UNIVERSITÄT POTSDAM Mathematisch-Naturwissenschaftliche Fakultät Institut für Physik und Astronomie

Transient Conductivity Measurements using Terahertz Time-Domain Spectroscopy

Diplomarbeit

von

Andreas Paulke

Gutachter: Prof. Dr. Matias Bargheer Zweitgutachter: Prof. Dr. Dieter Neher

Juli 2013

Zusammenfassung

Transiente Leitfähigkeitsmessungen mittels Terahertzspektroskopie in der Zeitdomäne

In der vorliegenden Arbeit wird der Aufbau eines Messplatzes zur Durchführung von Spektroskopie mit Terahertzstrahlung beschrieben. Durch Differenzfrequenzmischung innerhalb des breiten Spektrums optischer Femtosekundenlaserpulse werden Terahertzpulse im nichtlinearen Kristall Galliumselenid (GaSe) erzeugt. Die Pulse haben eine Zentralfrequenz von 1.5 THz und eine Bandbreite von etwa 2 THz. Die Messung des elektrischen Feldes der THz-Pulse erfolgt mittels elektrooptischem Abtasten in Zinktellurid (ZnTe). Durch Messung der von einer Probe transmittierten oder reflektierten THz-Pulse kann die frequenzabhängige dielektrische Funktion der vorliegenden Probe im THz-Bereich bestimmt werden. Aufgrund der Äquivalenz von dielektrischer Funktion und elektrischer Leitfähigkeit lässt sich auch die frequenzabhängige Leitfähigkeit einer Probe bestimmen. So kann etwa das Drude-Modell der Leitfähigkeit auf seine Gültigkeit hin untersucht werden. Die Pulslänge der Terahertzpulse beträgt etwa 500 fs, dies ermöglicht zeitaufgelöste Pump-Probe Spektroskopie mit einer Zeitauflösung im Subpikosekundenbereich. Hier wurden Optische-Pump / THz-Probe Experimente an den Halbleitern Galliumarsenid und Silicium durchgeführt. Ist die Photonenenergie des optischen Anregungspulses höher als die Bandlücke des Halbleiters können Elektron-Loch Paare erzeugt werden, es sind freie Ladungsträger vorhanden. Wird der abtastende THz-Puls in Abhängigkeit vom zeitlichen Abstand zum Anregungspuls gemessen kann daraus die transiente Leifähigkeit (bzw. Anzahl der Ladungstäger) bestimmt werden. So können die Zeitskonstanten der Rekombination von Elektron-Loch-Paaren bestimmt werden, was insbesondere für Anwendungen in der Photovoltaik interessant ist.

Contents

D	Deutsche Zusammenfassung i							
1	Introduction							
2	Theory							
	2.1	Gener	ation and Detection of THz Radiation	4				
		2.1.1	Difference-Frequency Generation	5				
		2.1.2	Detection: Electro-Optic Sampling - Pockels Effect	6				
	2.2	Equiv	alence of Conductivity and Dielectric Function	8				
	2.3	Model	s of Conductivity/ Dielectric Function	10				
		2.3.1	General Case - Lorentz Oscillator	11				
		2.3.2	Drude Model	13				
		2.3.3	Generalizations of the Drude Model	13				
		2.3.4	Drude Model with Restoring Force: Plasmon Model $\ . \ . \ .$	15				
3	Set	up		16				
	3.1	Laser	System	16				
	3.2	THz S	Setup	17				
		3.2.1	THz Generation and Electro-Optic Sampling	17				
		3.2.2	Optical-Pump / THz-Probe Spectroscopy (OPTP)	19				
		3.2.3	Improvements: Cross-Correlation and Fast Scanning	21				
4	Results I : Static THz Spectroscopy							
	4.1	Chara	cterization of THz Pulses	25				
		4.1.1	THz Electric Field and Spectrum	25				
		4.1.2	Water Absorption	26				
		4.1.3	Knife-Edge Measurement	28				
		4.1.4	Calibration of Field Strength	29				
	4.2	Test N	Measurements - Transmission	32				
		4.2.1	Doped Silicon - Drude Response	34				
		4.2.2	$LiNbO_3$ - Phonon Resonance	36				
		4.2.3	Highly Doped GaAs in Reflection	37				

	4.3 Preliminary Measurements				
		4.3.1 Undoped Silicon	40		
		4.3.2 Undoped GaAs	41		
5	\mathbf{Res}	ults II: Optical-Pump/THz-Probe Spectroscopy	43		
	5.1	General	44		
		5.1.1 Reflection from a Photoexcited Surface Layer	45		
		5.1.2 Transmission Through a Photoexcited Surface Layer	48		
		5.1.3 Carrier Dynamics	50		
		5.1.4 Temporal Resolution	53		
	5.2	Gallium Arsenide (GaAs)	56		
		5.2.1 Transmission Measurement	57		
		5.2.2 Reflection Measurement	60		
	5.3	Silicon	61		
	5.4	Poly-Si on Glass Substrate	63		
6	Cor	onclusion and Outlook			
Bi	bliog	graphy	67		
Selbstständigkeitserklärung					
D	anks	agung	68		

Chapter 1

Introduction

The terahertz band, also called the far-infrared band, lies in between the regions of optics and electronics of the electromagnetic spectrum (Fig. 1.1). For frequencies from 0.1 to 10 THz the photon energies are in the range of 0.4 to 40 meV. The wavelength lies in a range of 3 mm to 30 µm, i.e. in the sub-millimeter range. Due to the lack of coherent sources and detectors, the THz band is the least exploited region of the electromagnetic spectrum, known as the 'THz gap'. Advances have been made in coherently generating and detecting THz radiation in the last 20 years [1] [2]. Frequencies in the THz range are too fast for being recorded electronically, as the best achievable bandwidth of lab oscilloscopes reaches up to several GHz. One the other hand, the detection of THz radiation is also difficult with a bolometer because it will be totally overwhelmed by the black-body radiation at room temperature which corresponds to a frequency of 6 THz. The availability of ultrashort laser pulses enables coherent generation and detection of pulsed THz radiation. As ultrashort optical pulses cover a bandwidth of several THz difference-frequency generation and also time-domain sampling of the electric field of THz pulses is possible.

The electronic conductivity of a solid is determined by the density of free carriers. In contrast to visible light, THz radiation has much lower photon energies of several meV. Such low photon energies can only cause electronic transitions close to the Fermi edge, so only carriers that contribute to the conductivity are probed. The interaction of visible light (E > 1 eV) with the electronic system is dominated by interband transitions. Also carriers that lie deeper below the Fermi level do contribute to the optical response of the system although they do not contribute to the electrical conductivity. Broadband THz pulses combine the sensitivity to free carriers close to their equilibrium state with a picosecond temporal resolution.



FIGURE 1.1: THz radiation in the Electromagnetic Spectrum.

Generation and detection of THz pulses was first realized with photoconductive antennas[1]. Here, an above-band gap laser pulse generates free carriers in the conduction band of a semiconductor with an applied bias voltage. The photoexcited carriers are accelerated by the external field leading to the radiation of an electromagnetic pulse. For these antennas, semiconductors with sub-picosecond carrier lifetimes are used to generate THz pulses [3]. With amplified laser pulses differencefrequency generation in a nonlinear medium can be employed. Typical materials are ZnTe, GaSe and GaP. Here pairs of different frequencies within the broad laser spectrum create a nonlinear polarization with the difference of the two frequencies, which is then radiated. This is often synonymously called optical rectification because of the small generated frequencies in comparison to optical frequencies.

The aim of this thesis was to built a time-resolved THz spectroscopy setup, to establish this type of spectroscopy in UDKM group. In the first part, a setup for generation and detection of THz pulses from femtosecond amplified laser pulses was realized. The generation was done via difference-frequency generation in gallium selenide (GaSe) and the detection with electro-optic sampling in zinc telluride (ZnTe). Electro-optic sampling allows to measure the electric field of the THz pulse in the time-domain, therefore this type of spectroscopy is called THz time-domain spectroscopy (THz-TDS).

As a first test of the setup, static THz spectroscopy on samples with known dielectric function in the THz range has been performed. Since the electric field is recorded in the time-domain, the complex dielectric function of a sample can be obtained directly from the measurement. In the second part, the experimental setup was expanded with an additional optical pump beam path, including a delay line, to perform optical-pump/THz-probe experiments on semiconductors. The optical pump pulse is used to excite electrons from the valence band into the conduction band of the sample. A change in the dielectric function of a sample is caused by the presence of photoexcited free carriers, electrons in the conduction band and the remaining holes in the valence band. The THz pulse probes the change in the dielectric function of the sample or equivalently the change in the conductivity as a function of the temporal delay with respect to the pump pulse. From an optical-pump/THz-probe experiment the recombination dynamics of the photoexcited electron-hole pairs can be observed.

This thesis is subdivided in the following chapters. In chapter 2 the relevant theoretical background will be given. The nonlinear optical effects for the generation and detection of THz pulses, the relation between conductivity and dielectric function and some conductivity models will be discussed. In chapter 3 the experimental setup is described, this is the laser system and the optical-pump/THz-probe spectroscopy setup. In chapter 4, preliminary static THz spectroscopy measurements are shown. For testing the accuracy of the setup, the dielectric function of a doped silicon sample and a single crystal of LiNbO₃ have been determined, both showing strong variations of the dielectric function in the THz range. The static dielectric function was determined for the later dynamically examined GaAs and silicon samples. The results of the dynamical optical-pump/THz-probe (OPTP) measurements are discussed in chapter 5. For GaAs, the pump-probe experiment was carried out in transmission and reflection geometry to cross-check the results from both methods. The usefulness of an OPTP measurement in reflection will be demonstrated with an experiment on a polycrystalline silicon sample on a standard glass substrate, that could not be carried out as transmission experiment, because of the strong THz absorption of the glass substrate. The observed recombination dynamics of the photoexcited electron-hole pairs can be understood in terms of bulk and surface recombination taking place with different time constants.

Chapter 2

Theory

In this chapter the relevant theory needed to understand the generation and detection of THz-radiation will be briefly discussed. The underlying processes can be described in the framework of nonlinear optics, namely difference frequency generation and the Pockels effect, which are $\chi^{(2)}$ -processes. Transmission and reflection measurements of THz pulses can be fully described in the linear regime by applying the Fresnel equations and calculating the propagation through a medium using the dielectric function of the sample. The equivalence of the dielectric function and the conductivity will be derived, which allows to determine the frequency dependent conductivity of a sample from its dielectric function. To understand the mechanisms of charge carrier dynamics, some conductivity models are reviewed, which are the Drude model and possible extensions.

2.1 Generation and Detection of THz Radiation

The availability of sources of intense femtosecond laser pulses permits differencefrequency generation (DFG) within the broad spectrum of such laser pulses. As an example, a transform limited optical pulse centered at $\lambda_0 = 800 \text{ nm}$ and a temporal pulse width of $\tau_{FWHM} = 50 \text{ fs}$ covers a bandwidth of a $\Delta \nu \approx 11 \text{ THz}$. The corresponding center frequency is $\nu_0 = 375 \text{ THz}$. Thus THz-generation via differencefrequency generation within the spectrum of the pulse becomes possible (Fig. 2.1).

For THz pulses the electric field can be measured directly in the time domain by the electro-optic sampling technique. It supports a detection bandwidth of several THz, given by the temporal width of the probing optical pulse, which is around one order of magnitude higher than what is achievable with purely electronic devices, where bandwidths of several GHz, as for commercial available oscilloscopes, can be achieved.

2.1.1 Difference-Frequency Generation

Difference-frequency generation (DFG) is a result of the nonlinear-polarization occuring at high enough intensities of the applied electric field of the optical pulse. It is convenient to express the nonlinear polarization P^{nl} in terms of a power series in E with 'coefficients' $\chi^{(n)}$.

$$\mathbf{P}^{nl} = \epsilon_0 [\chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \dots]$$
(2.1)

DFG is a process that originates from the second-order susceptibility $\chi^{(2)}$, thus it can only occur in materials without inversion symmetry. This yields for different frequency components within the laser spectrum for the second order nonlinear polarization:

$$\mathbf{P}^{(2)}(\Omega) = \epsilon_0 \int d\omega_1 d\omega_2 \chi^{(2)}(\Omega; \omega_1, -\omega_2) \mathbf{E}(\omega_1) \mathbf{E}^*(\omega_2).$$
(2.2)

Where for the case of DFG the following abbreviation was used to ensure that only differences of two laser frequencies are generated (i.e. conservation of energy)

$$\chi^{(2)}(\Omega;\omega_1,-\omega_2) = \chi^{(2)}(\omega_1,-\omega_2)\delta(\Omega-|\omega_1-\omega_2|).$$
(2.3)

For an ideal non-dispersive medium the radiated THz pulse is proportional to the product of the nonlinear polarization $P^{(2)}(\Omega)$ and the square of the frequency Ω as $E(\Omega) \sim \Omega^2 \cdot P^{(2)}(\Omega)$ (Fig. 2.1). The Ω^2 dependence of the radiated electric field originates from the far field behaviour of a Hertz dipole [4].

Nevertheless, in a real experimental situation, propagation effects in the medium within the generation process of the difference frequency cannot be neglected. For an efficient generation process the optical pulse has to travel through a medium with finite thickness. This means the waves generated at different crystal positions have to add up constructively, 'phase matching' has to be fulfilled. For a difference frequency $\Omega = \omega_1 - \omega_2$ phase matching is given if for the resulting wave vector $\mathbf{K} = \mathbf{k}_1 - \mathbf{k}_2$



FIGURE 2.1: Principle of difference frequency generation: frequency pairs ω_1 and ω_2 of the laser spectrum create a nonlinear polarization at the difference frequency Ω , which is then radiated proportional to Ω^2 (adapted from [5]).

is fulfilled. In a situation where all beams are collinear and a medium without birefringence, using $|\mathbf{k}| = k = n\omega/c$ this leads to $n(\Omega)\Omega = n(\omega_1)\omega_1 - n(\omega_2)\omega_2$. This condition can also be written as $n(\Omega) = n(\omega) + \omega n'(\omega)$ with $\omega_1 = \omega + \Omega$ and $\omega_2 = \omega$ and the first order Taylor-expansion for $n(\omega + \Omega) = n(\omega) + n'(\omega)\Omega$. With the phase velocity $v_p = 1/n(\Omega)$ and the group velocity $v_g = c/(n(\omega) + \omega n'(\omega))$, this means that the phase velocity of the generated THz field and the group velocity of the optical pump pulse have to coincide. The phase matching condition is summarized in the following equation

$$K(\Omega) = k_2(\omega + \Omega) - k_1(\omega) \iff v_{ph}(\Omega) = v_{qr}(\omega).$$
(2.4)

A detailed calculation of the difference-frequency generation involving the dispersion of the nonlinear medium and treating the coupled wave equations can be found in [6].

