Above-band gap two-photon absorption and its influence on ultrafast carrier dynamics in ZnTe and CdTe

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We present measurements of transient carrier dynamics subsequent to intense above-band gap femtosecond excitation of the II–VI compounds ZnTe and CdTe, probed in the far infrared by transient terahertz time-domain spectroscopy. The intensity and temperature dependence of the carrier dynamics illuminates the role of two-photon absorption (TPA) of pump photons. At cold temperatures and high excitation intensities TPA results in a photoexcited carrier distribution which requires several picoseconds to thermalize. As a consequence, the dielectric function of the carrier distribution deviates strongly from the Drude model for as long as 20 ps after excitation. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1489480]

Two-photon absorption (TPA) is an important limiting factor in many practical applications of structured nonlinear optical materials, leading to effects such as gain limiting in optical amplifiers[1] and modification of the properties of semiconductor saturable absorbers on a subpicosecond time scale.[2] In the TPA process, a fraction of carriers already excited from the valence band to the conduction band by one-photon absorption (OPA) during pulsed optical excitation is lifted further up in the conduction bands by excitation photons from the same optical pulse. In situations where the additional excitation is carried out by photons from a pulse delayed with respect to the pump pulse the effect is normally referred to as free-carrier absorption.

In this letter we use transient terahertz (THz) time-domain spectroscopy[3,4] to probe ultrafast carrier thermalization and recombination dynamics in the direct-band gap semiconductors ZnTe and CdTe ($E_g = 2.3$ and 1.6 eV, respectively, at 300 K) subsequent to excitation by 3.1 eV (400 nm) femtosecond laser pulses, at temperatures between 10 and 300 K. We show that TPA can have dominating influence on carrier dynamics at even moderate excitation intensities, and that this influence is strongly temperature dependent. In both materials we observe that the temporal signature of TPA disappears at room temperature.

To shed further light on the relaxation of the initially very hot carrier distribution we have measured the transient frequency-dependent dielectric function (DF) of ZnTe in the spectral range between 0.3 and 2.5 THz at variable times Δt subsequent to optical excitation. Before all carriers are thermalized, the DF deviates strongly from the Drude theory of conduction.[5] In contrast to recent broadband measurements of the transient DF in GaAs[6] excited at similar intensities as used in our work we find that in the presence of significant TPA, carriers require up to 20 ps to thermalize to a distribution which can be described by the Drude model.

In the experiments presented here we excite crystalline ZnTe or CdTe samples [both (110)-cut] at normal incidence with 400 nm (3.1 eV), 100 fs pulses of energy up to 20 μJ, and probe the subsequent transient carrier dynamics with THz pulses. The THz probe pulses consist of a single cycle of the electromagnetic field, with a duration of less than 1 ps, covering the spectral range 0.1–2.7 THz (0.4–11 meV). The THz probe beam is attenuated in proportion to the product of instantaneous mobility $\mu(t)$ and concentration $N(t)$ of carriers located anywhere in the electronic band structure. Traditional pump-probe schemes utilizing visible- or near-infrared pulses are sensitive to $N(t)$ at the energetic position of the probe pulse, and may induce artifacts in the probe signal around $t=0$ (see, e.g., Refs. 1 and 2).

By measuring the temporal shape of the transmitted THz pulse with and without optical excitation of the sample, subsequent comparison of the spectral amplitude and phase of the two pulses allows calculation of the transient DF of the sample,[3,7] here represented as the absorption coefficient $\alpha(\omega,\Delta t)$ and the index of refraction $n(\omega,\Delta t)$.

In intrinsic ZnTe (CdTe), 3.1 eV photons excite electrons from the valence band into the conduction band (CB) with nominal excess energies of 0.7 (1.0) eV (OPA) and 3.9 (4.1) eV (TPA), as illustrated in Fig. 1, which shows the electronic band structure of ZnTe and CdTe, adapted from Ref. 8.

