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Citation: [Journal of Applied Physics](#) **115**, 053508 (2014); doi: 10.1063/1.4864017

View online: <https://doi.org/10.1063/1.4864017>

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Ultrafast dynamics of the dielectric functions of ZnO and BaTiO₃ thin films after intense femtosecond laser excitation

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(Received 19 December 2013; accepted 21 January 2014; published online 4 February 2014)

The ultrafast carrier dynamics of epitaxial ZnO and BaTiO₃ thin films after intense excitation at 3.10 eV and 4.66 eV photon energy has been studied by femtosecond absorption spectroscopy. Modelling the transient transmission changes on the basis of spectroscopic ellipsometry data and pertinent equilibrium model dielectric functions extended by additional terms for the effects at high carrier density (P-band luminescence and stimulated emission from electron-hole-plasma), a self-consistent parameterized description was obtained for both materials. Excited carrier lifetimes in the range of ≈ 2 to ≈ 60 ps and long-lived thermal effects after several hundred ps have been identified in both materials. These findings form a reliable basis to quantitatively describe future femtosecond studies on ZnO/BaTiO₃ heterolayer systems. © 2014 AIP Publishing LLC.
[\[http://dx.doi.org/10.1063/1.4864017\]](http://dx.doi.org/10.1063/1.4864017)

I. INTRODUCTION

Coupling effects at the interfaces of oxidic materials with different optical, electric, or magnetic properties promise novel functionality for future optoelectronic devices. For example, it has been shown recently that in heterostructures composed of thin films of ZnO and BaTiO₃ (BTO), ferroelectric polarization in the BTO layer influences the electrical¹ as well as optical behaviour² of the films, i.e., the dielectric function of the heterostructure. Since both materials are transparent in the visible range, such systems are quite attractive for opto-electronic and especially all-optical applications, allowing switching by ultrafast laser pulses.

Femtosecond pump-probe techniques are well-established and powerful tools to study the ultrafast properties of thin films. However, the interpretation of the physical processes leading to the ultrafast optical changes observed in such experiments depends, not least due to the interferometer character of thin films, on knowing as exactly as possible the dielectric function and its transient changes upon fs laser excitation. In the case of heterostructures, a comprehensive understanding of the single layers is a prerequisite, because the coupling between the layers is expected to add further effects.

As the material ZnO has remarkable application potential, e.g., as transparent electrodes or as light emitter showing stimulated emission and lasing in the high excitation regime,^{3–5} its carrier dynamics has been the subject of numerous studies in the last years.

For *bulk* ZnO, these activities have led to a fairly complete picture of the ultrafast processes after fs laser excitation, based on experimental techniques like time-resolved photoluminescence (PL),⁶ transient reflection^{7,8} or optical

pump-THz probe spectroscopy⁹ and corresponding theoretical work.¹⁰ For epitaxial ZnO *thin films*, the current picture of their carrier dynamics is still subject of some discussion, though several individual aspects like saturation of exciton absorption, band-gap renormalization, and stimulated emission (optical gain) have been deduced from experiments in the pico- and femtosecond time range.^{11–15} In the case of BaTiO₃, its ferroelectric properties are in the focus of interest; thus, femtosecond laser-based studies have so far only been conducted on the ultrafast switching properties^{16,17} rather than carrier dynamics.

In this work, we investigate the ultrafast carrier dynamics of epitaxial ZnO and BTO thin films by absorption spectroscopy after intense fs laser sub-band-gap ($h\nu_{\text{exc}} = 3.10$ eV) or above-band-gap ($h\nu_{\text{exc}} = 4.66$ eV) excitation. Goals are first to consolidate (ZnO) or acquire (BTO) the physical picture of the ultrafast dynamics after femtosecond excitation. Second, model descriptions based on the results of spectral ellipsometry will be developed for both materials, which allow comprehensive simulations of the transient optical changes in thin films after intense fs laser excitation. The simulation of (transient) spectra is done using the transfer matrix formalism based on model dielectric functions, so that this concept can easily be extended to multilayer systems. In view of the use for multilayer systems, we propose and employ a preferably simple description, with the main goal to parameterize the dynamics of individual physical processes in the single layers. This should open the way to easily identify interfacial or coupling effects in ZnO-BaTiO₃ heterostructures.

