Charge carrier dynamics in photovoltaic materials

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The THz frequency window can be considered as ranging from 100 GHz to 10 THz. THz frequencies lie between the infrared and microwave frequency regions in the electromagnetic spectrum shown in Figure 2.1. Spectroscopy in this frequency range is interesting not only because many molecular rotational and vibrational events happen at these frequencies, but also because the motion of electrons and holes in conductive materials give rise to dispersion of the optical properties in this frequency range. As the carrier momentum typically randomizes on $\sim$ps ($10^{-12}$ s) timescales via carrier-phonon interactions [42] and $1$ THz $= 10^{12}$ s$^{-1}$, the THz frequency range is ideal for studying these phenomena.

Historically, spectroscopy at THz frequencies has been limited by the lack of suitable emitters and detectors in the THz frequency region, which has come to be known as the “terahertz gap” [43]. The energy of a photon of frequency 1 THz is 4.2 meV, corresponding to a wavelength of 300 μm. This is below the electronic transitions typically used as emitters and detectors of optical light. On the other side, THz frequencies are above the megahertz and gigahertz frequencies achievable with electronic devices. The THz gap is thus said to be positioned between the realms of ‘electronics’ and ‘photonics’. Generation and detection of freely propagating THz pulses became possible in the late 1980s with the application of photoconductive antennas [44, 45] and later by the process of optical rectification [46] (explained below).

THz-time domain spectroscopy (THz-TDS) employs a freely propagating, long wavelength, electromagnetic pulse to probe charge carriers. The probe pulse can be seen as a wavepacket, typically consisting of frequencies in the 0.3–3 THz range and centered at 1 THz, see figure 2.2. The probe is sensitive to mobile charge carriers and can be used to investigate the photoconductive properties of a sample on sub-picosecond timescales [42]. THz spectroscopy thus provides access to electronic and optoelectronic properties on fast timescales without applying physical contacts to the sample. This is particularly useful for studies of nanostructured systems such as quantum dots where applying such
contacts would be impossible [47, 48, 49]. An advantage of THz-TDS is that the detection scheme allows for the recording of the field strength (not just the time integrated intensity) of the full transmitted THz waveform versus time [50, 51]. The experiment therefore gives access to both amplitude information from the absorption (or gain) of the THz probe in a given sample, and phase information obtained from the time-shift of the probe [52]. It is convenient to Fourier transform these waveforms to the frequency domain so that the electrooptic properties of the sample can be analyzed and reported as a function of probe frequency. Since the recorded time traces contain both amplitude and phase information, the data extracted from their Fourier transforms are complex valued. There are generally three ways of expressing this information, the refractive index $\hat{n}(\omega)$, the permittivity $\hat{\epsilon}(\omega)$ and the conductivity $\hat{\sigma}(\omega)$. $\omega$ denotes the angular frequency of the oscillating probe field, $\omega = 2\pi \nu$ where $\nu$ is the ordinary frequency. The complex refractive index $\hat{n}(\omega) = n(\omega) + i\kappa(\omega)$ consists of the real classical refractive index $n(\omega)$ related to the phase change in a given medium, and the imaginary component $\kappa(\omega)$ related to the amplitude absorption. The permittivity, the conductivity and the refractive index

Figure 2.1. Electromagnetic spectrum from radio waves to X-rays. The THz region is shown in shaded grey. Typical energy regions for molecular rotations and vibrations, intraband electronic motion, and interband transitions are also shown. Adapted from [43].
are related as
\[
\hat{\epsilon} = \hat{n}^2 \quad \hat{\sigma} = -i\hat{\epsilon}_0\omega = -i\hat{n}^2\hat{\epsilon}_0\omega
\] (2.1)

where \(\epsilon_0\) is the vacuum permittivity. It should be noted that the three complex quantities \(\hat{n}(\omega), \hat{\epsilon}(\omega)\) and \(\hat{\sigma}(\omega)\) hold exactly the same information and can be used interchangeably. In the following we leave out the \(^\ast\) to denote complex quantities except in cases where ambiguities may arise. Throughout this thesis we express the data obtained with the THz probe mostly as the complex conductivity \(\sigma\). The real part of \(\sigma\) is obtained from the amplitude change of the THz probe caused by the mobile charge carriers in the sample. These carriers are free to move in response to the THz field, and energy can therefore be transferred from the field to the carriers, causing the field to be attenuated. One can say that the real part of \(\sigma\) corresponds to the classical concept of conductivity where charge carriers can be driven by the field over a long range, causing a current. The imaginary part of \(\sigma\) is obtained from the time shift of the probe and yields information about the polarizability of the carrier population.