Since TPA is a second-order process it will be significant only in a thin surface layer compared to the penetration

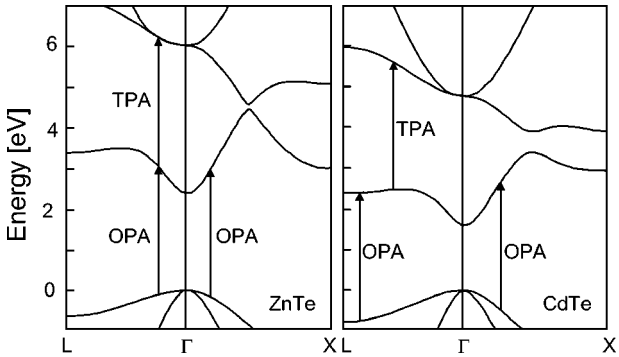

FIG. 1. Band structure of ZnTe and CdTe in the $\Gamma-L$ and $\Gamma-X$ directions (see Ref. 8). Vertical arrows indicate possible OPA and TPA of 400 nm (3.1 eV) photons.

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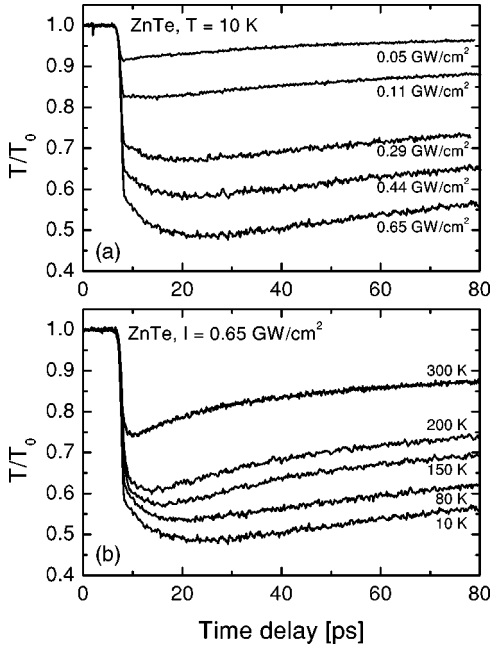

FIG. 2. Frequency-integrated transient transmission of ZnTe, recorded (a) at $T=10$ K with varying excitation intensity, and (b) at fixed excitation intensity with varying temperature.

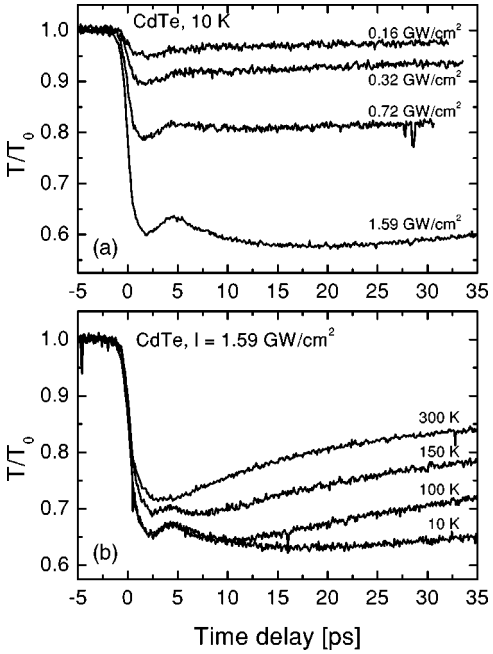

FIG. 3. Frequency-integrated transient transmission of CdTe, recorded (a) at $T=10$ K with varying excitation intensity, and (b) at fixed excitation intensity with varying temperature.

depth of the photons. Therefore, spatial diffusion of carriers created by TPA will be important for the understanding of the carrier dynamics on a picosecond time scale, whereas diffusion of OPA electrons may be neglected within the first 10–20 ps after excitation. Whereas the hole dynamics cannot be ignored for a full description of the experimental results, we will in the following qualitative discussion neglect the influence of holes due to their larger effective mass and lower mobility. Using an electron mobility of $500\ \mathrm{cm^2/V\,s}$ and the Einstein relation $D=kT\mu/e$ between diffusivity and mobility, and a penetration depth of 100 and 20 nm of the OPA and TPA carriers, respectively, injected at densities typical for the study presented here, a rough estimate shows that the distribution of electrons created by TPA can broaden to several microns within a few picoseconds.

In Fig. 2 two sets of transient transmission curves are shown for ZnTe, measured as the transmission at the peak of the THz pulse as function of delay between pump and probe pulse. At the peak of the THz pulse all frequencies within the bandwidth of the pulse are (by definition) in phase, and the transmission amplitude at this point can therefore be considered the average transmission within the detected bandwidth of the THz pulse.