II. EXPERIMENTAL

The experiments reported here have been performed on epitaxial, nominally undoped ZnO films (film thickness $d \approx 370$ nm) grown by pulsed laser deposition on *a*-plane

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sapphire substrates. All experiments were performed at room temperature. The thin films are *c*-axis oriented and are characterized by a smooth surface morphology with an r.m.s. roughness of ≈ 1.5 nm, determined by help of atomic force microscopy. The typical crystallite size, estimated from X-ray diffraction results, is ≈ 120 nm. PL measurements performed on the samples indicated the presence of shallow and deep defect states. BaTiO₃ films ($d \approx 82$ nm) were also grown by pulsed laser deposition on *a*-plane sapphire substrates.

Spectroscopic ellipsometry (cw) was performed on the ZnO and BTO samples in a wide spectral range from 0.75 eV to 4.55 eV. From the ellipsometry data, a dielectric function $\epsilon(\lambda)$ was obtained for each sample, by means of a model dielectric function approach

$$\epsilon_{\text{ZnO}} = \epsilon_{de} + \epsilon_{ce} + \epsilon_{fe} + \frac{A_{pol}E^2}{E_{pol}^2 - E^2}, \quad (1)$$

$$\epsilon_{\text{BTO}} = \epsilon_{cpm0} + \epsilon_{gau} + \frac{A_{pol}}{E_{pol}^2 - E^2}. \quad (2)$$

The model dielectric function suggested by Yoshikawa and Adachi¹⁸ was used for analysis of the ZnO data. From left to right in Eq. (1), the terms represent absorptive interaction due to discrete excitons (subscript “de”), continuum excitons (“ce”), and free electrons (“fe”). The valence band in ZnO is split into three doubly degenerate bands due to spin orbit and crystal field interactions,^{18,19} giving rise to three band-gap energies (E_{oA} , E_{oB} , and E_{oC}) at the Γ point. Band-to-band as well as excitonic transitions corresponding to each of the gaps has been considered. Core-excitonic transitions are also considered in form of an additional constant $\epsilon_{l_{off}}$ (real part only). To take into account transient thermal effects (which might arise after intense excitation), a formalism for temperature dependence of band gap and discrete exciton broadening was incorporated into the model;²⁰ the required coefficients are taken from Ref. 20. It should be noted that only the dielectric function for light polarized perpendicular to the *c*-axis is relevant for the used configuration of the pump-probe set-up. The dielectric function of BTO was modeled using three Gaussian shaped oscillators (“gau”) representing higher band-to-band transitions and the Adachi model²¹ for transitions at M0 critical point (“cpm0”). For both the cases, transitions at energies above the measured spectral range (i.e., with resonance deep into the UV) were accounted for by adding an undamped harmonic oscillator to the formalism²² (A_{pol} and E_{pol} are fit parameters while E is the photon energy).

Feeding this dielectric function together with film thickness and refractive indexes of air and sapphire substrate in a transfer matrix formulation, the ground state transmission $T_0(\lambda)$ (or the respective optical density (OD)) of the sample can be simulated in excellent agreement with the experimental spectra (see Fig. 1). The pertinent best fit parameters are well compatible to the ellipsometry data of the same sample. For reference, the respective band-gap energies of ZnO and BTO used for the simulation are tabulated in Table I.

By variation of parameters in the dielectric function and, if necessary, additional terms, this description is also used to model the laser-induced changes of OD in the pump-probe experiment (see below).

FIG. 1. Experimental and simulated linear extinction spectra of ZnO ($d \approx 365$ nm) and BTO ($d \approx 82$ nm) sample on sapphire substrates.

Physically, the strong absorption of ZnO at wavelengths shorter than 375 nm is due to transitions into the conduction band, with a pronounced exciton peak around $\lambda = 370$ nm. Toward longer wavelengths an Urbach tail of the absorption edge is clearly visible, followed by interference modulations in the transparency range. In the case of BTO, no excitonic absorption features are present.