2.1.2 Detection: Electro-Optic Sampling - Pockels Effect

A change in the refractive index of a material that depends linearly on the electric field is known as linear electro-optic effect, or Pockels effect. The effect is caused by the second order susceptibility $\chi^{(2)}$. For an applied DC-field and a field at optical frequencies a nonlinear polarization of the following form occurs:

$$P_{i}(\omega) = 2\sum_{jk} \chi_{ijk}^{(2)}(\omega = \omega + 0; \omega, 0) E_{j}(\omega) E_{k}(0).$$
(2.5)

In comparison to optical frequencies, $\nu = 375$ THz corresponding to $\lambda = 800$ nm, an electric field oscillating at a frequency of 1 THz can be treated as a quasi-DC field. Thus a sum or difference frequency generation of the two fields can be neglected (Eq. 2.5). The presence of the electric field can be rewritten as change in the refractive index for the optical field. For a linearly polarized incident THz field this causes a field dependent birefringence in a suitable crystal. This birefringence can be detected by means of the electro-optic sampling scheme shown in Figure 2.2. For the crystal ZnTe (point group $\bar{4}3m$) the resulting phase difference Γ for two perpendicular polarizations of the optical probe pulse accumulated over the crystal length d one gets the following result [7]:

$$\Gamma = \frac{2\pi d}{\lambda_{opt}} n_{opt}^3 r_{41} E_{THz}.$$
(2.6)

Here r_{41} is the electrooptic coefficient for the crystal ZnTe. This phase difference Γ can be transformed into an intensity difference which can be measured with the configuration shown in Figure 2.2.

$$\sin(\Gamma) \approx \Gamma = \frac{I_1 - I_2}{I_1 + I_2} \tag{2.7}$$



FIGURE 2.2: Principle of electro-optic sampling. A linearly polarized optical probe pulse and the THz pulse propagate through the sampling crystal. The electric field of the THz pulses causes a birefringence in the crystal that changes the polarization of the probe pulse from linear to elliptic. The quarter-wave plate sets the intensity difference on the balanced detector to zero (circular polarization before the Wollaston polarizer) with no field present, ensuring an almost background-free measurement. Scanning the delay between the two pulses the electric field of the THz pulse can be recorded in the time-domain (from [8]).

2.2 Equivalence of Conductivity and Dielectric Function

In the following, Maxwell's equations (macroscopic version) are given assuming conducting media without any net charge density ($\rho = 0$).

Further, the material equations are used. The electric field E and the displacement current D are linked via the dielectric function ε_L as $D = \varepsilon_L \varepsilon_0 E = \varepsilon_0 E + P$, where ε_0 is the permittivity of free space and P is the polarization of the medium. The magnetic flux density B is linked to the magnetic field H via the permeability μ as $B = \mu H = \mu_0 H + M$, where M is the magnetization of the medium and μ_0 is the permeability of free space. In the most general case, the medium consists of a lattice (i.e. nuclei) and more or less free carriers (electrons) that allow for charge carrier transport. The non-conducting lattice is characterized by the dielectric function $\varepsilon_L(\omega)$, whereas free carrier transport is characterized via the conductivity $\sigma(\omega)$. The dielectric function and the conductivity are in general frequency-dependent and complex-valued, a tilde will be used here to denote generalized quantities.

$$\nabla \cdot B = 0 \qquad (1) \qquad \nabla \cdot E = 0 \qquad (2)$$
$$\nabla \times E = \partial_t B \qquad (3) \qquad \nabla \times H = j_f + \partial_t D \quad (4)$$

Ohm's law which links the current density of free carriers (subscript f) to the applied electric field reads:

$$j_{\rm f}(\omega) = \sigma_{\rm f}(\omega) E(\omega).$$
 (2.8)

The concept of the conductivity is extended here to the frequency-dependent general case. The derivation given here follows the references [9] and [10]. Taking the curl of Eq. (3) and switching from time to frequency domain representation $(\partial_t \to -i\omega)$ leads to:

$$\nabla \times (\nabla \times E) = \nabla (\underbrace{\nabla \cdot E}_{=0}) - \nabla^2 E = -\nabla \times (\partial_t B) = -\partial_t (\nabla \times B)$$
$$= -\partial_t (j + \partial_t D) \mu = i\omega (j + \partial_t D) \mu = i\omega (\sigma_f(\omega) - i\omega \varepsilon_L(\omega) \varepsilon_0) \mu E$$
$$= -\omega^2 \varepsilon_0 (\varepsilon_L(\omega) + \frac{i\sigma_f(\omega)}{\omega \varepsilon_0}) \mu E.$$
(2.9)

The result is a wave equation for the electric field of the form:

$$\left[\nabla^2 + \omega^2 \varepsilon_0 \left(\varepsilon_L(\omega) + \frac{i\sigma_f(\omega)}{\omega\varepsilon_0}\right) \mu\right] E(x,\omega) = 0.$$
(2.10)

This wave equation can be brought into a more commonly known form via introducing a generalized dielectric function $\tilde{\varepsilon}(\omega)$ also accounting for conducting media. Thus the propagation and reflection/transmission can be described by means of $\tilde{\varepsilon}(\omega)$, as it is the only material property (for non-magnetic media $\mu = \mu_0$) in the wave equation

$$\left[\nabla^2 + \omega^2 \varepsilon_0 \tilde{\varepsilon}(\omega) \mu\right] E(x, \omega) = 0.$$
(2.11)

With

$$\varepsilon(\omega) := \varepsilon_L(\omega) + \frac{i\sigma_{\rm f}(\omega)}{\varepsilon_0\omega}$$
(2.12)

For a known lattice contribution the latter can be used to obtain the conductivity of free carriers of a composite system (e.g. for doped semiconductors).

The 4th Maxwell equation can be rewritten by introducing a generalized current J consisting of contributions from bound and free carriers

$$\nabla \times H = \underbrace{J}_{= j_{\text{free}} + j_{\text{bound}}}_{= j_{\text{free}} + j_{\text{bound}}}_{= (\tilde{\sigma}(\omega) - i\omega\varepsilon_0)E(x,\omega) = -i\omega\varepsilon_0 \underbrace{\left[\frac{i\tilde{\sigma}(\omega)}{\omega\varepsilon_0} + 1\right]}_{=:\tilde{\sigma}(\omega)}_{=:\tilde{\sigma}(\omega)}E(x,\omega). \quad (2.13)$$

This generalized current can then be assumed to be linked to an applied electric field via an generalized form of Ohm's law $J(\omega) = \tilde{\sigma}(\omega)E(\omega)$. By introducing this more general concept of conductivity and dielectric function Eq. 2.12 can be rewritten in a more general way by having introduced a generalized conductivity $\tilde{\sigma}(\omega)$ which is then linked to the generalized dielectric function as

$$\tilde{\varepsilon}(\omega) = 1 + \frac{i\tilde{\sigma}(\omega)}{\varepsilon_0\omega}.$$
 (2.14)

Putting together Eq. 2.12 and 2.14 shows that the generalized conductivity also includes a lattice contribution, as

$$\tilde{\sigma}(\omega) = \sigma_{\rm f}(\omega) - i\varepsilon_0 \omega(\varepsilon_L(\omega) - 1). \tag{2.15}$$

Which means that lattice oscillations can be regarded as bound oscillating currents.

It should be noted, that in an experiment only the complete generalized dielectric function can be measured, which includes the frequency dependent response of bound (i.e. lattice) and free carriers. For some cases the frequency dependence of both contributions might intersect on the frequency axis and cannot be clearly distinguished (Fig.). As an example, for non-magnetic media ($\mu_r = 1$), the reflection coefficient at normal incidence for the electric field is given by the following Fresnel equation, where the generalized dielectric function enters.

$$r(\omega) = \frac{1 - \sqrt{\tilde{\varepsilon}(\omega)}}{1 + \sqrt{\tilde{\varepsilon}(\omega)}}$$
(2.16)

2.3 Models of Conductivity/ Dielectric Function

Modeling the dielectric function ε or conductivity σ of a system is based on the linear response function approach. The polarization P is given by the average displacement x the of bound carrier density n_b and by the product of the external electric field Eand the electric susceptibility χ

$$P(\omega) = n_b e x(\omega) = \varepsilon_0 \chi(\omega) E(\omega).$$
(2.17)

The current density j (free carriers) is defined as the product of the carrier velocity \dot{x} , the density of free carriers n_f and the charge e and according to Ohm's law the product of the conductivity σ and the electric field E:

$$j(t) = n_{\rm f} e \dot{x}(t)$$

$$j(\omega) = -i\omega n_{\rm f} e x = \sigma(\omega) E(\omega).$$
(2.18)

Where from the first to the second line it was switched from the time to the frequency domain representation. From the definitions of P and j, by the division of Eq. 2.17 and Eq. 2.18 and regarding the both carrier densities as being equal, one can also obtain a general relation between the conductivity and the electric susceptibility χ . With the general relation $\chi = \varepsilon - 1$. This yields the exact same relation as derived from Maxwell's equations in the previous chapter

$$\sigma(\omega) = -i\omega\varepsilon_0\chi(\omega) = -i\omega\varepsilon_0(\varepsilon(\omega) - 1).$$
(2.19)

2.3.1 General Case - Lorentz Oscillator

The most simplified approach for modeling the response of a system to an electric field is to treat the system as an ensemble of damped harmonic oscillators with a resonance frequency ω_T , damping constant γ and an effective mass m^* . The subscript T for oscillator frequency accounts for the fact that a transverse electric field (e.g. plane wave) can only couple to transverse oscillation modes. The equation of motion for a damped harmonic oscillator in an electric field in the time and frequency domain reads

$$\ddot{x} + \gamma \dot{x} + \omega_T^2 x = \frac{eE}{m^*} = (-\omega^2 - i\omega\gamma + \omega_T^2)\tilde{x}.$$
(2.20)

The equation of motion is most easily solved in the frequency domain, and leads together with Eq. 2.17 to a frequency dependent susceptibility

$$x(\omega) = \frac{eE}{m^*(\omega_T^2 - \omega^2 - i\omega\gamma)},$$
(2.21)

$$\chi_{\rm osc}(\omega) = \frac{ne^2/m^*\varepsilon_0}{(\omega_T^2 - \omega^2 - i\omega\gamma)}.$$
(2.22)

In order to account for resonances at higher frequencies, one has to add another component to the dielectric function $\varepsilon = \chi_{\infty} + \chi_{\rm osc} + 1 = \varepsilon_{\infty} + \chi_{\rm osc}$. The plasma frequency $\omega_p^2 = ne^2/m^*\varepsilon_0$ is introduced here.

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\omega_p^2}{(\omega_T^2 - \omega^2 - i\omega\gamma)}$$
(2.23)

A set of eigenfrequencies can be included by taking the sum of the dielectric functions over different resonance frequencies $\omega_{T,j}$

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{j} \frac{\omega_{p,j}^2}{(\omega_{T,j}^2 - \omega^2 - i\omega\gamma_j)}.$$
(2.24)

For a system in which free carriers are present ($\omega_T = 0$) one might separate the contribution of the free carriers from the bound lattice carriers.

$$\varepsilon(\omega) = \varepsilon_{\infty} - \underbrace{\frac{\omega_p^2}{(\omega^2 + i\omega\gamma)}}_{Drude} + \underbrace{\sum_{j} \frac{\omega_{p,j}^2}{(\omega_{T,j}^2 - \omega^2 - i\omega\gamma_j)}}_{\omega_T \neq 0}$$
(2.25)

An example for the (generalized) dielectric function and conductivity is shown in Figure 2.3.



FIGURE 2.3: Real (blue) and imaginary part (red) of the dielectric function ε (a) and the conductivity σ (b) for a system with a Drude response (plasma frequency $\omega_p/2\pi = 5 \text{ THz}$, damping $\gamma/2\pi = 1 \text{ THz}$) and a phonon resonance at $\omega_T/2\pi = 6THz$ (damping $\gamma = 1 \text{ THz}$)) with $\varepsilon_{\infty} = 5$ (upper black dashed line in (a)). The dielectric function was calculated with Eq. 2.25 and is related to the conductivity via Eq. 2.14. The dashed lines in each graph indicate the free carrier (Drude) response.

2.3.2 Drude Model

The equation of motion of the charge carriers is simply that for a damped motion without a restoring force, or an harmonic oscillator with $\omega_0 = 0$. The damping frequency $\gamma = 1/\tau$ describes the collisions of the carriers with the lattice occuring in an average scattering time τ . Within such a carrier-lattice collision the carrier is assumed to loose its momentum.

$$\ddot{x} + \gamma \dot{x} = \frac{eE}{m^*} \tag{2.26}$$

$$\sigma(\omega) = \frac{ne^2}{m^*} \frac{\tau}{(1 - i\omega\tau)} = \frac{\sigma_{DC}}{(1 - i\omega\tau)}$$
(2.27)

Where the DC conductivity $\sigma_{DC} := \sigma(0)$ was introduced, which can also be defined involving the plasma frequency ω_p or the carrier mobility μ .

$$\sigma_{DC} = \frac{ne^2\tau}{m^*} = \varepsilon_0 \omega_p^2 \tau = ne\mu \tag{2.28}$$

2.3.3 Generalizations of the Drude Model

In various experiments is shown that the assumptions of the Drude model are oversimplified for describing the conductivity for general systems [11, 12]. An approach to generalize the Drude model is to add a continuous distribution of scattering times. In the Cole-Cole (CC) model a symmetric logarithmic distribution is assumed with a peak at $\ln \tau$ and a width that increases with the CC-parameter α and approaches a δ -distribution for $\alpha = 0$ [11]. The frequency dependent conductivity σ_{CC} for the Cole-Cole model reads

$$\sigma_{CC}(\omega) = \frac{\sigma_{DC}}{(1 - (i\omega\tau)^{1-\alpha})}.$$
(2.29)

For the Cole-Davidson (CD) model this is a one-sided logarithmic distribution, which is zero for $\tau > \tau_0$, with a peak at τ and with an increasing width for a decreasing CD-parameter $\beta < 1$. The conductivity is given as

$$\sigma_{CD}(\omega) = \frac{\sigma_{DC}}{(1 - i\omega\tau)^{\beta}}.$$
(2.30)

Both parameters are in the range $0 < \alpha < 1$ and $0 < \beta < 1$ and the Drude model is recovered for $\alpha = 0$ and $\beta = 1$. To account for symmetric and asymmetric distributions of relaxation times the CC and CD model can be put together to form a generalized Drude (GD) model [13]

$$\sigma_{GD}(\omega) = \frac{\sigma_{DC}}{(1 - (i\omega\tau)^{1-\alpha})^{\beta}}.$$
(2.31)

The conductivity is related to the electric susceptibility via $\sigma(\omega) = i\omega\chi(\omega)$. The inverse Fourier transform gives the time-domain response function $\chi(t)$. For the Drude theory the response function is an exponential decay, which is equivalent to the Debye theory of dielectric relaxation. For the Cole-Davidson model the response function has the form

$$\chi(t) = \frac{1}{\tau \Gamma(\beta)} \left(\frac{t}{\tau}\right)^{\beta-1} e^{-t/\tau}, \qquad (2.32)$$

where Γ denotes the gamma function. For the Cole-Cole model the response function also involves an exponential decay term, but can not be written in a closed form [14]. The generalized Drude model was confirmed experimentally with THz time-domain spectroscopy on doped semiconductors [15, 16] and photoexcited semiconductors [13, 17]. Also Monte-Carlo simulations of the carrier transport in doped semiconductors confirmed the GD model [18]. Figure 2.4 compares the conductivity from the CC and the CD model with the Drude model.