In section 2.1 below we describe how a THz-TDS experiment can be performed in praxis, and section in 2.2 we explain how the optical/electronic parameters of the measured system can be extracted from the obtained data.

## 2.1 Experimental setup

The experimental setup used for THz measurements is shown schematically in Figure 2.3. The system is based on an amplified Ti:sapphire mJ-class laser delivering pulses of center wavelength 800 nm and a pulse duration of 100 fs or
less at a repetition rate of 1 kHz. The laser output is split into three beams, the pump-, the generation- and the sampling beam.

![Diagram](image.png)

**Figure 2.3.** Optical pump - THz probe setup.

The pulses in the *pump* beam photoexcite the sample, and their wavelength (or equivalently photon energy) can be modified by one or more beta barium borate (BBO) crystals to generate higher harmonics of the fundamental 800 nm laser output, or by an optical parametric amplifier (OPA) which allows the wavelength to be tuned to virtually any value in the visible to near IR range. In cases where very homogeneous spatial pump profiles are required, such as the precise fluence determination used in the carrier multiplication (CM) experiments presented in chapters 3 and 4, an optical diffuser can be placed in the pump beam before the sample. The length of the pump path can be adjusted by a mechanical delay line in order to vary the time $\tau_{\text{pump}}$ when the pump pulse arrives at the sample, relative to the other beams.

The *generation* beam impinges on a ZnTe crystal where it generates the THz probe waveform by a second order nonlinear optical process called optical rectification [53]. Here a quasi-dc polarization is induced in the non-centrosymmetric generation crystal by the intense generation beam. The slow changes in this polarization is what generates the slowly oscillating, single cycle THz probe pulse. A parabolic mirror is used to collect and collimate the THz beam emitted from the crystal, and send it on to a second parabolic mirror which focuses it on to the sample. In order to ensure homogeneous pumping, the diameter of the pump spot (>3 mm) is significantly larger than the diameter of the THz beam at the focus (on the order of the wavelength, $\lesssim 300 \ \mu\text{m}$). The THz beam transmitted through the sample is collected and collimated by a third parabolic mirror which sends it to a fourth parabolic mirror, focusing it on a second ZnTe (detection) crystal. The entire THz beam path from the generation crystal to the detection

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...crystal is kept in a dry N₂ environment in order to avoid absorption caused by the rotational modes of water vapor [54].

In the detection crystal the field strength of the THz waveform is measured via the electro optic (EO) effect [55]: A third 800 nm beam, the sampling beam, passes through the detection crystal spatially overlapped with the focused THz probe beam. The electric field of the THz waveform causes a birefringence in materials without inversion symmetry such as ZnTe [42], the so called Pockels effect, which causes a rotation in the polarization of the sampling beam. For significantly small THz fields, causing a small birefringence in the detection crystal, the polarization change of the sampling beam is proportional to the THz field strength [42]. The EO effect is essentially the inverse of the optical rectification effect used for generating the THz pulse, which is why the same material is employed for both purposes [42]. After the detection crystal, the polarization change in the sampling beam is measured by splitting the beam in vertical and horizontal components in a Wollaston prism or polarizing beam-splitter, and detecting the intensity variations of both polarizations with a set of differential photodiodes. In a THz measurement, a differential signal can be read from the diodes which is proportional to the transmitted THz probe field [51]. This signal is acquired using lock-in detection, effectively frequency filtering the differential diode signal at the repetition frequency of the laser. As the photon energies in the THz spectral region are below the thermal energy at room temperature (1 THz ∼ 48 K) the coherent gated detection scheme with lock-in acquisition provides a major advantage as thermal noise can be strongly suppressed [42, 50]. Another advantage of the EO detection is that the time resolution is in principle limited by the duration of the sampling pulse which is typically on the order 50–100 fs. By consecutively scanning the arrival time τ_{samp} of this pulse in the detection crystal with a second delay stage, the transmitted THz waveform can be mapped out in time [51, 50], see figure 2.2. In a typical measurement the transmitted THz field is measured by placing a mechanical chopper in the generation beam and acquiring the signal from the differential diodes at the chopper frequency. Similarly, the pump-induced change in THz transmission can be measured by placing the chopper in the pump beam. A complication arises when the photoinduced THz response of the sample changes on timescales comparable to the THz probe pulse duration [56, 57]. In this case, resolving the photomodulated THz waveform by scanning τ_{samp} would yield measurement artifacts because the sample properties change between early and later sampling times. A solution to this problem is to scan the pump- and sampling delay lines synchronously so that τ_{pump} − τ_{samp} is held...
This is equivalent to having a delay line in the generation beam to vary only the delay of the probe field.