Femtosecond pump-probe measurements were performed in transmission geometry and the setup used was basically the same as described in detail in Ref. 23. Briefly, the frequency doubled ($\lambda \approx 400$ nm; $h\nu_{exc} = 3.10$ eV) or tripled ($\lambda \approx 266$ nm; $h\nu_{exc} = 4.66$ eV) output of a ≈ 150 fs, 1 kHz repetition rate *Spitfire* Ti:Sapphire regenerative amplifier was used as excitation pulses for the experiments. For convenience, they will be called Pu-400 and Pu-266 hereafter. Supercontinuum fs pulses generated by focussing a part of the Pu-400 beam to a sapphire plate were used as probe pulses, which are passing a delay line with a maximum pump-probe delay of ≈ 1 ns. After suppressing the strong residual intensity around $\lambda = 400$ nm with yellow coumarin dye solution, the resulting smooth broadband probe is split into a reference and a signal part. Using two identical grating spectrometers with detector arrays, a transmission spectrum of the sample is obtained for every individual laser shot. Blocking every second excitation pulse with a chopper, the sample transmission with (T) and without (T_0) excitation is measured, i.e., the change of optical density $\Delta OD = \log(T_0/T)$ is recorded with an effective repetition rate of 500 Hz. Time-resolved data shown below were recorded by averaging over 1000 laser shots. The chirp of the fs broadband probe pulses was determined using the ultrafast non-linear response of methanol,²⁴ yielding the zero time delay with an

TABLE I. Band-gap energies used for modelling ground state dielectric function of ZnO and BTO.

ZnO	E_{oA}	3.371 eV
	E_{oB}	3.380 eV
	E_{oC}	3.457 eV
BTO	E_{cpm0}	3.686 eV

accuracy of ≈ 50 fs at any wavelength within the broadband pulse. Over all, the setup provides a temporal resolution of ~ 150 fs for both excitation wavelengths.

All experiments were conducted using high pump intensity, addressing the high excitation regime of ZnO. For Pu-266, this was realized using laser pulse fluences in the range of 2–10 mJ/cm², which is at least one order of magnitude below the UV damage threshold of ZnO^{25,26} of ≈ 115 mJ/cm². Typically, the same distance to damage threshold (which is significantly higher at $\lambda = 400$ nm due to much lower absorption coefficient compared with $\lambda = 266$ nm) was kept for Pu-400 by using excitation energy densities in the range of 15–75 mJ/cm². The maximum charge density n_p achieved by the pump pulse can be estimated by^{9,14}

$$n_p = \frac{\Phi_{Pu} \cdot \alpha_{ZnO}(\lambda_{Pu})}{h\nu_{Pu}} \left(\frac{2}{1 + n_{ZnO}(\lambda_{Pu})} \right)^2. \quad (3)$$

Inserting the strongly different absorption coefficients of ZnO at $\lambda = 400$ nm ($\alpha_{400\text{ nm}} \approx 75 \text{ cm}^{-1}$) or $\lambda = 266$ nm ($\alpha_{266\text{ nm}} = 1.64 \times 10^5 \text{ cm}^{-1}$), the lowest laser fluences yield $n_p \approx 0.9 \times 10^{18} \text{ cm}^{-3}$ (Pu-400, $\Phi_{Pu} = 16 \text{ mJ/cm}^2$) or $n_p \approx 2.1 \times 10^{20} \text{ cm}^{-3}$ (Pu-266, $\Phi_{Pu} = 2 \text{ mJ/cm}^2$). Irrespective of a recent discussion about the correct value of the Mott density n_M of ZnO (Versteegh *et al.*¹⁰ argued that the established value at room temperature of $n_M \approx 3.7 \times 10^{19} \text{ cm}^{-3}$ is too large by a factor of 8π and should rather be $n_M \approx 1.5 \times 10^{18} \text{ cm}^{-3}$), our experiments are clearly performed in the region of the Mott density or even above. Thus, the well-known effects^{10,13,27} like screening of exciton resonances, band gap renormalization (BGR), and band filling (optical gain) have to be expected.

Fig. 2 shows examples for the transient spectral changes in ZnO after excitation at $\lambda = 400$ nm and 266 nm, respectively, referring to a few characteristic delay times up to 500 ps in each case.

The results for Pu-400 (fluence: 48 mJ/cm²) are given in Fig. 2(a), those for Pu-266 (fluence: 4 mJ/cm²) in Fig. 2(b). In the lower panel of Fig. 2(a), the main spectral changes at an early delay time of 400 fs after sub-bandgap excitation are observed at wavelengths shorter than the pump pulse: (i) a strong and rather narrow bleaching (negative ΔOD) at ≈ 375 nm, (ii) a strong increased extinction peaked at ≈ 382 nm, and (iii) a second, broader bleaching band around 390 nm. At wavelengths longer than 400 nm, a few broad modulations around $\Delta OD = 0$ are seen. Towards later time, the strong positive peak at ≈ 382 nm fades out within less than 1 ps, while the two bleaching bands are still rise until, after 1–2 ps, they start to decrease on a slower timescale of several picoseconds. Finally, an additional absorption increase centred at 377 nm is seen to emerge from ≈ 50 ps onwards, which later remains constant up to the maximum delay range accessible in our study (≈ 1 ns). The underlying dynamics will be discussed in Sec. IV.