FIGURE 2.4: Comparison of the real (a) and imaginary part (b) of the conductivity obtained from the Drude model ($\sigma_{DC} = 10 \,\text{S/cm}$, $\tau = 100 \,\text{fs}$) and the Cole-Cole (Eq. 2.29, $\alpha = 0.2$) and the Cole-Davidson model (Eq. 2.30, $\beta = 0.7$). The frequency dependence varies significantly as the value for the frequency $\nu = 0$ (DC) stays constant.

2.3.4 Drude Model with Restoring Force: Plasmon Model

For inserting a restoring force into the dynamic equation, the result is a vanishing conductivity for zero frequency and a peak of the real part of the conductivity for the resonance frequency (Fig. 2.5). A plasmon is the quantized plasma (free carriers) oscillation, resulting from the restoring force. The plasmon model becomes important for nanostructured systems where free carriers are confined to a certain spatial region [19].

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{eE}{m^*} \tag{2.33}$$

$$\sigma(\omega) = \frac{\sigma_{DC}}{1 - i\tau(\omega - \omega_0^2/\omega)}$$
(2.34)



FIGURE 2.5: Comparison of the real (a) and the imaginary part (b) of the conductivity obtained from the Drude (solid) and the plasmon model (dotted), with the parameters $\sigma_{DC} = 10 \text{ S/cm}$, $\tau = 100 \text{ fs}$ and a resonance frequency of $\omega_0/2\pi = 2 \text{ THz}$ for the plasmon model, for the latter the conductivity vanishes for $\nu = 0$.

Chapter 3

Setup

3.1 Laser System

The laser system consists of an Kerr-lens mode-locked Ti:sapphire oscillator operating at a repetition rate of 80 MHz and a two-stage amplifier system delivering amplified 40 fs pulses at a repetition rate of 1 kHz and a pulse energy of 7 mJ. The amplification process follows the chirped pulse amplification scheme [20]. The incoming oscillator pulse is stretched in time before it is amplified by stimulated emission in pumped Ti:Sa crystals in the amplification cavity and compressed in time after the amplification process (Fig. 3.1). The compression (and stretching) is done with a pair of diffraction gratings. Applying this technique makes such high pulse energies available, otherwise the active medium would be destroyed by the high peak light intensity. The amplification is split into two parts: A regenerative amplifier (RGA) where the amplification process is saturated after several roundtrips and a booster where it only passes once and the pulse energy is approximately doubled. The injection and release of only one seeding oscillator pulse into the RGA cavity within on amplification period T_{rep} is controlled with a pair high-voltage switched Pockels cells. In table 3.1 the specifications of the laser system are summarized, the pulse energy of the seeding oscillator pulse is approximately increased by a factor of $10^6.$



FIGURE 3.1: Schematic Drawing of the chirped pulse amplification scheme: the seeding oscillator pulse is stretched in time, amplified in a gain medium and compressed afterwards, yielding an ultrashort high-energy pulse (from [21]).

Laser Type	Oscillator	2-Stage Amplifier
Model	Coherent Mantis	Coherent Legend Duo
Center Wavelength	800 nm	800 nm
Bandwidth	80 nm	$30\mathrm{nm}$
Pulse Duration	$< 30 \mathrm{fs} \ \mathrm{(operating at} \ 50 \mathrm{fs})$	$40\mathrm{fs}$
Pulse Energy	$5\mathrm{nJ}$	$7\mathrm{mJ}$
Repetition Rate	$80\mathrm{MHz}$	1 kHz

TABLE 3.1: Summary of the specifications of the laser system

3.2 THz Setup

3.2.1 THz Generation and Electro-Optic Sampling

In the beginning of this thesis a simplified version of the final experimental setup was built (Fig. 3.2). The aim of this first setup was to generate THz pulses from the femtosecond optical laser pulses and to measure them. Since there was no power monitoring device for the low THz range available, the electric field of the generated pulses was measured by applying the electro-optic (EOS) sampling technique discussed in Section 2.1.2. Using a conventional bolometer as power monitoring device



the generated THz radiation would be overwhelmed by the black body radiation of the surrounding.

FIGURE 3.2: Setup for generation and detection of the THz pulses: amplified pulses passing a (100) GaSe crystal where THz generation via DFG occurs, the remaining 800 nm light is filtered out of the beam path with a silicon wafer at Brewster's angle for THz radiation. On a second silicon wafer the THz pulse and the optical sampling pulse from the oscillator are combined and focussed into an (110) ZnTe crystal. The THz pulse induces a birefringence in the crystal that is transformed to an intensity difference of the probe pulse by a quarter-wave plate and a polarizing beam splitter, the intensity difference is measured with a balanced photodetector.

For generating the THz pulses the amplified 50 fs laser pulses (s-polarized) were passed through a [001] GaSe crystal with a thickness of d = 0.5 mm. GaSe is suitable for generating low frequency THz radiation at normal incidence, since it fulfils the phase-matching condition (Sec. 2.1.1). The remaining 800 nm pump light is filtered out of the beam path with a silicon wafer placed at Brewster's angle θ_B for the generated p-polarized THz radiation. The refractive index for crystalline silicon is almost constant for low THz-frequencies $(n_{Si} = 3.41, \text{ Sec. } 4.3.1)$, so the silicon wafer was placed at $\theta_B = 73^\circ$. The THz pulse is then combined with the sampling pulse with another silicon wafer, also placed at θ_B , and focused together with an off axisparabolic gold mirror into the [110] ZnTe sampling crystal. S-polarized pulses of the oscillator were taken as sampling pulses, since a perpendicular polarization of the two beams gives the maximum signal [22]. A quarter-wave plate after the crystal is used to circularly polarize the probe beam, so that without any electric field present the polarizing beam splitter splits the beam in two parts of equivalent intensity hitting the balanced detector. When the THz field is present, the polarization of the probe beam will get elliptically polarized due to the induced birefringence and this

can be subsequently detected as intensity difference with the balanced detector. By scanning the delay between the oscillator pulse and the THz pulse, the electric field of the THz pulse can be scanned in the time domain.

Since the THz pulses arriving at a repetition rate of 1 kHz are sampled with the 80 MHz (T = 12.5 ns) oscillator pulse train, a boxcar integrator is used to pick out only the signal change of the one probe pulse overlapping with the THz pulse. The application of the boxcar integration gate is illustrated in Figure 3.3. The balanced detector was built from high speed photodiodes with rise times smaller than 1 ns, so that the ocillator pulse train can be fully resolved.



FIGURE 3.3: THz pulse ($f_{rep} = 1 \text{ kHz}$) sampled with optical pulse of the oscillator ($f_{rep} = 80 \text{ MHz}$), to only measure the signal from the pulse overlapping with the THz pulse a boxcar integration gate of width $T < T_{rep} = 12.5 \text{ ns}$ is applied. The temporal pulse width of the THz and the sampling pulse have been exaggerated as they are in reality shorter than 1 ps.

3.2.2 Optical-Pump / THz-Probe Spectroscopy (OPTP)

As a next step the THz beam path was extended by another off-axis parabolic mirror for measuring THz transients reflected from a sample. The sample is placed in the focal plane of the parabolic mirror and fixed on a kinematic mirror mount. The reflected pulse from the sample was aligned in a way to hit the parabolic mirror at a different height than the incoming pulse as indicated in Figure 3.4. This results in a reflected pulse traveling parallel at a different height as the incoming pulse after the parabolic mirror, which can be send to the 'spectrometer' with a pick-up mirror. To perform the alignment of the THz beam path, an extra adjustment diode-laser was aligned collinear to the optical beam that generates the THz pulse. If the pulse from the amplifier would be taken for this purpose, the sample at the focus of the parabolic mirror would be destroyed due to the high peak intensity, that is high enough to generate a plasma in ambient air. The angle of incidence onto the sample was kept as small as possible and large enough to separate the incoming from the reflected beam ($\theta < 5^{\circ}$), so that the reflection can still be treated as a normal incidence reflection. To also perform transmission experiments another parabolic mirror behind the sample was added to the setup, so it is possible to switch from one to the other geometry within a few minutes. The reflection and transmission beam paths are shown in Figure 3.4. For an OPTP experiment the amplified pulse was split into two parts where one part is used to pump the sample and is sent to a 1 ns delay stage and subsequently onto the sample.



FIGURE 3.4: Schematic drawing of the experimental optical-pump/THz-probe setup in reflection (transmission) geometry, the dashed line after the sample shows the transmission beam path.

Since the electric field of the probing THz pulse is recorded in the time domain, within a pump-probe scan a two-time dataset of the electric field $E_{\text{THz}}(t_{EOS}, \tau_{pp})$

has to be recorded. Here t_{EOS} is the time of the THz pulse scanned with the EOSdelay stage (Fig. 3.4) and τ_{pp} is the delay of the THz pulse with respect to the optical pump pulse scanned with the second delay stage. The temporal delays involved are shown in Fig. 3.5.



FIGURE 3.5: Temporal delays for an optical-pump/THz-probe experiment: the sampling pulse is used to scan the electric field of the THz pulse, delay $t_{\rm EOS}$, for every delay with respect to the optical pump pulse $\tau_{\rm pp}$, which gives a 2D-dataset $E_{\rm THz}(t_{EOS}, \tau_{pp})$.

3.2.3 Improvements: Cross-Correlation and Fast Scanning

The previously used step-by-step electro-optic sampling technique has the big disadvantage that for typical sampling parameters ($\Delta t = 25$ fs) only around one tenth of the used measurement time is used for acquiring data points of the THz electric field. The rest of the time is 'wasted' due to driving the EOS-delay stage to the next position. Therefore a continuous-driving and continuous measurement scheme was implemented, which decreased the required measurement time significantly. This becomes very important when performing pump-probe scans, where THz transients for several pump-probe delays $\tau_{\rm PP}$ have to be recorded. As an example, acquiring a THz waveform $(T = 10 \text{ ps}, \Delta t = 25 \text{ fs})$ in the step-by-step mode takes around 60 seconds, in the continuous driving mode, this can be done in less than 10 seconds. As a limiting factor here the repetition rate of the laser system comes into play, which determines the measurement time needed to record a data point with sufficient signal-to-noise ratio. The stage repeatedly drives back and forth between the two endpoints of the selected temporal range at constant velocity and the measurement software continuously reads out the signal of the balanced detector and the position of the stage. After each run the THz transient is put together by putting the measured points into the predefined temporal grid of fixed step width. The velocity

of the stage movement is chosen so that a defined number of averages is achieved for a defined step width. Figure 3.6 shows a sketch of the continuous measurement mode compared to the stepwise measurement.



FIGURE 3.6: Stepwise data acquisition (a) vs. Continuous Driving (b) shows the amount of time saved, the THz pulses that are measured are indicated at the bottom (spikes). For the stepwise measurement there is always some down time between the scanning steps, as for the continuous driving every THz pulse is measured, which decreases the amount of time needed to record a single waveform.

It was recognized that there is a certain physical jitter in between the sampling oscillator pulse and the THz pulse of several 100 fs within one hour, which is attributed to thermal drifts of the whole system. One approach to avoid this is to do the EOS with a small portion of the amplified pulse, but unfortunately this results in a much lower signal-to-noise ratio, since the shot-to-shot fluctuations are much higher within the amplified pulses. For correcting this physical jitter an additional non-collinear second-harmonic generation in a BBO crystal was measured as cross correlation. This defines the time zero between the optical sampling pulse and the THz pulse for every scan of the THz waveform. Figure 3.7 shows the implementation of the cross-correlation beam path into the setup. For this purpose the residual optical pulse from the THz generation is used and the oscillator pulse is split into two parts. In Figure 3.8 the correction of the temporal drift is demonstrated for a pump-probe scan repeated over four consecutive loops.



FIGURE 3.7: Setup with implemented cross-correlation measurement: a noncollinear second-harmonic generation in a BBO crystal between the residual optical pulse from the THz generation and a portion of the oscillator pulse is measured. This cross-correlation is used to define the time zero between both pulses and to correct for the physical jitter.



FIGURE 3.8: Recorded pump-probe scans (a), cross correlation scans (b) for 4 consecutive loops over the pump-probe delay of 1 ns and corrected and averaged field transients (c). The raw data (a),(b) shows a correlated drift which can be corrected using the cross-correlation measurement (b).

Chapter 4

Results I : Static THz Spectroscopy

In this section the results of the static THz time-domain spectroscopy measurements are presented. The generated THz pulses were characterized regarding their waveform, peak electric field strength and spatial profile. To test the accuracy of the setup, transmission and reflection measurements on samples with known response were performed. As preliminary measurements for the dynamic experiments shown in chapter 5, the dielectric function of the undoped semiconductors silicon and GaAs was determined.

4.1 Characterization of THz Pulses

4.1.1 THz Electric Field and Spectrum

The THz pulses were generated via difference-frequency generation in an 0.5 mm thick (001) GaAs crystal and detected via electro-optic sampling in an 0.5 mm thick (110) ZnTe crystal. The electric field of the THz pulse shows an almost single-cycle like behaviour with a center frequency of 1.5 THz and a bandwidth of 2 THz. The measured THz time domain waveform and its spectrum (Fig. 4.1) are in good agreement to the theoretical calculations for the difference-frequency generation in GaSe (Fig. 4.2) given in [6]. The phase matching condition for the difference-frequency generation in GaSe (Sec. 2.1.1) is limited by a transverse optical phonon resonance at 6 THz, which explains why only such a small bandwidth compared to the laser

bandwidth (10 THz) is converted efficiently into THz radiation for a crystal thickness of 0.5 mm. The refractive index for GaAs at THz frequencies [23] compared to the optical group index at 800 nm is shown in Figure 4.3.



FIGURE 4.1: Electric field of the THz pulse generated from 50 fs, 800 nm pulses in an 0.5 mm GaSe crystal in the time domain (a) shows an almost single cycle behavior and frequency domain (b) with a center frequency of 1.5 THz covering a bandwidth of 2 THz.



