation and diffusion dynamics in ZnO. *Proc. SPIE*, 7603:7603–7603–14, 2010. doi:10.1117/12.845636.