For BTO, the same fluence ranges have been applied; this causes again high carrier density under Pu-266, but no considerable carrier excitation for Pu-400 because of the large distance to the BTO band gap. In view of experiments on multilayer samples, this choice of excitation wavelengths

FIG. 2. Transient spectral changes in ZnO at selected delay times for excitation with (a) Pu-400 and (b) Pu-266; individual curves vertically shifted for visibility.

allows selective injection of carriers in only one material by irradiating with Pu-266 from either side of a two-layer structure; Pu-400 in contrast allows, due to the different transmission properties at this wavelength, selective excitation of ZnO even in multilayer structures.

III. MODELLING OF TRANSIENT SPECTRAL DATA

In this chapter, we will demonstrate exemplarily our modelling approach, and at the same time identify the main ultrafast physical contributions in ZnO after intense excitation. The general spectral features of the transient spectra after above band-gap excitation (Pu-266) are similar to the Pu-400 case, though with differing relative amplitudes (upper panel in Fig. 2(b)). The most prominent difference, however, is seen at the earliest delay time (lower panel in Fig. 2(b)): instead of the two bleaching peaks, only a very strong band of increased optical density is seen at 380 nm, neighboured by a very broad and negligibly weak transmission increase (negative ΔOD) at ≈ 450 nm. Apparently, the complex overlap of several effects constituting the transient spectral data discourages analysing the dynamics of the underlying physical processes directly from time-resolved data at fixed wavelength positions. Instead, a model-based simulation was used starting with the dielectric function $\epsilon(\lambda)$ of the ZnO layer as detailed above.

The straightforward approach to synthesize the experimentally observed spectral changes induced by the pump pulse is modifying the parameters of the ground state dielectric function such that the transient sample transmission $T(\lambda, t)$ at time t after pump pulse provides a good simulation of the transient ΔOD spectra at all delay times t by using the equation

$$\Delta OD_{sim}(\lambda, t) = \log \left(\frac{T_0(\lambda)}{T(\lambda, t)} \right). \quad (4)$$

However, trying to fit the available data with this approach, it turned out that neither the induced absorption at 382 nm nor the increased transmission around 390 nm can be explained by any parameter in the model dielectric function. Obviously, these changes are not related to ground state transitions, but must be due to transitions starting from excited levels or many body effects. As has been previously emphasized, the intention is to keep the approach preferably simple, for application to multilayer systems. Therefore, to incorporate these high excitation density effects into the mathematical framework, we chose the empirical approach to simply add Gaussian functions at the appropriate spectral positions

$$\Delta OD_{sim}(\lambda, t) = \Delta OD_{Ad}(\lambda, t) + \sum_i G_i(\lambda, t). \quad (5)$$

The additional i Gaussians have to be understood as tools to parameterize the dynamics at the respective spectral position; the physical meaning of these contributions is then identified by comparison to literature results. With these ingredients, the nonlinear least square trust-region optimization routine was implemented to optimize the parameters in the model to fit the experimental spectrum for any delay time. As an illustration, the simulated spectra along with individual contributions for the spectral changes measured at a delay time of 0.5 ps are shown in Fig. 3.

The main contributions stemming from the model dielectric function of ZnO are the following: (i) Variation of the amplitude of discrete exciton-A (transitions corresponding to the components A, B, and C of the valence band to the

lowest conduction band in ZnO are included in the model) to explain the transmission increase at $\lambda \approx 375$ nm. (ii) Variation of the amplitude of ϵ_{1off} (labelled as “refr. index” in Fig. 3) is required for simulating the modulations in the visible region of the spectrum ($\lambda \geq 400$ nm). However, it also results in a positive component in the spectral region of $\lambda < 375$ nm; a correlated contribution “cont.ex-A” (amplitude of continuum exciton-A) provides the necessary compensation. The required additional Gaussian curves at $\lambda \approx 382$ nm and $\lambda \approx 390$ nm are tentatively assigned to “BGR” and stimulated emission (“electron-hole plasma (EHP)”), as will be discussed below. The positive ΔOD band at $\lambda = 377$ nm occurring at later delay times is attributed to a small temperature rise in the focal volume after carrier relaxation, which can approximately be modelled through the temperature dependent band-gap and exciton broadening.²⁰ Using all these contributions, simulated spectra obtained by the optimization routine are in good agreement with the experimental time resolved spectra; the sum of squared residuals is of the order of 10^{-3} .