### 2.2 Extracting the Conductivity

In the following we describe how the frequency resolved complex material parameters $n(\omega)$, $\epsilon(\omega)$ and $\sigma(\omega)$ can be extracted from a THz-TDS measurement. We start by considering a THz waveform with frequency dependent electric field $T(\omega)$ which we propagate through a region $j$ of length $l_j$ and (complex) refractive index $n_j$. We approximate the THz pulse by a plane wave and let $T_{j-1}$ denote the initial waveform in region $j-1$ which propagates through the interphase between regions $j-1$ and $j$, through region $j$, and then through the interphase between regions $j$ and $j+1$. We obtain the waveform in region $j+1$ 

$$T_{j+1}(\omega) = T_{j-1} \cdot t_{j-1,j} \cdot \exp\left(i n_j \omega l_j / c\right) \cdot t_{j,j+1} \cdot MR_j$$

where $MR_j$ is a factor that accounts for multiple reflections in the region $j$ given by

$$MR_j = \left[1 + r_{j-1,j} \cdot r_{j,j+1} \cdot \exp\left(2i n_j \omega l_j / c\right)\right]^{-1}$$

and the Fresnel transmission and reflection coefficients for normal incidence are given by

$$t_{j,j+1} = \frac{2n_j}{n_j + n_{j+1}}, \quad r_{j,j+1} = \frac{n_{j+1} - n_j}{n_{j+1} + n_j}.$$ 

The expression (2.2) is valid when the leading edge of the THz pulse probes the same dielectric function as the trailing edge, that is, a steady state approximation is valid.

In optical pump-THz probe experiments the analysis can be complicated by the spatial variation in excitation density along the propagation direction of the THz pulse. For linear (one-photon) excitation, the excitation density decays as $N(z) = N_0 e^{(-z/l)}$ with a characteristic optical penetration depth $l$ [56]. If the penetration depth is significantly shorter than either the sample thickness or the wavelength of the THz probe, the excited region can be approximated by a homogeneous region of width $l$ [60].

Figure 2.4 shows the general layout of a sample as a stack of layers of varying optical properties. Using (2.2) we model the propagation of the THz probe from an air phase of refractive index $n_1$ through a second phase of refractive index $n_2$ and thickness $l_2$, which can be either a cuvette window or another air phase depending on the sample, then the photoactive region of thickness $l$ and (complex) refractive index $n_3$ when unexcited, and $n_3^*$ when photoexcited,
Figure 2.4. General layout of a sample: Typically, medium 1 is air, medium 2 is a cuvette window, or in the case of a sample deposited directly on a substrate, medium 2 is also air and \( n_2 = n_1 \), medium 3 is the photoactive region characterized by complex refractive \( n_3^* \) when photoexcited and \( n_3 \) when unexcited, medium 4 is another cuvette window or a sample substrate, and medium 5 is another air phase.