FIGURE 4.2: Electric field in the time domain (a) and frequency domain compared to the theoretical calculation (solid line) for difference-frequency generation in 0.5 mm GaSe of amplified 30 fs pulses (from [6]). The calculation involves coupled nonlinear wave equations and the dispersion of GaAs.

4.1.2 Water Absorption

Since there are a lot of rotational and vibrational transitions for water vapor in the THz band [24], the whole setup had to be purged with nitrogen. The importance of this is shown in Figure 4.4. The water absorption in ambient air (rH = 20%) leads to a pulse spectrum with very deep absorption dips as shown in Fig. 4.4 (b),



FIGURE 4.3: Refractive index of GaSe at THz frequencies (blue) compared to the group index at 800 nm (red) $n_g = 3.13$ for a electric field polarization perpendicular to the c-axis. The THz refractive index increases towards higher frequencies due to a transverse optical phonon resonance at 6 THz, therefore THz generation is only efficient for low THz frequencies.

corresponding to a loss of the single cycle nature of the initial pulse in the time domain. So the temporal width of the THz pulse increases according to its nonsmooth envelope which is undesirable for performing pump-probe measurements. It was also observed that the water absorption is very sensitive to fluctuations in the humidity so this would introduce an unwanted uncertainty for spectroscopic applications.



FIGURE 4.4: Effect of water vapor absorption: the electric field in the time domain (a) shows a longer pulse duration (red curve) compared to the pulse propagating in a nitrogen atmosphere (blue curve). In the frequency domain (b) the presence of water vapor causes deep absorption dips in the pulse spectrum (red curve).

4.1.3 Knife-Edge Measurement

For determining the spot size of the THz field focused by a parabolic mirror with a focal length of f = 75 mm onto the sample, a knife-edge measurement was performed. A D-shaped mirror was put in the focal plane of the parabolic mirror and moved out of the beam path to act as a reflecting knife. The resulting peak electric field amplitude was recorded as function of the lateral mirror position. From the fit of the data with an error function (Fig. 4.5) the spot size of the focused THz pulse was found to be FWHM = 1.3 mm. For an optical-pump/THz-probe measurement the optical pump beam should have at least twice the beam waist as the spot size of the probe beam.



FIGURE 4.5: Result of the Knife edge measurement of the focused THz pulse and fit with an error function yields spot size of FWHM = 1.3 mm.

From electrodynamics it is known that a plane wave with beam waist w_0 can be focused by an optical element with focal length f to a focused beam width of w_f proportional to its wavelength λ .

$$w_f = \frac{\lambda f}{\pi w_0} \tag{4.1}$$

For a central frequency of 1.5 THz and the applied parabolic mirror this yields an initial width of $w_0 = 5 \text{ mm}$ of the THz pulse. This matches the width of the generating optical beam, as it is expected from the parallel beam during the generation in the GaSe crystal. Equation 4.1 implies that the different spectral components of

the pulse are focused to different spot sizes that are proportional to the THz frequency. Between the lowest frequency in the spectrum of 0.5 THz and the highest frequency of 2.5 THz, there is a factor of 5, which is a totally different situation as for optical experiments. So the focused spot size of the lowest an highest frequency do also differ in a factor of 5, which has always to be kept in mind when performing pump-probe experiments since it might lead to undesirable artifacts in the measured signals [25].

4.1.4 Calibration of Field Strength

With the balanced detection scheme (Sec. 2.1.2) a relative intensity difference of the oscillator pulses on the balanced detector is measured. The intensity difference is proportional to the electric field of the THz pulse. As the actual measured quantity is a voltage proportional to the intensity difference this voltage was calibrated. For this purpose a defined intensity difference was introduce on the balanced detector with a half-wave plate mounted on a high precision rotation mount. To find out the peak electric field strength one could just use Eq. 2.6 that relates the electric field to the measured intensity difference and the electro-optic coefficient of ZnTe. But it is also worth having a look at the transfer function of the THz detection system.

For the electro-optic sampling of the THz electric field in ZnTe a frequency dependent transfer function can be calculated which accounts for phase mismatching effect during the detection process, the co-propagation of the THz and the optical pulse, and Fresnel losses at the interface of the crystal [26].

The phase matching, reflection and absorption losses can be described by the following transfer function:

$$G(\omega) = \frac{2}{(n(\omega)+1)\delta(\omega)} \frac{\exp(i2\pi\omega\delta(\omega)) - 1}{i2\pi\omega}$$
(4.2)

with the abbreviation

$$\delta(\omega) = \frac{n_g - n(\omega)}{c} d, \qquad (4.3)$$

where n is the refractive index at THz frequencies, n_g the optical group index of ZnTe and d the crystal thickness.

One also has to account for the frequency dependence of the relevant electro-optic coefficient r_{41} of ZnTe

$$r_{41}(\omega) = r_e \left\{ 1 + C \left(1 - \frac{\omega^2 - i\omega\gamma}{\omega_{TO}^2} \right) \right\},\tag{4.4}$$

where r_e is the purely electronic nonlinearity, C is the Faust-Henry coefficient that represents the ratio between the ionic and the electronic part of the electro-optic coefficient, ω_{TO} is the transverse optical resonance frequency in ZnTe and γ is the lattice damping. The specific values are given in [26].

The full transfer function is given as

$$R(\omega) = G(\omega) \times r_{41}(\omega). \tag{4.5}$$

The optical group index, the refractive index at THz frequencies and the resulting transfer function are shown in Fig. 4.6. The transfer function is almost flat up to 3 THz and the average value of 0.5 originates from the reflection loss at the first interface of the sampling crystal.



FIGURE 4.6: Refractive index of ZnTe for THz frequencies (blue) and optical group index at 800 nm (dashed)(a). Due to the phonon resonance at 5 THz the refractive index increases towards higher frequencies and effects the detection efficiency shown as transfer function (b) for a 0.5 mm thick ZnTe crystal. The transfer function is almost flat up to 3 THz.

Using Eq. 2.6 allows to calculate the peak value of the THz electric field to be around $50 \,\mathrm{kV/cm}$ which is a quite high field strength. For a further cross-checking of this value, a pulse energy measurement with a He-cooled bolometer could be performed. The value of the peak field strength is in good agreement to what was reported in

[6] for this type of THz generation. Since the THz pulse was planned to act as a probe pulse, a higher field strength was not desirable, but could be reached with a higher intensity of the generating optical pulse, as it leads to a nonlinear sample response [27]. Given the peak electric field of the pulse, its time domain waveform and the spatial profile from the knife-edge measurement, the total energy of the THz pulse can be calculated to be $W_{\text{pulse}} \approx 50 \,\text{nJ}$, which corresponds to an energy conversion efficiency of 5×10^{-5} for a generating pulse energy of 1 mJ. For a pulse repetition rate $f_{\text{rep}} = 1 \,\text{kHz}$ an average THz power of $\bar{P} = 50 \,\mu\text{W}$ is radiated. For comparison, the Stefan-Boltzmann law states that the total radiated power of a black body at room temperature with an area of the size of the focused THz spot $(1 \,\text{mm}^2)$ is $P_{\text{rad}} = 1 \,\text{mW}$, which is much higher than the generated THz radiation.

4.2 Test Measurements - Transmission

To test the accuracy of the THz setup, transmission measurements on samples with known response have been performed. For performing THz-TDS (time-domain spectroscopy) experiments in transmission, different samples were placed into the beam path and the electric field was recorded with and without the sample in the beam path. The exact sample thickness has to be known for being able to determine the dielectric function of the sample with high accuracy. Figure 4.7 shows the transmission beam path including multiple reflections inside of the sample and the resulting transmitted pulse train in the time-domain.



FIGURE 4.7: Transmission through a homogeneous plate (a) and resulting multireflections in the time-domain (b) for $d = 500 \,\mu\text{m}$ and a refractive index of n = 3. E_0 is the electric field without the sample in the beam path, $E_t^{(1)}$ is the first transmitted pulse through the sample and $E_t^{(2)}$ includes an extra roundtrip arriving 10 ps later at the detector, the multi-reflections can be separated in the time-domain if temporal difference fulfills $\Delta T > \tau_{\text{pulse}}$.

If the investigated sample is sufficiently thick the occurring multi-reflections can be neglected, since the transmitted THz pulse is measured in the time domain temporal windowing can be applied. As an example, for a sample thickness of 500 µm and a refractive index of n = 3 the first and second transmitted pulse are separated by 10 ps which is much longer then a typical THz pulse length of $\tau_{\text{pulse}} < 1 \text{ ps}$. The transmission of an electric field through the interfaces of the sample for normal incidence from refractive index $n_i \rightarrow n_j$ is described by the Fresnel equation $t_{ij} = E_t/E_{in} = n_i/(n_i + n_j)$. The propagation of a distance d through a medium is calculated via $\exp(i\tilde{k}d)$, with the complex wave vector $\tilde{k} = \omega \tilde{n}/c$ which is given
by the refractive index $\tilde{n} = n_r + in_i$. For a complex-valued refractive index the propagation factor includes the phase shift and absorption within the medium. In the frequency domain, neglecting multiple-reflections, the electric field with E_s and without the sample E_{air} in the beam path are related to the incoming electric field E_0 by

$$E_{air}(\omega, d) = E_0 \exp(+i\omega d/c) \tag{4.6}$$

$$E_s(\omega, d) = E_0 \frac{4n_s}{(1+n_s)^2} \exp(+i\omega \tilde{n}_s d/c).$$
 (4.7)

The complex-valued ratio of the two fields $\tilde{T}(\omega)$ can be split into an amplitude $A(\omega)$ and a phase factor $\exp(i\phi(\omega))$

$$\tilde{T}(\omega) = \frac{E_{\rm s}(\omega)}{E_{\rm air(\omega)}} = \frac{4n_{\rm s}}{(1+n_{\rm s})^2} e^{-\alpha d/2} e^{i\omega(n_r-1)d/c} = A(\omega)e^{i\phi(\omega)}.$$
(4.8)

The absorption coefficient α is related to the imaginary part of the refractive index n_i via $\alpha = 4\pi n_i/\lambda$, where λ is the vacuum wavelength of the incoming wave. For samples with low absorption $n_r \gg n_i$ holds, which is usually the case when performing a transmission measurement. The phase shift at the interfaces from the Fresnel term $4\tilde{n}_{\rm s}/(1+\tilde{n}_{\rm s})^2 \approx 4n_{\rm r}/(1+n_{\rm r})^2$ can be neglected. For this approximation the solution for the real part of the refractive index n_r and the power absorption coefficient α of the sample can be directly calculated [28] from the Fourier-transformed measured waveforms as

$$n_r(\omega) = 1 + \frac{c}{\omega d} \phi(\omega)$$

$$\alpha(\omega) = -\frac{2}{d} \ln \left[A(\omega) \frac{(n_r(\omega) + 1)^2}{4n_r(\omega)} \right].$$
(4.9)

4.2.1 Doped Silicon - Drude Response

THz time-domain spectroscopy has been widely applied to characterize the frequencydependent conductivity of doped semiconductors [15, 29] and the Drude model and its generalizations were successfully employed to describe the frequency-dependent conductivity for these type of samples. For doped semiconductors, depending on the doping concentration, the plasma frequency typically lies in the THz band which makes THz spectroscopy a suitable tool. This is in contrast to metals for which the plasma frequency usually lies in the visible up the ultraviolet range. For gold, the plasma frequency is $\omega_p = 2.18 \times 10^3$ THz [30] which corresponds to a wavelength of $\lambda = 137$ nm, which is in the UV. The transmitted THz field through an n-type phosphor-doped silicon wafer with a resistivity of $\rho = 0.3 \Omega$ cm and a thickness of d = 375 µm was measured. The electric field in the time and frequency domain are shown in Fig. 4.8.

Using equation 4.9, the complex refractive index \tilde{n} of the sample is calculated from the ratio of the reference and the transmitted THz spectra. In Fig. 4.9 the refractive index of the sample is shown. The imaginary part n_i (absorption) increases and the real part n_r decreases towards low frequencies in comparison to undoped silicon due to the additional free carrier contribution. It also shows that the assumption $n_r > n_i$ is valid.

The conductivity σ can be calculated from the refractive index $\sigma(\omega) = i\varepsilon_0\omega(n_L^2 + \tilde{n}^2(\omega))$ with the knowledge of the lattice contribution $n_L^2 = \varepsilon_L$ to the dielectric function (Sec. 2.2). The lattice contribution $n_L = 3.41$ can be obtained by measuring the transmission through an undoped silicon wafer as shown in Sec. 4.3.1. The frequency-dependent conductivity was fit with the Drude model and the parameters $\sigma_{DC} = 2.7$ S/cm for the DC-conductivity and $\tau = 171$ fs for the scattering time. From the fit parameters the plasma frequency can be calculated to be $\omega_p = \sqrt{\sigma_{DC}/\varepsilon_0\tau} = 13.4$ THz. The fit parameter σ_{DC} of is in good agreement to the specification of the manufacturer ($\sigma_{DC}^* = \rho^{-1} = 3.3$ S/cm).



FIGURE 4.8: Reference (blue) and transmitted THz pulse through the doped silicon wafer (red) in the time domain (a) and in the frequency domain (b) with the calculated absolute transmission $|\tilde{T}(\omega)|$ (dashed line). The silicon wafer acts as an high pass filter as frequencies lower than 0.5 THz are totally absorbed in the sample, the vertical lines mark the region of interest with sufficient spectral intensity for further data evaluation.



FIGURE 4.9: Real (blue) and imaginary (red) part of the refractive index $n = n_r + in_i$ (c) with indicated lattice contribution (dashed line). Real (blue) and imaginary (red) part of the conductivity $\sigma = \sigma_r + i\sigma_i$ (d) fitted with the Drude model, with parameters $\sigma_{DC} = 2.7 \,\text{S/cm}$ and $\tau = 171 \,\text{fs}$.

4.2.2 LiNbO₃ - Phonon Resonance

Another useful application of THz-TDS is to determine the dielectric function, i.e. the real part of the refractive index n_r and the power absorption α , for materials that have a transverse optical (TO) phonon resonance in the THz band. The transmitted THz field through a 500 µm thick z-cut LiNbO₃ wafer was measured and is shown in Fig. 4.10. In the time domain the transmitted pulse shows a significantly different shape which is caused by additional dispersion and the increasing absorption towards higher THz frequencies in the sample. From the complex-valued transmission $\tilde{T}(\omega) = \tilde{E}_s(\omega)/\tilde{E}_0(\omega)$ the dielectric function can be calculated with Eq. 4.9.