To extract the dynamics, the changes of optical density at all delay times have been fitted. For that, the same (selected) set of parameters was consistently varied over the entire time sequence. For the contributions from the model, dielectric function only amplitude (of discrete and continuum exciton-A, ϵ_{1off}) and temperature are allowed to vary; for the two Gaussian bands, also a small variation (corresponding to the experimental accuracy of the spectra) of position and spectral width was allowed. For each contribution, its temporal evolution is then obtained by plotting the area under the curve as a function of delay time; the decay of these curves was fitted with single or multi exponential functions (wherever applicable) in order to make a quantitative approximation of the relaxation time scales. The accuracies of parameters specified below refer to the statistical errors of this procedure. Finally, the assignment of the empirically introduced additional terms to the corresponding physical processes was done on the basis of their spectral position, width, and temporal behaviour.

IV. RESULTS AND DISCUSSION

A. Excitation process and short time dynamics in ZnO

Before discussing the dynamical evolution of the physical effects occurring after strong excitation, we want to analyse the excitation process itself in more detail. In particular, the low absorption coefficient of ZnO at $\lambda = 400$ nm ($\alpha_{400 \text{ nm}} \approx 75 \text{ cm}^{-1}$) forces the question if the below bandgap pump causes a mainly linear excitation directly to the band edge, or involves a significant contribution of nonlinear excitation to higher band states. To get a hint, we analyse the bleaching peak at 375 nm (at a delay time of ≈ 1 ps) which corresponds to the position of discrete exciton-A. No matter if this bleaching is caused by transient population or reduction of the exciton resonance via screening, its amplitude can be taken as a relative measure of the charge density n_p . Fig. 4 shows the respective peak amplitude (here a negative ΔOD) to increase clearly more than linearly with increasing laser pulse fluence, as illustrated by the linear (red dashed line)

FIG. 3. (a) Different contributions to the transient spectra of ZnO (delay time: 0.5 ps, ν_{pu} : 400 nm), vertically shifted for visibility; (b) simulated (dashed curve) and experimental transient spectrum at a delay time of 0.5 ps.

FIG. 4. Maximum of transmission increase at 375 nm as a function of pump fluence (excitation $\lambda = 400$ nm).

and second-order polynomial (blue solid line) best fit curves. For the latter, the relative weight of the quadratic term (given individually as dashed-dotted line together with the linear term—short dashed curve) is 13% to 42% of the total amplitude, respectively, for lowest and highest fluence. Thus, apparently the Pu-400 experiments feature not only direct excitation to the conduction band edge, but also an additional nonlinear, most probably two-photon absorption (TPA) process^{28–30} higher into the conduction band states.

In contrast, Pu-266 is exciting carriers definitely to states higher in the conduction band, from where they first have to relax down to the band minimum to have an effect on the optical properties at the optical frequencies near the band gap.¹⁰ It has been reported that this carrier thermalization, occurring mainly via interaction with LO (longitudinal optical) phonons and acoustical phonons, may take between several hundred femtoseconds¹⁰ and a few picoseconds.^{31,32} The time evolution of the build-up of bleaching observed at $\lambda \approx 375$ nm can be used to verify these ideas: Fig. 5 shows the relative amplitude changes of the exciton-A term in the model dielectric function needed for the best fit of experimental data, plotted as a function of delay time. Clearly the exciton absorption decreases immediately with the pump

FIG. 5. Early time behaviour of exciton bleaching for excitation of the ZnO sample by Pu-400 and Pu-266.

pulse around delay time zero for Pu-400, indicating that a part (at least about 50%) of the excited carriers is delivered directly to exciton states. The peak value however is only achieved after 1 ps, indicating an additional, delayed source of the bleaching—most probably the carriers excited by TPA.

For Pu-266, bleaching only starts with a delay of ≈ 700 fs (the open symbols at earlier delay times indicate that positive values have been suppressed in the fit procedure), reaching its maximum after about 2 ps. As these experiments definitely refer to carrier concentration above Mott density, the observed bleaching must be attributed to screening of the exciton resonance by highly excited carriers, which relax to the conduction band minimum within 2 ps to form EHP there.