In Fig. 3 the transient transmission of the THz pulse is shown for CdTe. In part (a) of Figs. 2 and 3 the crystal temperature is 10 K, and the excitation intensity is varied. In part (b) of the figures the crystal temperature is varied at constant excitation intensity.

The most prominent features of the traces shown in Figs. 2 and 3 are the fast initial transmission decrease, and the appearance of a second, delayed transmission minimum, most prominent at low temperatures and high excitation intensities. Interestingly, it is clear in both Figs. 2 and 3 that a decrease of temperature from 300 to 10 K qualitatively leads to the same modification of the transient signal as an increase of excitation intensity at low temperature.

We interpret the fast initial decrease and the delayed minimum as direct visualization of the cooling of the two carrier distributions excited by the OPA and TPA processes, respectively. The second transmission minimum is in both ZnTe and CdTe delayed by approximately 20 ps.

The absorption of the THz probe beam is strongest for electrons with high mobility, i.e., electrons near the minimum of a steep parabolic band. In both ZnTe and CdTe, electrons in the Γ valley of the lowest conduction band have the largest mobility. Additionally, there is a higher-lying parabolic valley in both materials (see Fig. 1). In ZnTe, this valley is populated near its minimum by TPA, which can explain the instantaneous onset of absorption by carriers created by TPA in Fig. 2. In contrast to this, carriers excited by TPA in CdTe are born 0.8 eV above the higher-lying band minimum, and it may therefore be expected that there is no instantaneous absorption from the TPA distribution of electrons in CdTe. This may explain why we observe that the initial absorption by the OPA electrons starts to recover before the onset of absorption by electrons returning to the lowest Γ valley after excitation by TPA.

Tentative fitting of a multiparameter rate equation model give good agreement with the picture of the general carrier dynamics outlined earlier. The TPA coefficient β could in ZnTe be estimated to (5.5 ± 0.5) cm/GW at 10 K, in good agreement with values reported for excitation below the band gap.[9]

To shed further light on the influence of TPA on the carrier dynamics we measured the frequency-resolved absorption coefficient $\alpha(\nu)$ and index of refraction $n(\nu)$ of ZnTe subsequent to excitation with an intensity of $I_0=0.5\ \mathrm{GW/cm^2}$ and $T=10$ K, as shown in Fig. 4. Solid symbols are data recorded at $\Delta t=2$ ps, open symbols are data recorded at $\Delta t=20$ ps after excitation. The solid curves are results of a fitting of the DF predicted by the Drude theory to the experimental data. The Drude model fit in Fig. 4(a) was

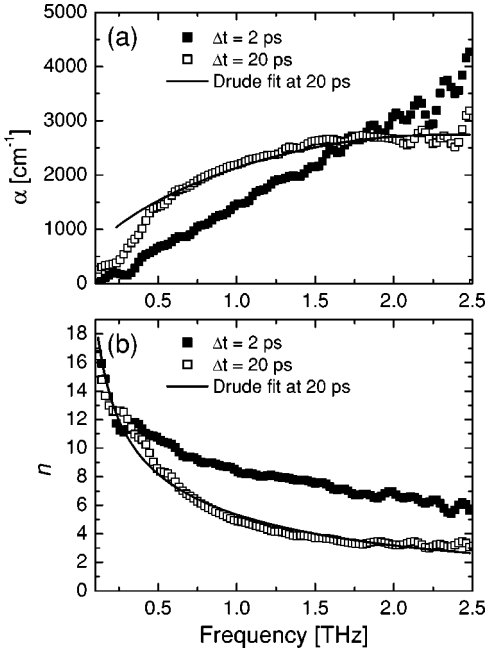

FIG. 4. Frequency-dependent transient absorption coefficient and index of refraction of ZnTe, recorded 2 ps (solid squares) and 20 ps (open squares) after excitation. Solid curves: Drude model fits at 20 ps.