The real part of the refractive index n_r and the power absorption α increase towards high frequencies due to an TO phonon resonance at 4.5 THz. The refractive index and power absorption, i.e the dielectric function, are in good agreement to what was reported in [31], as shown in Fig. 4.11. For the dielectric function only the values up to 2 THz are considered to be accurate because for higher frequencies the transmitted power already reaches the noise floor of the spectrum. This is indicated with the vertical lines in the frequency domain data, where also a low-frequency cut-off is introduced due to the initial THz spectrum.



FIGURE 4.10: Reference electric field of the THz pulse without the sample in the beam path (blue) and transmission through a 0.5 mm z-cut LiNbO₃ wafer (red) in the time domain (a) and in the frequency domain (b). The absolute value of the transmission $|\tilde{T}(\omega)|$ (circles) is indicated in (b). The sample acts as an low-pass filter as the transmission decreases for increasing frequencies and vanishes for $\nu > 2$ THz.



FIGURE 4.11: The real part of the refractive index n_r (a) and the absorption coefficient α (b) for LiNbO₃ increase towards higher frequencies due to a TO phonon resonance at 4.5 THz. The solid line shows the calculated values from [31] to which the measurement agrees well within the interval indicated by the dashed vertical lines.

4.2.3 Highly Doped GaAs in Reflection

For highly doped semiconductors a THz-TDS transmission measurement is not possible for a typical wafer thickness of several 100 µm, because of the high plasma frequency and the resulting power absorption in the THz band. As shown in [32, 33] THz-TDS in reflection serves as a useful tool to study the conductivity of highly doped semiconductors.

Performing a THz-TDS experiment in reflection is a quite difficult task because one cannot switch easily from a measurement of the incoming to the reflected pulse from the sample, which would be necessary to determine the dielectric function of the sample with great accuracy. The solution of this problem is to measure the reflection from a reference (e.g. metallic) mirror and compare it to the sample response. The crucial task here is to put the reference and the sample into the exact same position with micrometer precision. A misalignment of 10 µm causes a temporal shift of 66 fs, this alters the obtained results dramatically. Nevertheless for highly absorbing samples reflection spectroscopy is the method of choice. The refractive index of the sample can be calculated from the Fresnel reflection formulas. For normal incidence the reflected electric field E_r from a sample (**R**eference, **S**ample) with the refractive index n_i is related to the incoming field E_{in} via

$$\frac{E_{r,i}(\omega)}{E_{in}(\omega)} := r_i(\omega) = \frac{1 - n_i(\omega)}{1 + n_i(\omega)} \quad ; \quad i = R, S.$$

$$(4.10)$$

The incoming electric field can be cancelled out by dividing the equations for the reference and the sample, yielding the relative complex-valued reflectivity $Q(\omega)$

$$Q(\omega) := \frac{r_S(\omega)}{r_R(\omega)} = \frac{(1 - n_S(\omega))(1 + n_R(\omega))}{(1 + n_S(\omega))(1 - n_R(\omega))}.$$
(4.11)

This can be directly inverted for the complex-valued refractive index of the sample n_S if the refractive index of a reference sample n_R is given

$$n_S(\omega) = \frac{1 + n_R(\omega) - Q(\omega) + Q(\omega)n_R(\omega)}{1 + n_R(\omega) + Q(\omega) - Q(\omega)n_R(\omega)}.$$
(4.12)

As an example, a highly n-type Si-doped GaAs sample $(n_c = (4.2 - 6.3) \cdot 10^{16} \text{ cm}^{-3})$ from *MTI Corp.* was studied. A transmission measurement for this sample was not possible since all radiation gets absorbed within the sample. As reference sample a gold mirror served as an almost perfect reflector. The reference mirror and the sample were mounted on a kinematic mirror mount which was then attached to a manual linear stage, to switch from one to the other. For the THz beam alignment the beam from a laser diode was overlapped collinearly with the THz beam, so that the alignment could be done with a visible beam. The recorded waveforms in the time domain are shown in Fig. 4.12

For the dielectric function of gold in the THz range the values from [30] were taken.

All though the quality of the data is not satisfactory, the absolute reflectivity shows the form of a Drude response. The absolute reflectivity fits quite well to the Drude response but the calculated conductivity differs significantly caused by the phase uncertainty. But with taking some bigger efforts it should be possible to determine the conductivity with higher precision with this setup. From the plasma frequency $\omega_p/2\pi = 8.7$ THz and with the effective mass of electrons in the conduction band of GaAs $m^* = 0.067m_e$ [34] the carrier density can be calculated to be $n = \varepsilon_0 \omega_p^2 * m^*/e^2 = 6.1 \times 10^{16} \text{ cm}^{-3}$. This value fits into the specified range of the wafer manufacturer. The mobility $\mu = e/\gamma m^* \approx 4 \times 10^4 \text{ cm}^2$ / Vs from the fitted damping rate γ comes out one order of magnitude too high from this measurement as it should have a value of $\mu \approx 6 \times 10^3 \text{ cm}^2$ / Vs [35].



FIGURE 4.12: Electric field reflected from a gold mirror (blue) and a doped GaAs wafer (red) in the time domain (a) and the frequency domain (b). The absolute value of the reflectivity (black dots) was fit with the Drude model with a plasma frequency of $\omega_p/2\pi = 8.7$ THz and a damping rate of $\gamma = 0.66$ THz (solid black line).



FIGURE 4.13: Real (blue) and imaginary (red) of the dielectric function ε (a) and conductivity σ (b) for highly doped GaAs. A relative time shift of $\Delta t = 65$ fs between both THz pulses was manually introduced to fit the Drude model (solid lines).

4.3 Preliminary Measurements

For the undoped silicon and GaAs samples that have also been investigated in optical-pump/THz-probe experiments, the static dielectric function in the THz range has been determined. The undoped semiconductor wafers were investigated by THz time-domain spectroscopy in transmission.

4.3.1 Undoped Silicon

The transmitted electric field through a high resistivity silicon wafer with thickness of $d = 500 \ \mu m$ was measured. In the time domain (Fig. 4.14) it shows that the transmitted pulse through the wafer arrives approximately 4 ps later at the ZnTe crystal ('detector') with respect to the probing optical pulse. This would give rise to a refractive index of n = 3.4 of the sample. The amplitude ratio in the frequency domain shows an almost constant value which is due to the additional surface reflection losses. The fluctuations around the constant amplitude ratio should vanish if the measurement is repeated for several times and an averaging over the recorded data is performed. A transmission measurement here is performed without an additional reference beam, which is the common technique in optical measurements. Here the electric field was recorded without the sample, then the sample was moved into the beam path and the electric field was recorded, so there were several minutes between both measurements. So fluctuations (drifts) in the laser output and the resulting THz waveform could not be avoided. The phases of the two pulses show a linear frequency dependence with different slopes as this is a general feature of the Fourier-transformation for a time shift $\tilde{E}(\omega, \Delta t) = \tilde{E}(\omega, \Delta t = 0)e^{-i\omega\Delta t}$. From Eq. 4.9 the phase shift is related to the real part of the refractive index as $\Delta\phi(\omega) = \phi_S(\omega) - \phi_0(\omega) = (n_r(\omega) - 1)\omega d/c$ from which the frequency dependent refractive index can be calculated. The best agreement to previously reported values for the refractive index of silicon [36–38] was obtained for a thickness of $d = 525 \, \mu m$, which is within the uncertainty specified by the manufacturer. The real part of the refractive index is almost constant within the THz range and there is no absorption observable despite some fluctuations that result from intensity fluctuations of the laser system.



FIGURE 4.14: Electric field with (red) and without (blue) the undoped silicon wafer in the beam path in the time domain (a) and frequency domain in amplitude (b), where also the absolute value of the transmittance (dots) is shown, which is almost constant, despite some fluctuations.



FIGURE 4.15: The spectral phase (a) $\phi(\omega)$ of the THz pulse with (red) and without (blue) the undoped silicon wafer in the beam path shows different slopes, which corresponds to refractive index of the sample as $\Delta\phi(\omega) = \phi_S(\omega) - \phi_0(\omega) = (n_r(\omega) - 1)\omega d/c$. In (b) the real (blue) and imaginary part of the refractive index of the silicon sample is shown. Both values are constant as $n = 3.41 + i \cdot 0$, the deviations in the low frequency range might be a result of a free carrier contribution because of crystal impurities.

4.3.2 Undoped GaAs

Also the transmission through a semi-insulating GaAs wafer with a thickness $d = 500 \,\mu\text{m}$ was measured, for which the results are very similar to that of the silicon sample. In Fig. 4.16 the measured THz pulses are shown. The real part of the dielectric function has an average value of $\langle \varepsilon_r \rangle = \langle n_r \rangle^2 = 3.63^2$ and increases

slightly towards higher frequencies, as shown in Fig. 4.17. This due to a phonon resonance at 8 THz and agrees well with previously reported values [38, 39]. The imaginary part of the dielectric function is almost zero within the bandwidth of the THz pulse, which shows that there is no absorption, i.e. free carriers, in the sample.



FIGURE 4.16: Electric field with (red) and without (blue) the semi-insulating GaAs wafer in the beam path in the time domain (a) and frequency domain in amplitude (b). The absolute value of the transmittance (dots) is shown, which decreases for higher frequencies.



FIGURE 4.17: The spectral phase (a) $\phi(\omega)$ of the THz pulse with (red) and without (blue) the GaAs wafer in the beam path shows different slopes, which corresponds to refractive index of the sample as $\Delta\phi(\omega) = \phi_S(\omega) - \phi_0(\omega) = (n_r(\omega) - 1)\omega d/c$. In (b) the real (blue) and imaginary part (red) of the dielectric function of the GaAs sample are shown. The real part increases for higher frequencies due to a phonon resonance. The vertical lines indicate the region for which the average of the dielectric function is $\langle \varepsilon_r \rangle = 3.63^2$.

Chapter 5

Results II: Optical-Pump/THz-Probe Spectroscopy



FIGURE 5.1: Sketch of an optical-pump/THz-probe experiment in reflection geometry

5.1 General



FIGURE 5.2: Sample response (e.g. reflectivity) after excitation with an optical pump pulse at t = 0, measured by a THz probe pulse with subpicosecond duration as a function to the pump-probe delay τ_{pp} .

Optical-pump/THz-probe (OPTP) experiments on semiconductor samples were performed to investigate carrier dynamics with picosecond temporal resolution. A sketch of such an experiment is shown in Fig. 5.2.

If the photon energy of the optical pump pulse is larger than the band gap of the semiconductor, an absorbed pump photon leads to an electronic transition within the band structure of the sample. For a semicondutor, an electron is excited from the valence band into the conduction band. The remaining electrons minus the excited electron in the valence band behave collectively equivalent to a charged particle of charge +e, thus forming a hole, an electron hole-pair is created. With an OPTP experiment one can distinguish between bound and free charges, i.e. the difference between a sample that behaves dielectric-like and metal-like. The optical excitation of free carriers in a semiconducting sample leads to an increase in the reflectivity of the probing THz pulse and a decrease in the transmission of the probe pulse, as metals reflect electromagnetic radiation better than dielectrics. Measuring the sample response for different pump-probe delays τ_{pp} , the temporal evolution (e.g. the recombination) of the photoexcited carrier density can be measured with a temporal

resolution determined by the probing THz pulse ($\tau < 1 \,\mathrm{ps}$). The duration of the optical pump pulse was always kept shorter than 100 fs, so the temporal resolution is determined by the THz pulse length. The probing THz pulses are recorded in the time-domain with the electro-optic sampling (EOS) technique as shown in Sec. 2.1.2. The measured pump-probe signal is the electric field $E(t_{EOS}, \tau_{pp})$ dependent on the EOS delay t_{EOS} and the pump-probe delay τ_{pp} (Fig. 3.5). Thus one has access to the amplitude A and phase ϕ of the pump-induced change in the reflectivity (or transmission) $\frac{\tilde{r}(\omega, \tau_{pp})}{\tilde{r}_0(\omega)} = \frac{\tilde{E}(\omega, \tau_{pp})}{\tilde{E}_0(\omega)} = A(\omega)e^{-i\Delta\phi(\omega)}$. From the Fourier-transformed electric field $\tilde{E}(\omega, \tau_{pp})$ for all pump-probe delays τ_{pp} the change in the dielectric function of the sample can be calculated. The time-dependent dielectric function of the sample is given by the static lattice contribution ε_L and the time-dependent photo-induced conductivity σ as $\tilde{\varepsilon}(\omega, \tau_{pp}) = \epsilon_L(\omega) + i\sigma(\omega, \tau_{pp})/\omega\varepsilon_0$ (Sec. 2.2). If the static dielectric function of the sample is known, the frequency-dependent photo-induced conductivity $\sigma(\omega, \tau_{pp})$ can be calculated for all pump-probe delays τ_{pp} .

5.1.1 Reflection from a Photoexcited Surface Layer

The investigated samples are semiconductor wafers with a thickness of $d = 500 \,\mu\text{m}$. The typical penetration depth of the optical pump pulse ($\lambda = 800 \,\text{nm}$) is $D = 10 \,\mu\text{m}$, which is much shorter than the sample thickness. resulting in a reflection from a strongly varying refractive index within the propagation direction z of the probing pulse. Directly after the excitation the carrier density n will be proportional to the absorbed energy in the depth of the sample z as $n(z) = n_0 \exp(-z/D)$ which leads to a z-dependent conductivity $\sigma(\omega, z)$ or equivalently to a dielectric function $\varepsilon(\omega, z)$.

For the case of the reflection from an exponential carrier density profile an analytical solution of the wave equation was given in [40] in terms of modified Bessel functions of complex order. Due to the inhomogeneous excitation the photoexcited carriers will diffuse into the depth of the sample, which alters the carrier distribution. The solution for an exponential profile will only be applicable for short pump-probe delays. As the ongoing carrier diffusion introduces an additional degree of freedom into the data analysis it is convenient to treat the actual carrier density distribution as a thin homogeneously excited layer with fixed thickness d of the order of the penetration depth $d \approx D$. It is shown in Figure 5.3 that exact solution and thin film approximation agree very well.

For the calculation of the reflectivity of a homogeneous layer only multiple reflections within the thin layer on top of the wafer (Fig. 5.4) have to be considered because the



FIGURE 5.3: Amplitude (a) and phase (b) of the reflectivity change 30 ps after 800 nm excitation of GaAs wafer fitted with the exact solution of an exponential carrier density profile (solid line, $n_c = 9.5 \cdot 10^{16} cm^{-3}$, $\tau = 150 \text{ ps}$, d = 1.44 µm) compared to the thin film approximation and a Drude conductivity (dashed line, $n_c = 5.5 \cdot 10^{16} cm^{-3}$, $\tau = 160 \text{ ps}$, d = 2.3 µm). Both models agree well with each other and also to the measured data.

time domain measurement of the THz field allows temporal windowing of only the main reflection. As seen in previous experiments the reflection from the backside of the wafer arrives around 10 ps later at the detector which is much longer than the THz pulse duration. The reflection from such a system can be calculated by taking the sum over an infinite number of multiple reflections (geometric series) or calculated within a transfer matrix formalism which is basically the same [41].