The occurrence of EHP or, more general, band-filling can be the origin of optical gain, which is the obvious explanation for the other observed bands of negative ΔOD : the one seen at 390 nm for Pu-400 can be explained by stimulated emission corresponding to the P-band of ZnO which owes its origin to exciton-exciton scattering,^{33,34} to include this in our model, a simple Gaussian at 390 nm was sufficient.

The positive ΔOD band around $\lambda = 382$ nm is attributed to BGR, which causes a red-shift of the absorption edge³⁵ for high density of excited charge carriers. Simulation of the contribution by a simple variation of band gap energies (in the formalism for ground state dielectric function) is not possible, because band-structure calculations have shown that the effect cannot be described as a rigid shift of the band-edges.³⁶ Even more important concern regarding inclusion of BGR into the formalism is that, various vastly different models for the BGR of ZnO are reported in literature.¹⁰ Therefore, to simply handle the BGR transient effects in the fitting process, a Gaussian curve (or a convolution of Gaussians to fit the asymmetric line shape of the contribution when necessary) has been included in the model. Using a fixed position, variable width and allowing only positive amplitude for this band, very satisfactory fit quality could be achieved.

As shown in Fig. 6 for Pu-400, the BGR is the fastest effect rising immediately with the generation of free carriers.

FIG. 6. Early time evolution of band gap renormalization, exciton bleaching and stimulated emission (excitation $\lambda = 400$ nm) in ZnO.

As soon as these carriers have formed excitonic states and/or EHP, the BGR effect does not have to be included any more to achieve good fit quality for delay times larger than ≈ 1 ps. Most probably, band filling and the resulting optical gain are over-compensating the BGR effect after that time. The slightly delayed growth of stimulated emission compared with exciton bleaching confirms that the latter has a significant contribution from direct population of the exciton states by linear absorption of Pu-400 photons.

For completeness, the time behavior due to the term $\varepsilon_{1\text{off}}$ (compare Fig. 3), is given by the black squares in Fig. 6. A distinct physical interpretation cannot be given: every excitation of an electron will cause changes in the available transitions; and the real parts of the dielectric function of the respective transitions to higher bands (UV absorption) are in the visible range mainly seen as refractive index change. Roughly spoken, the term $\varepsilon_{1\text{off}}$ represents the total number of excited carriers, but is insensitive to their special energetic state. The changed refractive index is observed as a shifted interference pattern in the linear transmission spectra after pump excitation, and hence as spectral modulations in the differential spectra.

B. Excitation process and short time dynamics in BaTiO₃

Conducting pump-probe experiments on a BTO sample using Pu-400 pulses in the same intensity range as for ZnO yielded no indication for carrier excitation: only a weak signal around delay time zero (“coherent artifact”) has been observed, which is mainly due to the sapphire substrate. For delay times ≥ 200 fs, no signal (ΔOD) was found within experimental accuracy in this case.

For Pu-266, however, the above band-gap excitation leads to considerable transient changes also in the spectral range accessible with our setup, as shown in Fig. 7: within the first 500 fs, a broad induced absorption around $\lambda \approx 520$ nm (2.38 eV) arises. Within the next picosecond, this band broadens further towards shorter wavelengths and starts to decrease; while at ≈ 340 nm another induced absorption starts to increase. The latter effect can be modelled by a combined variation of the band-gap (E_g) and broadening of band-to-band transitions (Br_0) in the dielectric function of

FIG. 7. BTO: Transient spectral changes at selected delay times for excitation with Pu-266; individual curves vertically shifted for visibility.

BTO. Thus, this effect can be assigned to a temperature rise in the sample as a consequence of the relaxing carriers. The band around 2.38 eV, however, is not included in the ground state dielectric function. Since impurities like Mn can give rise to acceptor levels ≈ 1.3 eV above the valence band edge of BTO,³⁷ the broad induced extinction is most probably caused by excited electrons relaxing from the conduction band to these acceptor levels. The spectral shift and broadening of the band observed within the first 1-2 ps indicate that the higher-lying impurity states are populated faster than those with larger energy distance to conduction band—which is quite plausible assuming a non-radiative, phonon-assisted process. For the fit procedure, we parameterize this band by using a single Gaussian with variable central position and width. An example for the fitting is given in Fig. 8, referring to a delay time of 3 ps.

C. Carrier relaxation dynamics in ZnO

After identifying the different contributions to the transient spectra and their build-up after excitation, we can now analyse the relaxation dynamics of the excited carriers (excitons). We restrict the discussion for ZnO to the Pu-400 results, where only one well-defined band of stimulated emission is present and, more generally, we can assume constant excitation density through the whole sample thickness because of the low linear absorption coefficient. It should be stated here that we have evaluated the Pu-266 results in the same way, and the results are fully compatible to the findings detailed below.