then through another window (or substrate) of index \( n_4 \) and thickness \( l_4 \) into air again (\( n_5 = n_1 \)). Letting \( T_0 \) denote the wave transmitted through air in the absence of a sample, we get the transmission through the unexcited sample:

\[
T_{\text{calc}}^{\text{unexc}}(\omega) = T_0(\omega) \cdot t_{12} e^{i\omega n_2 l_2/c} \cdot t_{23} e^{i\omega n_3 l_3/c} \cdot t_{34} e^{i\omega n_4 l_4/c} \cdot t_{41} e^{-i\omega n_1 (l_2 + l_3 + l_4)/c} \cdot \text{MR}_3^* \tag{2.5}
\]

where the fourth exponential factor compensates for propagation through the air displaced by the sample. Here we consider the effect of multiple reflections only in the photoactive region. Similarly, for the wave transmitted through the excited sample we get:

\[
T_{\text{calc}}^{\text{exc}}(\omega) = T_0(\omega) \cdot t_{12} e^{i\omega n_2 l_2/c} \cdot t_{23}^* e^{i\omega n_3^* l_3/c} \cdot t_{34}^* e^{i\omega n_4 l_4/c} \cdot t_{41} e^{-i\omega n_1 (l_2 + l_3 + l_4)/c} \cdot \text{MR}_3^* \tag{2.6}
\]

Here \( t_{23}^* \), \( t_{34}^* \) and \( \text{MR}_3^* \) are the transmission and multiple reflection coefficients modified through the photoinduced change in \( n_3^* \). Taking the ratio \( T_{\text{calc}}^{\text{exc}}(\omega)/T_{\text{calc}}^{\text{unexc}}(\omega) \) yields the strongly simplified expression

\[
\frac{T_{\text{calc}}^{\text{exc}}(\omega)}{T_{\text{calc}}^{\text{unexc}}(\omega)} = \frac{t_{23}^* t_{34}^*}{t_{23} t_{34}} e^{i\omega \Delta n l/c} \frac{\text{MR}_3^*}{\text{MR}_3} \tag{2.7}
\]

where we have defined \( \Delta n \equiv n_3^* - n_3 \). The corrections \( \text{MR}_3^* \) and \( \text{MR}_3 \) are necessary when region 3 is thin enough that the reflected THz waveforms overlap in time with the transmitted ones as is the case for thin film samples or samples.
where the pump penetration depth is short. In contrast, for e.g. solution samples in a cuvette, the optical path length \( l \) is typically long enough that the reflected waveforms can be filtered out temporally, and the \( MR \) factors are not included in the analysis.

Experimentally, we measure in the time domain the THz field transmitted through the unexcited sample \( T_{\text{meas \ unexc}}(t) \), and the photoinduced change in the field \( \Delta T_{\text{meas}}(t) = T_{\text{exc}}(t) - T_{\text{meas \ unexc}}(t) \), see Figure 2.5. The corresponding frequency resolved waveforms \( T_{\text{meas \ unexc}}(\omega) \) and \( \Delta T_{\text{meas}}(\omega) \) are obtained by Fourier transformation. Taking the ratio between these we obtain

\[
\frac{\Delta T_{\text{meas}}(\omega)}{T_{\text{meas \ unexc}}(\omega)} = \frac{T_{\text{exc}}(\omega) - T_{\text{meas \ unexc}}(\omega)}{T_{\text{meas \ unexc}}(\omega)} = \frac{T_{\text{exc}}(\omega)}{T_{\text{meas \ unexc}}(\omega)} - 1 \tag{2.8}
\]

which can be directly related to the calculated quantity in (2.7). The photoinduced change in the complex refractive index of the sample region \( \Delta n(\omega) \) can now be found by numerically minimizing the difference between \( T_{\text{calc \ exc}}(\omega)/T_{\text{calc \ unexc}}(\omega) \) and \( T_{\text{exc}}(\omega)/T_{\text{meas \ unexc}}(\omega) \). From the corresponding dielectric functions \( \epsilon = (n_3)^2 \) and \( \epsilon^*(\omega) = (n_3^*(\omega))^2 = (n_3 + \Delta n(\omega))^2 \), the complex photoconductivity can be found (see (2.1)).
\[ \Delta \sigma(\omega) = -\left( \epsilon^*(\omega) - \epsilon \right)i\epsilon_0 \omega \] 
(2.9)

Thus the complex photoconductivity can be extracted from the measured THz waveform transmitted through the unexcited sample and the photoinduced change therein given prior knowledge of the refractive indices of the medium before the sample \( n_2 \), usually air or a window, of the unexcited sample \( n_3 \), and of the medium after the sample \( n_4 \), usually a window or substrate, plus the thickness \( l \) of the sample region.