The coefficients $t_{ij} = 2n_i/(n_i + n_j)$ and $r_{ij} = (n_i - n_j)/(n_i + n_j)$ denote the Fresnel transmission and reflection coefficients for the electric field at normal incidence for the boundary $n_i \rightarrow n_j$. As the refractive index is in general complex-valued this is also true for the Fresnel coefficients. Propagation through a medium of thickness d and refractive index n_i is described with a complex-valued propagation factor $p_i = \exp(-i\omega \tilde{n}_i d/c)$. All coefficients are meant to be frequency-dependent and complex-valued which will be dropped in the following notation. The refractive index in the conducting layer can be expressed as $n_2(\omega) = \sqrt{n_3^2 + i\sigma(\omega)/\omega\varepsilon_0}$ with the refractive index of the unexcited sample n_3 frequency-dependent conductivity $\sigma(\omega)$.

The reflection from the top surface is given by

$$r_0 = E_r^{(0)} / E_{in} = r_{12}.$$



FIGURE 5.4: Photoexcited layer n_2 of thickness d on top of semiconductor wafer with thickness L. For $d \ll L$ only multiple reflections within the top layer are considered due to the temporal windowing of the measured THz pulses. The black area indicates the exact initial exponential carrier density distribution due to the optical pump pulse absorption.

The first multiple reflection including one extra round trip in the thin layer is

$$r_1 = E_r^{(1)} / E_{in} = t_{12} p_2^2 r_{23} t_{21}$$

and the nth multiple reflection including n extra round trips

$$r_n = E_r^{(n)} / E_{in} = r_1 (\underbrace{r_{21} p_2^2 r_{23}}_{=:p_R})^{n-1} = r_1 p_R^{n-1}.$$

All reflection can be summed up by employing the geometric series with the factor p_R accounting for an extra round trip in the photoexcited layer

$$\sum_{n=0}^{\infty} E_r^{(n)} / E_{in} = r_0 + r_1 \frac{1}{1 - p_R}.$$
(5.1)

Figure 5.5 shows the calculated reflectivity for various conducting film thicknesses compared to the reflection from a bulk sample. It is clearly shows that for an increasing film thickness the response approaches that of a bulk conducting sample with only one surface reflection. It also shows that for a typical penetration depth of 10 µm the deviations from the bulk reflection cannot be neglected.



FIGURE 5.5: Comparison of the reflectivity in amplitude (a) and phase (b) from a thin conducting layer with Drude parameters ($\sigma_{DC} = 30 \,\text{S/cm}, \tau = 150 \,\text{fs}$) on substrate with $n_L = 3.6$ (GaAs) for different layer thicknesses, showing the deviations from a homogeneously excited sample(dotted line). For thicker layers the deviations from the bulk sample become smaller.

5.1.2 Transmission Through a Photoexcited Surface Layer

Following the same procedure as for the reflection case (Fig. 5.4) the pump-induced relative change in the transmission $T^{(exc)}$ can be written with transmitted electric field through the unexcited E_t^0 and the excited sample $E_t^{(exc)}$ as

$$T^{(exc)}(\omega) = \frac{E_t^{(exc)}(\omega)}{E_t^0(\omega)} = \frac{t_{12}p_2t_23p_3(-d)}{(1 - r_{23}p_2^2r_{21})t_{13}}.$$
(5.2)

The problem of equation 5.2 that it can not be solved directly for the refractive index of the conducting layer n_2 because it occurs in an exponential $p_j = \exp(-i\omega \tilde{n}d/c)$ and in the Fresnel coefficients $t_{ij} = n_i/(n_i + n_j)$. But it could be solved numerically which was not done here as the change in the transmission was fit with a suitable model for the conductivity of the photoexcited layer, which was easier to apply.

There exists a thin-film approximation for the transmission of a thin conducting film on an insulating substrate with refractive index n of EM-waves [42] which is only valid if the wavelength λ of the incoming wave is much larger than the thickness dof the conducting layer $\lambda \gg d$. The large benefit of this relation is that it can be directly inverted for the conductivity σ .

$$\frac{E_t^{(exc)}(\omega)}{E_t^0(\omega)} = \frac{1+n}{1+n+Z_0\sigma(\omega)d},$$
(5.3)

where $Z_0 = 376.7 \Omega$ denotes the impedance of free space. For the investigated frequency range of several THz it was observed that this simplification only holds for film thicknesses with $d \ll 1 \,\mu\text{m}$, so it is not applicable for the cases investigated here. Fig. 5.6 shows the change in the transmission through a photoexcited conducting layer with a thickness of $d = 5 \,\mu\text{m}$ calculated with the exact formula (Eq. 5.2) and the approximation (Eq. 5.3). The calculation from the thin-film approximation differs significantly from the exact calculation. The vacuum wavelength for 1 THz is 300 μm , which is much larger than the estimated layer thickness, so this deviation from the approximation is quite surprising.



FIGURE 5.6: Relative change in the transmission in amplitude (a) and phase (b) as calculated with the thin-film approximation (Eq. 5.3) and the exact formula (Eq. 5.2). Both results differ significantly so the approximation is not valid for this frequency range. The thickness of the conducting layer is 5 µm, the Drude parameters for the conductivity are $\sigma_{DC} = 40 \text{ S/cm}, \tau = 150 \text{ fs}$ and the refractive index of the substrate is $n_L = 3.6$.

For the case of small changes in the transmitted electric field $\Delta E \ll E$ transfer functions for several cases of layered sample geometries are given in [43], but are not applicable here, either. Here pump induced changes of the probing THz field of approximately a factor of 2 were investigated.

5.1.3 Carrier Dynamics

Photoexcited electron-hole pairs in the bulk of a sample will recombine with a characteristic time constant τ_b . This radiative transition this can be observed by timeresolved photoluminescence measurements. For samples with a thickness larger than the penetration depth of the optical pump pulse carrier diffusion into the depth of the sample will take place which is described by a diffusion equation $(\partial_t n = D\partial_x^2 n)$. The diffusivity is given by the Einstein relation $D = \mu_{ab}k_BT/e$, where μ_{ab} is the ambipolar mobility given through the electron and hole mobilities $1/\mu_{ab} = 1/\mu_e + 1/\mu_h$. The recombination on the surface of a semiconductor is known to be totally different from the bulk material. A reason for that is that dangling bonds can act as surface recombination centres where non-radiative recombination takes place trough defect levels.[44]

It is customary to relate the time constant of the surface recombination τ_s to the sample thickness d via $\tau_s = d/2$, where the quantity s is the surface recombination velocity (the factor 2 refers to the two wafer surfaces).

The effective carrier lifetime is related to the two recombination mechanisms as follows [45]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} = \frac{1}{\tau_b} + \frac{2s}{d},$$
(5.4)

so the surface recombination is important for small sample thicknesses and equivalently for thin photoexcited layers.

An analytical solution of the diffusion equation 5.5 was given in [46] involving the surface recombination velocity s, a slower bulk recombination time τ_b and the diffusivity D. For the initial condition the optical penetration depth $1/\alpha$ of the pump pulse is needed and the pump pulse is assumed to be a $\delta(t)$ -pulse. The diffusion equation reads

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2} - \frac{n}{\tau_b} + \delta(t) \exp(-\alpha z).$$
(5.5)

With the following boundary conditions:

$$n(0,t) = \frac{D\partial n(z,t)}{s \ \partial x}|_{z=0}$$
(5.6)

which states that carrier at the surface will recombine (Fig. 5.7), and

$$n(L,t) = 0 \tag{5.7}$$

$$n(z,0) = 0 (5.8)$$

(5.9)

stating that there are no excess carriers before the excitation and for a sufficient distance L in the depth of the sample.

The solution can be found by a Laplace transform method [46]:

$$n(x,t) = \phi(x,t) \exp(-t/\tau_b)$$

$$\phi(x,t) = \exp\left(-\frac{x^2}{4Dt}\right) \left\{\frac{1}{2} \left[\omega \left(\alpha \sqrt{Dt} - \frac{x}{2\sqrt{Dt}}\right) + \frac{\alpha D + s}{\alpha D - s}\omega \left(\alpha \sqrt{Dt} + \frac{x}{2\sqrt{Dt}}\right)\right] - \frac{s}{\alpha D - s}\omega \left(s\sqrt{\frac{t}{D}} + \frac{x}{2\sqrt{Dt}}\right)\right\},$$
(5.10)
(5.10)
(5.11)

where ω denotes the exponentially scaled complementary error function $\omega(z) = \exp(z^2)[1 - \operatorname{erf}(z)]$ The solution for some specific time steps is shown in Fig. 5.7, where also the first boundary condition (Eq. 5.6) was indicated.

The total carrier density for this model is given is given by:

$$n(t) = \int_{0}^{L} dx \ n(x,t)$$

= $\exp(-t/\tau_{b}) \left\{ \frac{s}{\alpha(s-\alpha D)} \omega(\alpha \sqrt{Dt}) - \frac{D}{s-\alpha D} \omega\left(s\sqrt{\frac{t}{D}}\right) \right\}$ (5.12)

In the following it will be shown that the response (transmission/reflection) from such an inhomogeneous carrier density profile, resulting from the bulk and surface recombination and the carrier diffusion, can be well described by a thin homogeneous film. For this calculation it also was ensured that the total number of carriers is the same for both cases (Fig. 5.8(a)). The space-dependent Drudeconductivity $\sigma(\omega, z) \sim \frac{n_c(z)}{1-i\omega\tau}$ is used for calculating the THz response in a transfer matrix formalism.[41] The general dependence of the scattering time τ on the carrier density was neglected here.



FIGURE 5.7: Initial exponential carrier density profile (dashed line) for a penetration depth of 1 µm and carrier density profiles for 10, 50, 100, 300 and 1000 ps after photoexcitation calculated with a bulk lifetime $\tau_b = 2$ ns, surface recombination velocity $s = 8 \times 10^5$ cm/s and a diffusivity $D = 100 \text{ cm}^2/\text{s}$, the straight dashed lines indicate the boundary condition (Eq. 5.6) for the surface recombination at z = 0.

For the example shown in Figure 5.8, a carrier density profile was chosen that deviates significantly from the initial profile as surface recombination has taken place and so the 'center of charge' has moved into the sample. The calculation shows that even for this case the reflectances/ transmittances agree reasonably well in amplitude and phase. For carrier distributions agreeing more closely with the step function, the accordance in the response increases.



FIGURE 5.8: Calculation of the amplitude (b) and phase (c) of the THz reflection/transmission resulting from a inhomogeneous carrier density profile (a) (dots) compared the response of thin homogeneous layer with a thickness of 1 µm (red line in (a)), the dots in the normalized carrier density plot (a) correspond to the step width applied in the transfer matrix calculation. The absolute relative deviation (d) from the response of the real profile stays below 3%. The Drude parameters for the conducting layer are $\sigma_{DC} = 40$ S/cm and $\tau = 200$ fs.

5.1.4 Temporal Resolution

The achievable temporal resolution of a pump-probe experiment is determined by the temporal length of both the probe and the pump pulse. In the case of the OPTP experiments performed here, the THz-probe pulse has a length of $\tau_{\text{probe}} \approx 500 \,\text{fs}$ which is much longer than the length of the optical pump pulse $\tau_p < 100 \,\text{fs}$. If both pulses impinge non-collinearly on the sample, an additional geometrical smearing decreases the temporal resolution. A schematic drawing of a probe pulse at normal incidence and a pump under an angle α is shown in Figure 5.9. In this configuration, the temporal smearing can be estimated to be $\Delta t = \tan(\alpha) w_{probe}/c$. For a typical focused spot size of a THz pulse of $w = 1 \,\text{mm}$ (Sec. 4.1.3) and an angle of incidence

of $\alpha = 30^{\circ}$, this leads to an additional smearing of $\Delta t = 2 \text{ ps}$, which is much larger then the temporal THz probe pulse width.



FIGURE 5.9: Non-collinear pump probe geometry and resulting temporal smearing Δt that is related to the angle of incidence of the pump pulse α and the spatial probe pulse width w_{probe} as $\Delta t = \tan(\alpha) w_{probe}/c$.

Observed Signal Rise Time

Figure 5.10 shows the rise in the reflectivity for short times before and after the excitation in an OPTP experiment in reflection geometry on a semiconductor sample (Si). The observed transient signal R can be treated as a convolution of an instantaneous(electronic) response (Heaviside function H) and Gaussian pump and probe pulses plus some additional smearing that might occur for geometrical reasons. As electronic transitions happen on much shorter time scales (sub-fs) than what is accessible in this experiment the electronic transition can be treated as instantaneous.

$$R = H * I_{pump} * I_{probe} * I_{smearing}$$

$$(5.13)$$

$$= H * I_{eff} \tag{5.14}$$

$$\sim \operatorname{erf}(\tau/\sigma_{eff}) \quad ; \ \sigma_{eff}^2 = \sum_i \sigma_i^2$$
 (5.15)

The observed onset in the reflectivity was fitted with an error function of the form $\operatorname{erf}(\tau/\sigma)$ which yields the width of the effective probing Gaussian with FWHM = $2\sqrt{\ln 2\sigma}$. It was observed that the measured width of the rising edge of 2 ps is much broader than the pulse width of the THz pulse of $\tau = 0.5$ ps would suggest. This can be explained fully geometrically by the non-collinear setup. The measured width



FIGURE 5.10: Pump-probe scan of the electric field of the THz pulse (a) for the optical excitation at $\tau_{pp} = 0$ of a silicon wafer measured in reflection. The integrated probe pulse intensity (b) shows a rise time of 2 ps, the dashed red line shows the derivative of the rising edge compared to the THz envelope (blue), the rise time is increased due to an additional temporal smearing that can be explained geometrically.

corresponds exactly to the value calculated in the previous paragraph. If pump and probe beam are arranged collinearly, the observed temporal resolution should be determined solely by the width of the THz pulse.

To increase the temporal resolution even further one can also do some additional data processing - Finite-difference time-domain analysis [47] of the dataset $E(t, \tau)$. The key idea is that usually the optical pump pulse ($\tau_p < 100 \,\text{fs}$) is much shorter than the THz pulse, so different parts of the THz pulse in reality 'see' different pump probe delays and this information is contained in such a two-time measurement.