The main effects observable for delay times larger than 1 ps (i.e., when the BGR effect is no longer required in our model), namely, exciton bleaching and stimulated emission, reach their maximum amplitude via carrier thermalization only after 1 ps to ~ 2 ps, and then relax on a slower time scale stretching out to several hundred picoseconds, so that their decay dynamics can be traced very well. As can be clearly seen on the examples in Fig. 9, double-exponential decays provide very reasonable fits of the data, at least for delay times ≥ 2.5 ps (which was the range used for our fits). The

FIG. 8. (a) Different contributions to the transient spectra of BTO (delay ≈ 3 ps, ν_{pu} : 266 nm); (b) comparison of simulated and experimental spectral changes.

FIG. 9. Temporal evolution of exciton bleaching and stimulated emission (fluence: 48 mJ/cm²).

obtained fast and slow time constants, within experimental accuracy independent of laser fluence are $\tau_{1b} = (2.1 \pm 0.2)$ ps and $\tau_{2b} = (29 \pm 1)$ ps for exciton bleaching; $\tau_{1s} = (6.5 \pm 0.6)$ ps and $\tau_{2s} = (62 \pm 5)$ ps for stimulated emission at $\lambda = 390$ nm. The relative amplitude of the fast component (τ_{1x}) grows in both cases towards higher fluence. It should also be mentioned that the stimulated emission band develops an earlier peak towards higher fluence (at $t_{Del} = 0.6$ ps applying 80 mJ/cm²), followed by a fast decay until $t_{Del} = 2$ –2.5 ps.

The interpretation of the time constants depends partially on the correct value of the Mott density of ZnO (see Sec. II). We tend to follow the arguments of Versteegh *et al.*¹⁰ and thus take their value of $n_M \approx 1.5 \cdot 10^{18}$ cm⁻³ as basis of our discussion. Then, the peak carrier density achieved in our Pu-400 experiments ranges from slightly below to clearly above n_M for the range of laser fluences applied.

Under those circumstances, the initially high carrier density n_p would suppress the exciton-A absorption, and the fast decay ($\tau_{1b} \approx 2$ ps) can be understood as decrease of n_p by trapping of carriers at intrinsic defect states (the observed decay times are consistent with the trapping time reported in literature^{10,38}) leading to recovery and population of the exciton states. The slow decay (τ_{2b}) is then attributed to the exciton recombination. The measured lifetime of 29 ps is considerably smaller than the ≈ 90 ps reported in the literature for bulk ZnO³⁹ or much thicker films.¹³ A possible explanation for that is found in the crystallite size of ≈ 120 nm in our sample, which may give rise to additional non-radiative recombination processes at the grain boundaries.

For the stimulated emission, the initial fast component at high fluence is most probably due to recombination directly out of the EHP, while the two obtained time constants τ_{1s} and τ_{2s} of the bi-exponential decay possibly describe different processes. It has been observed before that for moderate to high intensity excitation in ZnO different recombination mechanisms can contribute to the emission at the same spectral position.²⁹ The slower decay time of ≈ 60 ps can be identified with the recombination of shallow trapped electrons with deep trapped holes; time-resolved measurements of the visible emission band in ZnO showed that these processes occur within a time scale of several

hundred picoseconds.^{39,40} Consequently, the faster decay with $\tau_{1s} \approx 6.5$ ps can be attributed to the exciton-exciton scattering process of the P-band luminescence leading to recombination of one of the interacting excitons.

Although radiative recombination is an important part of the carrier relaxation, a considerable part of the initially absorbed laser pulse energy will be transferred to the lattice by carrier-phonon scattering. The resulting temperature rise ΔT in the focal volume and the resulting change of the electron distribution is the apparent reason for the weak band of induced absorption around $\lambda \approx 377$ nm observed as the only remaining spectral feature at late delay time $t_{Del} \geq 500$ ps. The magnitude of ΔT can be estimated by

$$\Delta T = (\Phi_{Pu})_{eff} / c \cdot \rho \cdot d, \quad (6)$$

where ρ and c are density and heat capacity of ZnO, d is the layer thickness, and $(\Phi_{Pu})_{eff}$ denotes the part of the laser pulse fluence which is actually absorbed and converted into phonons (heat). For Pu-400 and the intermediate fluence of 48 mJ/cm², one obtains a value of $\Delta T = 1.3$ K, regarding that under linear absorption only less than 0.3% of the pulse energy is absorbed, and neglecting the energy being re-emitted in form of photons. Fig. 10 compares a numerical simulation calculated assuming a temperature increase of 1 K with the experimental spectrum obtained at $t_{Del} = 500$ ps after Pu-400 excitation with the above specified fluence. It is seen that the position and spectral shape of measured and simulated induced absorption correspond fairly well to each other.