For sufficiently thin samples for which the photoexcited region \( l \) is on the order of micrometers or less \([60]\), which is fulfilled in semiconductors with strong optical absorption or in very thin samples such as graphene deposited on a non-absorbing substrate, an analytical expression can be applied to extract the optical functions of the sample \([61]\). In these samples the complex photoconductivity can be calculated as \([62, 63]\)

\[ \Delta \sigma(\omega) = -\frac{n + 1}{Z_0 \cdot l} \frac{\Delta T_{\text{meas}}}{T_{\text{meas} \text{unexc}}} \] 
(2.10)

Here it is assumed that the medium before the photoexcited region is air. \( l \) is the thickness of the photoexcited region, \( n \) is the refractive index of the medium after the photoexcited region (typically a supporting substrate or an unexcited region of the same material), and \( Z_0 = 377 \, \Omega \) is the impedance of free space. The SI unit for the photoconductivities extracted using either (2.9) or (2.10) is S/m.

2.3 Pump-probe conductivity dynamics

In order to get the full amount of information obtainable from an optical pump-THz probe measurement, one needs to measure the full 2-dimensional map of photoconductivity versus both sampling delay \( \tau_{\text{samp}} \) and pump delay \( \tau_{\text{pump}} \) to obtain the frequency resolved photoconductivity at all pump delays \( \Delta \sigma(\omega, \tau_{\text{pump}}) \). However, much information can be obtained by fixing one of the measurement parameter and scanning the other. Figure 2.6 shows how the sampling delay can be fixed at different positions relative to the THz probe in order to be sensitive to the different components of the complex conductivity: On the peak of the THz waveform the derivative is zero, and the \( \Delta T \) value measured here is, in the limit of small differential signals, primarily sensitive to changes in the magnitude of the THz probe. \( \Delta T \) recorded on the THz peak can then be assumed to be proportional to the real component of the photoconductivity.
When fixing $\tau_{\text{samp}}$ at the THz peak, the photoinduced change in THz transmission ($\Delta T$) will scale approximately linearly with the magnitude change of the THz waveform and therefore give information about the real part of the photoconductivity. When setting $\tau_{\text{samp}}$ at the zero crossing after the peak, $\Delta T$ will scale with the time shift of the THz waveform and give information about the imaginary part of the photoconductivity.

1-D pump-probe scans have been widely used to study the rates of generation and recombination of photoexcited charge carriers in bulk semiconductors as well as trapping and exciton condensation \[57, 64\]. Additionally, pump-probe delay measurements have been applied to study the injection of charge carriers from light absorbing materials such as molecular dyes \[65, 66, 67\] or semiconductor quantum dots (QDs) \[68, 69\] into mesoporous oxide films in excitonic solar cell geometries like the ones presented in section 1.3. In these systems THz-TDS presents an advantage over other spectroscopic techniques such as time resolved photoluminescence (PL) or transient absorption (TA). In the latter two techniques, charge injection is indirectly inferred by probing the number of excited carriers in the donor (dye or QD). However, a reduction in the photoexcited carrier population in the donor can also be caused by recombination processes, and does not constitute unambiguously proof that injection into the oxide is taking place \[6\]. In THz-TDS the carrier population in the oxide can be monitored directly. As charge carriers confined in a molecular dye or a QD do not display a real conductivity component (section 2.4.3), the appearance of real conductivity after photoexcitation is a direct indication of an increase in the number of mobile carriers in the oxide phase, provided that the energy of the photons exciting the dye or QD is below the bandgap energy of the oxide so that direct excitation is avoided. Figure 2.7 from \[69\] shows THz pump
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Figure 2.7. THz probed photoconductivity versus pump-probe delay for a mesoporous SnO$_2$ film sensitized with PbSe quantum dots of varying size. From [69].

delay measurements performed on mesoporous SnO$_2$ sensitized with PbSe QDs of varying size. The injection rates inferred from the ingrowth of the THz conductivity increase with decreasing QD size as stronger quantum confinement increases the driving force for the injection process.