5.2 Gallium Arsenide (GaAs)

GaAs is a III/V direct band gap semiconductor ($E_g = 1.42 \,\mathrm{eV}$) that crystallizes in the zinc blende structure. Semi-insulating GaAs crystals have very low carrier concentrations, resulting from crystal defects, leading to a resistivity up to $1 \times 10^9 \,\Omega$ cm which is still lower than the resistivity of true insulator. A semi-insulating (100) GaAs wafer ($d = 500 \,\mu$ m) was optically excited by an 800 nm (50 fs) pump pulse. Figure 5.11 shows the simplified band structure of GaAs and the possible above band gap excitation. The OPTP experiments were performed in transmission and reflection geometry. Although examples of transmission measurements have been reported very frequently in the literature, this is not the case for reflection measurements. Here experiments in both geometries were performed to cross-check the results by both methods . The absorption for GaAs at 800 nm is $\alpha = 1.3 \times 10^4 \,\mathrm{cm}^{-1}$ [48] which corresponds to an optical penetration depth of $d = 0.7 \,\mu$ m.



FIGURE 5.11: Simplified band structure of GaAs [49] showing only the first valence band and the conduction band and a possible vertical above band gap excitation of an electron-hole pair in the proximity of the Γ -point with an 800 nm pump pulse.

5.2.1 Transmission Measurement

In the transient THz transmission experiment an initial decrease of the transmission due to the additional photocarrier absorption was observed. A subsequent increase in the transmission for longer times after the photoexcitation within several 100 ps could be observed caused by electron-hole pair recombination.

The model of a thin conducting layer of approximately the optical penetration depth $(d = 1 \,\mu\text{m})$ on an insulating substrate was employed to fit the photoinduced change in transmission. The dielectric function of the conducting film was calculated as $\varepsilon(\omega) =$ $\varepsilon_{GaAs} + i\sigma(\omega)/\varepsilon_0\omega$. It was observed that the Drude model was not sufficient to fit the data so the generalized Drude model of the form $\sigma(\omega) = \sigma_0/(1-(i\omega\tau)^{1-a})$ (Cole-Cole model Sec. (2.3.3) with the additional parameter a was employed. As a result shown in Figure 5.12, the pump induced change in transmission $t_{exc}(\omega)/t_0(\omega) = A(\omega)e^{i\Delta\phi(\omega)}$ could be well described by the model of a thin homogeneous layer in amplitude and phase. For evaluating the data, a constant layer thickness was assumed to simplify the curve fitting procedure at all pump-probe delays τ_{pp} . Since the change in transmission should be proportional to the total amount of carriers, N the carrier dynamics are assumed to come out right ($\Delta T/T \sim \exp(-N)$). For GaAs the mobility of electrons in the conduction band is much larger than the hole mobility [50] so the effective mass for the conduction band electrons $m^* = 0.067m_e$ is used for the calculation of the carrier density ($\sigma_{DC} = ne^2 \tau / m^*$). The fitting procedure yields time dependent values for the carrier density n_c , the scattering time τ and the CC-parameter a which are shown in Fig. 5.13. As expected, the total transmission in Fig. 5.13(a) shows a behaviour that corresponds to the carrier density in Fig. 5.13(c).

As a result it can was observed that the decay in the total number of carriers can not be described by a single exponential decay, but by an biexponential decay indicating that there must exist at least two different relaxation mechanisms. This can be explained by the occurrence of surface and bulk recombination on different time scales and carrier diffusion into the depth of the sample. The pump pulse creates an exponential carrier density profile while being absorbed on its way into the depth of the sample. Then the fast surface recombination, diffusion of carriers into the bulk of the sample and the slower bulk recombination are taking place. The fast surface recombination should be the dominant process for short times after the excitation and for later times the bulk recombination rate should be observable, as there are almost no more remaining surface carriers.



FIGURE 5.12: Amplitude (a) and phase (b) of the spectral change in transmission $E_{exc}(\omega)/E_0(\omega) = t_{exc}(\omega)/t_0(\omega) = A(\omega)e^{i\Delta\phi(\omega)}$ for GaAs 30 ps after photoexcitation with an 800 nm pulse and a fluence of 40 µJ / cm². In (a) also the initial (dashed) and less intense THz spectrum after photoexcitation (solid) are indicated. The measured data (dots) agrees well with the fit of an 1 µm thick conducting (Cole-Cole model) layer with $n_c = 7 \times 10^{17} \,\mathrm{cm}^{-3}$, $\tau = 150 \,\mathrm{fs}$ and a = 0.1.

Figure 5.14 shows the total number of carriers fitted with equation 5.12 accounting for bulk and surface recombination. Beard et al.[13] found slightly different fit parameters which might result from the higher pump fluence applied here, the obtained bulk lifetime $\tau_b = 1.33$ ns here is about half of the value they found ($\tau_b = 2.1$ ns). Also the surface recombination velocity of s = 19.2 cm/s found here is much higher than what they have found $(s = 8.5 \times 10^5 \text{ cm s}^{-1})$. This should also result from the high number of carriers of $1 \times 10^{18} \,\mathrm{cm}^{-3}$ which is two orders of magnitude higher than in their study $(2 \times 10^{16} \text{ cm}^{-3})$. The diffusion coefficient of $D = 11.2 \text{ cm}^2/\text{s}$ matches quite well their result of $D = 10 \,\mathrm{cm}^2/\mathrm{s}$, in [51] a value of $D = 20 \,\mathrm{cm}^2 \,\mathrm{s}$ was reported. The absorbed fluence of $40 \,\mu\text{J} / \text{cm}^2$ corresponds to a photon flux of 1.6×10^{14} cm⁻². Making the assumption that all photons are absorbed within the first 1 µm of the sample this would lead to an initial average carrier (e-h pair) density of 16×10^{17} cm⁻³. So the estimated initial carrier density is approximately 2 times higher than obtained via the fitting procedure of the data for short times after the photoexcitation. The reason for this might be that the surface recombination is that fast enough to decrease the number of carriers within a few picoseconds. A step size of 20 ps was not sufficient to capture the whole dynamics of the carriers for short times after the excitation.



FIGURE 5.13: Results of the OPTP transmission experiment on GaAs pumped with a fluence of 40 µJ / cm² at 800 nm: averaged change in transmission (a) (<>:= $\int d\omega |E(\omega)|^2$). Obtained fit parameters for the various pump-probe delays: collision time τ (b), carrier density n_c (c), Cole-Cole parameter a (d), for a thickness of the conducting layer of $d = 1 \,\mu\text{m}$. The transmission corresponds to the carrier density which shows a biexponential behaviour with $\tau_1 = 659 \,\text{ps}$ and $\tau_2 = 45 \,\text{ps}$. The scattering time and also the Cole-Cole parameter increase for lower carrier concentrations .



FIGURE 5.14: Total carrier density as fitted with the surface recombination and diffusion model(a) (Eq.5.12) and corresponding carrier density profiles for selected time steps after the photoexcitation (b). After 100 ps there are no more carriers at the surface so only the bulk recombination rate affects the total number of carriers.

5.2.2 Reflection Measurement

Additionally for the almost the same fluence as in the transmission measurement the experiment was also done in the reflection geometry. A photoinduced onset and decay in the THz reflectivity was observed, caused by photoexcitation and recombination of electron-hole pairs. For fitting the change in reflectivity the same model as for the previous measurement was employed to check if the results match. Again the thickness of the photoexcited layer was fixed at 1 µm to reduce the number of fitting parameters. Figure 5.15 shows the fit for one selected time step which shows good agreement within the spectral width of probing THz pulse. The time dependence of the obtained fit parameters n_c , τ and a, as shown in Fig. 5.16, matches well with the results from the transmission measurement. The absorbed fluence of $36 \,\mu\text{J} / \text{cm}^2$ corresponds to a photon flux of $1.4 \times 10^{14} / \text{cm}^{-2}$. With the assumption that all photons are absorbed within the first 1 µm of the sample this leads to an initial average carrier (e-h pair) density of $14 \times 10^{17} \text{ cm}^{-3}$. So the estimated initial carrier density is again approximately 2 times higher than obtained via the fitting procedure of the data for short times after the photoexcitation.



FIGURE 5.15: Amplitude (a) and phase (b) of the spectral change in reflection $E_{exc}(\omega)/E_0(\omega) = r_{exc}(\omega)/r_0(\omega) = A(\omega)e^{i\Delta\phi(\omega)}$ for GaAs 20 ps after photoexcitation with an 800 nm pulse and a fluence of $36\,\mu\text{J}$ / cm². In (a) also the initial (dashed) and more intense THz spectrum after photoexcitation (solid) are indicated, which shows an increased reflection due to the photoexcitated carriers. The measured data (dots) agrees well with the fit of an 1 µm thick conducting (Cole-Cole model) layer with $n_c = 6 \times 10^{17} \,\text{cm}^{-3}$, $\tau = 150 \,\text{fs}$ and a = 0.1.



FIGURE 5.16: Results of the OPTP reflection experiment on GaAs pumped with a fluence of $36 \,\mu\text{J} / \text{cm}^2$ at 800 nm: averaged change in reflection (a) (<>:= $\int d\omega |E(\omega)|^2$), obtained fit parameters dependent on the pump-probe delay collision time τ (b), carrier density n_c (c), Cole-Cole model parameter a (d), for a thickness of the conducting layer of $d = 1 \,\mu\text{m}$, the carrier density shows a biexponential behaviour with $\tau_1 = 681 \,\text{ps}$ and $\tau_2 = 91 \,\text{ps}$. The scattering time increases for lower carrier concentrations and also does the Cole-Cole parameter. The results agree well to the transmission measurement.

5.3 Silicon

OPTP experiments on silicon have also been performed in transmission (and reflection) geometry on an undoped single crystal wafer with a thickness of $d = 500 \,\mu\text{m}$. Silicon is an indirect band gap semiconductor with a band gap of $E_g = 1.11 \,\text{eV}$ [52]. The band structure of silicon and a possible indirect excitation with an 1.55 eV pump photon is shown in Figure 5.17. The absorption coefficient at 800 nm is $\alpha = 1 \times 10^3 \,\text{cm}^{-1}$ which corresponds to a penetration depth of 10 µm.

As the penetration depth of the pump pulse is $10 \,\mu\text{m}$, the photoexcited conducting layer is assumed to have thickness of the order of this penetration depth. However, the best fit results for the complex change in transmission were achieved assuming a constant thickness of $d = 5 \,\mu\text{m}$. Again Figure 5.18 shows a very good agreement between the fit and the measured data. The number of carriers shows an single exponential decay with a time constant of $\tau = 2.5 \,\text{ns}$. As known from other methods (Microwave-Detected Photoconductance Decay $\mu - PCD$,Optical pump-probe) the bulk carrier lifetime in silicon is on the order of a few μs [53]. It was shown that the surface recombination can be suppressed by chemical surface passivation techniques



FIGURE 5.17: Band structure of Silicon [52] and a possible indirect phonon assisted electron transition for a photon energy of $E_{\gamma} = 1.55 \text{ eV}(800 \text{ nm})$.

[54]. so the decay seen here is attributed to the surface recombination at the wafer surface. It was also observed that silicon shows far slower recombination velocities which explains why the decrease observed here happens on a much slower time scale than for GaAs.



FIGURE 5.18: Amplitude (a) and phase (b) of the spectral change in transmission $E_{exc}(\omega)/E_0(\omega) = t_{exc}(\omega)/t_0(\omega) = A(\omega)e^{i\Delta\phi(\omega)}$ for Si 30 ps after photoexcitation with an 800 nm pulse and a fluence of 100 µJ / cm². In (a) also the initial (dashed) and the less intense THz spectrum after photoexcitation are indicated. The measured data (dots) agrees well with the fit of an 5 µm thick conducting (Cole-Cole model) layer with $n_c = 18 \times 10^{17} \,\mathrm{cm}^{-3}$, $\tau = 230 \,\mathrm{fs}$ and a = 0.25.



FIGURE 5.19: Results of the OPTP transmission experiment on Si pumped with a fluence of 100 µJ / cm² at 800 nm. Averaged change in transmission (a) (<>:= $\int d\omega |E(\omega)|^2$), obtained time dependent fit parameters: collision time τ (b), carrier density n_c (c), Cole-Cole parameter a (d), for a thickness of the conducting layer of $d = 1 \,\mu$ m. The transmission corresponds to the carrier density which shows an exponential behaviour with a time constant of $\tau_s = 2.5 \,\mathrm{ns}$. The scattering time and the Cole-Cole parameter increases for lower carrier concentrations.

5.4 Poly-Si on Glass Substrate

An OPTP measurement was performed on an 10 µm thick poly-Si layer on a standard glass substrate (*Corning*). This measurement also serves as an example for the usefulness a reflection measurement, since the THz transmission through a standard glass plate (soda-lime glass) of 1 mm thickness almost vanishes $(T < 10^{-3})$. Thus performing the experiment in transmission would not be possible. But the experiment can be easily be done applying a reflection geometry. The sample was provided by D.Amkreutz (HZB) and is similar to that reported in [55]. The change in reflectivity was again fitted with a layered system model with a thickness of the silicon layer of $d = 8 \,\mu\text{m}$ and a refractive index of the glass substrate of n = 2.5. The refractive index of the glass substrate is assumed to match basically that of BK7 which was reported in [56]. For BK7, refractive index is almost constant for the THz range with n = 2.5 and the absorption coefficient increases quadratically with frequency, having a value of $100 \,\mathrm{cm}^{-1}$ for 1 THz. Also for this sample the fit suits quite well for change the in reflectivity in amplitude and phase (Fig. 5.20). The carrier lifetime here was found to be 5.9 ns, as in previous experiments by timeresolved photoluminescence the lifetime was found to be $\tau = 8 \,\mu s$ [55]. This leads to the conclusion that again surface recombination was observed here, since the bulk

recombination in silicon happens on the μs -time scale. Surface recombination is very important for thin layers as the surface recombination time constant can be related to the thickness of the sample d and the recombination velocity s as $\tau_s = d/s$. From the carrier lifetime and the layer thickness, the surface recombination velocity can be estimated to be $s = 4 \times 10^5$ cm/s.



FIGURE 5.20: Amplitude(a) and phase (b) of the spectral change in reflection $E_{exc}(\omega)/E_0(\omega) = t_{exc}(\omega)/t_0(\omega) = A(\omega)e^{i\Delta\phi(\omega)}$ for poly-Si on glass 30 ps after photoexcitation with an 800 nm pulse and a fluence of 450 µJ / cm². In (a) also the initial (dashed) and the more intense THz spectrum after photoexcitation (solid) are indicated. The measured data (dots) agrees well with the fit of an 8 µm thick conducting (Cole-Cole model) layer with $n_c = 1.3 \times 10^{18} \,\mathrm{cm^{-3}}$, $\tau = 230 \,\mathrm{fs}$ and a = 0.25.