Conduction of heat to the substrate will result in an actual lattice temperature lower than the estimated one, which explains the relatively smaller amplitude of the experimental peak. Another plausible reason for the discrepancy could be that the signal is averaged over the heated volume as well as non-illuminated areas, due to the slightly larger spot size of the probe relative to the pump at the sample. As can be expected, the amplitude of the contribution is relatively higher for the spectra pumped by Pu-266.

D. Carrier relaxation dynamics in BaTiO₃

Due to the absence of excitons, the carrier relaxation in BTO is quite clear: after excitation into the conduction band,

FIG. 10. Comparison of numerically simulated spectra assuming a temperature increase of 1 K to experimental spectra of ZnO at a time delay of 500 ps (ν_{Pu} : 400 nm).

FIG. 11. Temporal evolution of induced absorption in BTO (fluence: 48 mJ/cm²).

the electrons relax to the band minimum and are getting trapped into defect states within a few hundred femtoseconds, leading to the broad induced absorption around a wavelength of ≈ 520 nm. In line with the decay of this broad absorption, another band of positive ΔOD at $\lambda = 340$ nm is increasing, which can be explained by a temperature rise and the resulting effects to band gap and band-to-band transitions.

The dynamical behaviour of the broad 520 nm band is plotted in Fig. 11 as a function of delay time; the experimental points given there represent the area under the Gaussian curve that has been used to fit ΔOD at the respective time. That is, the signal refers to the total number of electrons being trapped at different defect states. Thus, it is not surprising that the relaxation cannot be explained by a mono-exponential decay. A very reasonable fit is possible with a sum of two exponentials with the decay time constants (2.6 ± 0.4) ps and (9.7 ± 2.6) ps, indicating that at least two different types of defects are contributing to the broad band.

The effects observed around 340 nm rise with approximately the same time constants as the induced absorption decays, and then remain constant for the whole delay range accessible in our experiments. This confirms that this band is due the temperature increase after relaxation of the excited carriers.

V. CONCLUSION

In conclusion, the ultrafast carrier dynamics of epitaxial ZnO and BaTiO₃ thin films has been studied by femtosecond absorption spectroscopy in the strong excitation regime, using photon energies for excitation below and above the material's band gap (3.10 eV and 4.66 eV, respectively). The observed transient spectral changes have been modelled in a transfer matrix formalism on the basis of spectral ellipsometry data of any individual thin layer. Using established model dielectric functions extended by additional terms for the effects at high carrier density (for ZnO around and above Mott density), self-consistent pictures of the ultrafast carrier dynamics could be established for both materials. In particular, a direct population of exciton states was observed for the below-band gap pumping in ZnO. Mediated by an additional two-photon absorption process, carrier excitation above Mott density could be achieved, leading to exciton bleaching and

stimulated emission from either P-band luminescence or directly from electron-hole plasma. Carrier lifetimes in the range of approximately 2–60 ps have been determined for these effects. For BTO, only above-band gap pumping caused measurable carrier excitation, which decay via traps with time constants of approximately 10 ps or faster. In both materials, long-lasting (nanosecond range) absorption increase at photon energies slightly below the band gap due to a small temperature increase in the focal volume has been observed.

These parameterized descriptions form a good basis for a quantitative simulation of ultrafast dynamics in multilayer systems prepared from the two materials by help of the transfer matrix formalism. Using the identified contributions and the obtained relaxation time constants, additional effects due to coupling at the interface(s) can easily be identified. A special aspect is the contribution of direct exciton excitation in ZnO at a pump photon energy of 3.10 eV (where BTO did not show any carrier excitation), which allows to selectively inject carriers into ZnO also in heterostructures. Corresponding studies on BTO/ZnO double layer samples are in progress; the results will be reported in a forthcoming publication.

ACKNOWLEDGMENTS

This work was financially supported by the Deutsche Forschungsgemeinschaft through SFB 762 “Functionality of Oxidic Interfaces.”

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