obtained using a plasma frequency $\omega_p=(85.2\pm4.2)\times10^{12}\ \mathrm{s}^{-1}$ and damping rate $\Gamma=(22.3\pm2.5)\times10^{12}\ \mathrm{s}^{-1}$, whereas the best fit in Fig. 4(b) was obtained with $\omega_p=(95.9\pm1.9)\times10^{12}\ \mathrm{s}^{-1}$ and $\Gamma=(19.5\pm1.0)\times10^{12}\ \mathrm{s}^{-1}$. Using $\omega_p=90\times10^{12}\ \mathrm{s}^{-1}$, we obtain $N=\omega_p^2\epsilon_0 m^\star/e^2=4.2\times10^{17}\ \mathrm{cm}^{-3}$, in agreement with the experimental excitation density if a realistic diffusion depth of 4 μm is used. The calculated mobility $\mu=e/m^\star\Gamma=5.1\times10^2\ \mathrm{cm}^2/\mathrm{V\,s}$ is in agreement with typical electron mobilities in ZnTe.[10]

Shortly after excitation but after several LO-phonon collision times, the measured $\alpha(\omega)$ and $n(\omega)$ cannot be fitted by the Drude model. Based on the arguments presented earlier we conclude that both the OPA and TPA carrier distributions must thermalize to the CB minimum before the carrier dynamics can be modeled as an electron gas described by a single plasma frequency and damping rate. In the warm crystals, where the TPA process is suppressed, we do not observe this delayed thermalization. This behavior is in agreement with several recent studies of room-temperature carrier dynamics in other semiconductor materials.[6,11]

The origin of the TPA suppression at room temperature is subject of further studies, but we tentatively suggest that the following may explain our observations qualitatively. The electron-phonon scattering time $\tau_s=1/\Gamma$ is strongly temperature dependent. According to the classical Drude model the absorption coefficient of carriers already in the conduction band is $\alpha\propto\tau_s^{-1}$,[12] leading to reduced TPA efficiency at low temperatures, in contrast to our observations. However, the Drude model assumes that interaction with phonons is required to conserve momentum in the conduction band during TPA, which is the case if the photon energy is small. In our situation the photon energy is large enough to give access to higher-lying bands via direct transitions, therefore not involving phonon interactions. Hence, a long phonon scattering time may lead to the effect of increasing the TPA efficiency at low temperatures, in agreement with our observations.

In conclusion, we have demonstrated that the TPA process in ZnTe and CdTe is strongly temperature dependent and leads to a significant modification of carrier dynamics at low crystal temperatures. As the single-wavelength-channel speed of optical communication systems is moving into the terabit/s range[13,14] it becomes increasingly important to increase the understanding of carrier dynamics on the femtosecond time scale in order to allow optoelectronic components of such systems to keep up with the all-optical components. Our results show that TPA limits the ultrafast response time of II–VI semiconductor materials and that the effects of TPA must be considered in the design of optoelectronic components with operational bandwidth approaching the terahertz range.

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[1] J. Mørk, J. Mark, and C. P. Seltzer, Appl. Phys. Lett. **64**, 2206 (1994).
[2] M. Joschko, P. Langlois, E. R. Thoen, E. M. Koontz, E. P. Ippen, and L. A. Kolodziejski, Appl. Phys. Lett. **76**, 1383 (2000).
[3] M. Schall and P. Uhd Jepsen, Opt. Lett. **25**, 13 (2000).
[4] P. Uhd Jepsen, W. Schairer, I. H. Libon, U. Lemmer, N. E. Hecker, M. Birkholz, K. Lips, and M. Schall, Appl. Phys. Lett. **79**, 1291 (2001).
[5] N. W. Ashcroft and D. N. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).
[6] R. Huber, F. Tauser, A. Brodschelm, M. Bichler, G. Abstreiter, and A. Leitenstorfer, Nature (London) **414**, 286 (2001).
[7] M. C. Beard, G. M. Turner, and C. A. Schmuttenmaer, Phys. Rev. B **62**, 15764 (2000).
[8] E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. B **43**, 9700 (1991).
[9] A. A. Said, M. Sheik-Bahae, D. J. Hagan, T. H. Wei, J. Wang, J. Young, and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 405 (1992).
[10] H. E. Ruda, J. Phys. D **24**, 1158 (1991).
[11] K. P. H. Lui and F. Hegmann, Appl. Phys. Lett. **78**, 3478 (2001).
[12] P. Y. Yo and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, Berlin, 1999), pp. 296–300.
[13] M. Nakazawa, T. Yamamoto, and K. R. Tamura, Electron. Lett. **36**, 2027 (2000).
[14] T. Yamamoto and M. Nakazawa, Opt. Lett. **26**, 647 (2001).