FIGURE 5.21: Results of the OPTP reflection experiment on poly-Si pumped with a fluence of 450 µJ / cm² at 800 nm: averaged change in reflection (a) (<>:= $\int d\omega |E(\omega)|^2$) and obtained time dependent carrier density n_c (b), for a thickness of the conducting layer of $d = 8 \,\mu\text{m}$. The transient reflectivity corresponds to the carrier density which shows an exponential behaviour with a time constant of $\tau_s = 5.9 \,\text{ns}$. $N_{\gamma} = 2.3 \times 10^{18} \,\text{cm}^{-3}$ denotes the number of absorbed photons within the layer and is almost twice the value obtained from the fit.

Chapter 6

Conclusion and Outlook

During this thesis a THz time-domain spectroscopy setup was built allowing to perform optical-pump / THz-probe experiments in transmission and reflection geometry, which was shown for GaAs and silicon samples. From those measurements the bulk lifetime and surface recombination rate of the photoexcited carriers could be determined. For GaAs surface and bulk recombination could both be observed on the experimental available timescale and for the silicon samples the observed recombination is attributed to the surface recombination only. The surface recombination was observed here because the recombination in thin photoexcited layers with a thickness of several μm was investigated. For thin layers surface properties play an important role and particularly for photovoltaic applications. The time needed for recording a full 2D OPTP scan was improved significantly by implementing a fast THz-sampling mode. A large benefit of the reflection geometry is that it offers the possibility to examine highly absorbing samples. Usually, samples for OPTP experiments in transmission have to be prepared on expensive quartz glass substrates due to their low THz absorption. It should also be possible to investigate samples that actually work as photovoltaic devices in reflection and not only the active layers prepared on a substrate. As the signal change from thin conducting films is of the order 10^{-2} and lower, it is necessary to implement a chopper into the optical pump beam path for measuring such small pump induced changes. For the measurements reported here, the pump fluence was chosen high enough that still a pump induced signal was observable. To my knowledge OPTP experiments in reflection have rarely been analyzed and published so far to this extent (only one example in [57]). The obtained pump-induced change in THz reflection and transmission could be well described within a layered system model for the examined semiconductor samples.

For examining samples that show a fast photoconductive decay it could become important to arrange the pump and probe beams collinearly to increase the temporal resolution. Also the spectral bandwidth of the THz radiation could be increased by applying a different generation mechanism (e.g. generation in air plasma) which then also increases the temporal resolution. It could also be interesting to generate THz radiation with high peak electric field strengths to use them as pump pulses or to probe nonlinear carrier dynamics.

Selbstständigkeitserklärung

Hiermit erkläre ich, dass ich die vorliegende Diplomarbeit selbstständig verfasst habe. Es wurden keine anderen als die in der Arbeit angegebenen Quellen und Hilfsmittel benutzt. Die wörtlichen oder sinngemäß übernommenen Zitate habe ich als solche kenntlich gemacht. Diese Arbeit wurde in gleicher oder ähnlicher Form noch keiner anderen Prüfungsbehörde vorgelegt und auch noch nicht veröffentlicht.

Ort, Datum:

Unterschrift:

Danksagung

An dieser Stelle möchte ich mich bei denjenigen bedanken die wesentlich zum Gelingen dieser Arbeit beigetragen haben:

Peter Gaál für die Einführung in den Bereich der Terahertzspektroskopie und die Vermittlung seiner langjährigen experimentellen Erfahrungen auf diesem Gebiet. Daniel Schick für die Hilfe bei der Erstellung der Messprogramme in *Lab View* und bei technischen Fragen zum Versuchsaufbau. André Bojahr für zahlreiche ausführliche Diskussionen der experimentellen Resultate. Matias Bargheer die Möglichkeit meine Diplomarbeit in seiner Arbeitsruppe anfertigen zu können.

Und natürlich meinen Eltern für die langjährige Unterstützung.
Bibliography

- P.R. Smith, D.H. Auston, and M.C. Nuss. Subpicosecond photoconducting dipole antennas. *Quantum Electronics, IEEE Journal of*, 24(2):255–260, 1988.
- [2] Q. Wu and X.-C. Zhang. Free-space electro-optic sampling of terahertz beams. Applied Physics Letters, 67(24):3523, 1995.
- [3] C. A. Schmuttenmaer. Exploring dynamics in the far-infrared with terahertz spectroscopy. *Chemical Reviews*, 104(4):1759–79, April 2004.
- [4] John David Jackson. Classical Electrodynamics Third Edition. Wiley, 1998.
- [5] T. Kampfrath. Charge-Carrier Dynamics in Solids and Gases Observed by Time-Resolved Terahertz Spectroscopy. Dissertation, FU Berlin, 2005.
- [6] K. Reimann. Table-top sources of ultrashort THz pulses. Reports on Progress in Physics, 70(10):1597–1632, October 2007.
- [7] C. Winnewisser, P. U. Jepsen, M. Schall, V. Schyja, and H. Helm. Electro-optic detection of THz radiation in LiTaO_3, LiNbO_3 and ZnTe. *Applied Physics Letters*, 70(23):3069, 1997.
- [8] Yun-Shik Lee. Principles of Terahertz Science and Technology. Springer, 2009.
- [9] N.W. Ashcroft and N.D. Mermin. Solid State Physics. Saunders College Publishing, 1976.
- [10] H. Kuzmany. Solid-State Spectroscopy. Springer, 1998.
- [11] Kenneth S. Cole and Robert H. Cole. Dispersion and Absorption in Dielectrics I. Alternating Current Characteristics. *The Journal of Chemical Physics*, 9(4): 341, 1941.
- [12] D. W. Davidson and R. H. Cole. Dielectric Relaxation in Glycerol, Propylene Glycol, and n-Propanol. *The Journal of Chemical Physics*, 19(12):1484, 1951.

- [13] M. Beard, G. Turner, and C. A. Schmuttenmaer. Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy. *Physical Review* B, 62(23):15764–15777, December 2000.
- [14] C.J.F. Böttcher and P. Bordewijk. Theory of electric polarization, Vol.2, Dielectrics in time-dependent fields. Elsevier, New York, 2nd edition, 1978.
- [15] Tae-In. Jeon and D. Grischkowsky. Nature of conduction in doped silicon. *Physical Review Letters*, 78(6):1106–1109, 1997.
- [16] Tae-In Jeon and D. Grischkowsky. Observation of a ColeDavidson type complex conductivity in the limit of very low carrier densities in doped silicon. *Applied Physics Letters*, 72(18):2259, 1998.
- [17] M. C. Beard, G. M. Turner, and C. A. Schmuttenmaer. Subpicosecond carrier dynamics in low-temperature grown GaAs as measured by time-resolved terahertz spectroscopy. *Journal of Applied Physics*, 90(12):5915, 2001.
- [18] K. J. Willis, S. C. Hagness, and I. Knezevic. A generalized Drude model for doped silicon at terahertz frequencies derived from microscopic transport simulation. *Applied Physics Letters*, 102(12):122113, 2013.
- [19] Han-Kwang Nienhuys and V. Sundstr. Influence of plasmons on terahertz conductivity measurements. Applied Physics Letters, 87(012101), 2005.
- [20] J.C. Diels and W. Rudolph. Ultrashort Laser Pulse Phenomena. Acad. Press/Elsevier, 2nd edition, 2006.
- [21] M Perry. Multilayer dielectric gratings: increasing the power of light. Science & Technology Review, (September), 1995.
- [22] P. C. M. Planken, Han-Kwang Nienhuys, H. J. Bakker, and T. Wenckebach. Measurement and calculation of the orientation dependence of terahertz pulse detection in ZnTe. Journal of the Optical Society of America B, 18(3):313, 2001.
- [23] N. Piccioli, R. L. Toullec, M. Mejatty, and M. Balkanski. Refractive index of GaSe between 0.45 m and 330m. *Applied Optics*, 16(5):1236–1238, 1977.
- [24] X. Xin, H. Altan, A. Saint, D. Matten, and R. R. Alfano. Terahertz absorption spectrum of para and ortho water vapors at different humidities at room temperature. *Journal of Applied Physics*, 100(9):094905, 2006.

- [25] G. L. Dakovski, B. Kubera, S. Lan, and J. Shan. Finite pump-beam-size effects in optical pump-terahertz probe spectroscopy. *Journal of the Optical Society* of America B, 23(1):139, 2006.
- [26] A. Leitenstorfer, S. Hunsche, J. Shah, M. C. Nuss, and W. H. Knox. Detectors and sources for ultrabroadband electro-optic sampling: Experiment and theory. *Applied Physics Letters*, 74(11):1516, 1999.
- [27] W. Kuehn, P. Gaal, K. Reimann, M. Woerner, T. Elsaesser, and R. Hey. Terahertz-induced interband tunneling of electrons in GaAs. *Physical Review B*, 82(7):075204, August 2010.
- [28] P. U. Jepsen and B. M. Fischer. Dynamic range in terahertz time-domain transmission and reflection spectroscopy. *Optics Letters*, 30(1):29–31, January 2005.
- [29] M. V. Exter and D. Grischkowsky. Carrier dynamics of electrons and holes in moderately doped silicon. *Physical Review B*, 41(17):140–149, 1990.
- [30] M.A. Ordal, R. J. Bell, R.W. Alexander, L. L. Long, and M.R. Querry. Optical properties of fourteen metals in the infrared and far infrared: Al, Co, Cu, Au, Fe, Pb, Mo, Ni, Pd, Pt, Ag, Ti, V, and W. Applied Optics, 24(24):4493, December 1985.
- [31] M. Schall, H. Helm, and S.R. Keiding. Far infrared properties of electro-optic crystals measured by THz time-domain spectroscopy. *International Journal of Inrared and Millimeter Waves*, 20(4):595–604, 1999.
- [32] Tae-in Jeon and D. Grischkowsky. Characterization of optically dense, doped semiconductors by reflection THz time domain spectroscopy. *Applied Physics Letters*, 72(23):3032–3034, 1998.
- [33] S. Nashima, O. Morikawa, K. Takata, and M. Hangyo. Measurement of optical properties of highly doped silicon by terahertz time domain reflection spectroscopy. *Applied Physics Letters*, 79(24):3923, 2001.
- [34] A. Raymond, J.L. Robert, and C. Bernard. The electron effective mass in heavily doped GaAs. *Journal of Physics C: Solid State Physics*, 2289, 1979.
- [35] P. G. Huggard, J. a. Cluff, G. P. Moore, C. J. Shaw, S. R. Andrews, S. R. Keiding, E. H. Linfield, and D. a. Ritchie. Drude conductivity of highly doped GaAs at terahertz frequencies. *Journal of Applied Physics*, 87(5):2382, 2000.

- [36] E. V. Loewenstein, D. R. Smith, and R. L. Morgan. Optical constants of far infrared materials. 2: crystalline solids. *Applied Optics*, 12(2):398–406, February 1973.
- [37] M. V. Exter and D. Grischkowsky. Optical and electronic properties of doped silicon from 0.1 to 2 THz. Applied Physics Letters, 1990.
- [38] D. Grischkowsky and S.R. Keiding. Far-infrared time-domain spectroscopy with terahertz beams of dielectrics and semiconductors. *Journal of the Optical Soci*ety of America B, 7(10):2006–2015, 1990.
- [39] R. H. Stolen. Far-Infrared Absortion in High Resitivity GaAs. Applied Physics Letters, 15(2):74, 1969.
- [40] J.Y. Vinet, M. Combescot, and C. Tanguy. Influence of the electron-hole density profile on the reflectivity of laser irradiated silicon. *Solid state communications*, 51(3):171–173, 1984.
- [41] E. Hecht. Optics. Addison Wesley, 3rd edition, 1998.
- [42] F.A. Hegmann, O. Ostroverkhova, and D.G. Cooke. Probing Organic Semiconductors with Terahertz Pulses. In G. Lanzani, editor, *Photophysics of Molecular Materials From Single Molecules to Single Crystals*, chapter 7, page 398. Wiley-VCH, Weinheim, 2006.
- [43] P. Kuzel, F. Kadlec, and H. Nmec. Propagation of terahertz pulses in photoexcited media: analytical theory for layered systems. *The Journal of Chemical Physics*, 127(2):024506, July 2007.
- [44] J.M. Langer and W. Walukiewicz. Surface Recombination in Semiconductors. 18th ICDS, Sendai, July 24-28, 1995.
- [45] William Shockley. Electrons and Holes in Semiconductors. D. Van Nostrand Company, Inc., Princeton, 1950.
- [46] J. Vaitkus. The nonequilibrium hall effect and related transport phenomena in semiconductors under inhomogeneous excitation by a laser pulse. *Physica Status Solidi* (a), 34(2):769–775, April 1976.
- [47] C. Larsen, D.G. Cooke, and P.U. Jepsen. Finite-difference time-domain analysis of time-resolved terahertz spectroscopy experiments. *Journal of the Optical Society of America B*, 28(5):1308, April 2011.

- [48] D.E. Aspnes and A.A. Studna. Dielectric Function and optical parameters of Si, Ge, GaP, GaAs, GaSb. *Physical Review B*, 27(2):985–1009, 1983.
- [49] I. Vurgaftman, J.R. Meyer, and L.R. Ram-Mohan. Band parameters for III V compound semiconductors and their alloys. *Journal of Applied Physics*, 89 (5815), 2001.
- [50] S.M. Sze and J.C. Irvin. Resistivity, mobility and impurity levels in GaAs, Ge, and Si at 300 K. Solid-State Electronics, 11:599–602, 1968.
- [51] B. A. Ruzicka, L.K. Werake, H. Samassekou, and H. Zhao. Ambipolar diffusion of photoexcited carriers in bulk GaAs. *Applied Physics Letters*, 97(26):262119, 2010. doi: 10.1063/1.3533664.
- [52] M.L. Cohen and J.R. Chelikowsky. *Electronic Structure and Optical Properties of Semiconductors*. Springer, 2nd edition, 1989.
- [53] O. Palais and A. Arcari. Contactless measurement of bulk lifetime and surface recombination velocity in silicon wafers. *Journal of Applied Physics*, 93(8):4686, 2003.
- [54] E. Yablonovitch, D.L. Allara, and C.C. Chang. Unusually low surfacerecombination velocity on silicon and germanium surfaces. *Physical Review Letters*, 57(2):249–252, 1986.
- [55] D. Amkreutz and J. Müller. Electron-beam crystallized large grained silicon solar cell on glass substrate. *Progress in Photovoltaics: Research and Applications*, 2011.
- [56] M. Naftaly and R.E. Miles. Terahertz time-domain spectroscopy of silicate glasses and the relationship to material properties. *Journal of Applied Physics*, 102(4):043517, 2007.
- [57] I-Chen Ho, Xiaoyu Guo, and X-C Zhang. Design and performance of reflective terahertz air-biased-coherent-detection for time-domain spectroscopy. *Optics Express*, 18(3):2872–83, February 2010.