Another way to perform 1-D pump-probe scans is to fix $\tau_{\text{samp}}$ to the point where the probe field crosses zero (Figure 2.6). As the field vs. $\tau_{\text{samp}}$ can be approximated as a straight line in the close vicinity of the zero crossing, the $\Delta T$ value recorded here is proportional to the time shift of the THz waveform, and therefore to the imaginary component of the conductivity.

The 1-dimensional pump delay measurements described above provide information on the magnitude of the real or the imaginary part of the photoconductivity as a function of pump-probe delay. Measuring the photoconductivity magnitude generally gives information about the product of the number of photoinduced charge carriers and their average mobility. In order to separate these two factors and obtain information about the nature of the photoexcited charge carriers and the mechanism of conductivity, measurement and analysis of the probe frequency resolved photoconductivity $\sigma(\omega)$ is necessary.

Below we present a few models for frequency resolved conductivity that can be used to distinguish between free charge carriers and carriers experiencing various degrees of confinement.
2.4 Conductivity models

2.4.1 The Drude model

A simple model for describing the complex conductivity of free carriers accelerated by an oscillating electric field is the Drude model. Here the electrons and holes are treated as an ideal classical gas, not interacting with each other, and interactions with the lattice are assumed to take place only through momentum randomizing scattering events occurring with a mean scattering time $\tau_s$. In the absence of an applied field, the charge carriers move with the thermal velocity $v_t = \sqrt{3k_BT/m^*}$ (for a 3-dimensional system). Here $k_B$ is the Boltzmann constant, $T$ is the temperature, and $m^*$ is the effective mass of the carrier. As the thermal motion can be described as a random walk, the mean velocity of the carriers in the absence of a field is zero. When applying a time varying electric field $E(t)$, the carriers will acquire a mean drift velocity $v_d$. For field strengths typically used in THz experiments, the interaction with the field is non-perturbative: $v_d$ is typically on the order of millimeters per second whereas $v_t$ is on the order of a hundred thousand of meters per second in a typical semiconductor at room temperature. The equation of motion for the ensemble of electrons is

$$-\frac{e}{m^*}E(t) = \frac{d}{dt}v_d(t) + \frac{1}{\tau_s}v_d(t)$$  \hspace{1cm} (2.11)

where $e$ is the elementary charge.

For an external electric field oscillating with angular frequency $\omega$, $E(t) = E_0 e^{-i\omega t}$, the expression (2.11) has the solution

$$v_d(t) = -\frac{e\tau_s}{m^*} \frac{1}{1 - i\omega\tau_s} E_0 e^{-i\omega t}.$$  \hspace{1cm} (2.12)

The carrier mobility $\mu$ can be defined as the proportionality factor between the drift velocity and the applied electric field:

$$\mu(\omega) = \frac{v_d(t)}{E(t)} = -\frac{e\tau_s}{m^*} \frac{1}{1 - i\omega\tau_s}.$$  \hspace{1cm} (2.13)

The conductivity of the material is then simply the (average) mobility of an electron times its charge times the density of electrons $N$

$$\sigma_{\text{Drude}}(\omega) = N(-e)\mu(\omega) = \frac{Ne^2\tau_s}{m^*} \frac{1}{1 - i\omega\tau_s}.$$  \hspace{1cm} (2.14)

Here the conductivity can be found in S/m. This is the main result of the
Drude model. It can be rewritten by introducing the plasma frequency

$$\omega_p = \sqrt{\frac{e^2 N}{\epsilon_0 m^*}}$$

(2.15)

so that (2.14) becomes

$$\sigma_{\text{Drude}}(\omega) = \frac{\omega_p^2 \epsilon_0 \tau_s}{1 - i \omega \tau_s}. \tag{2.16}$$

The expression for the conductivity now consists only of natural constants and the two variables $\omega_p$ and $\tau_s$. Thus by measuring the complex THz frequency resolved conductivity and fitting to (2.16), these two parameters can be extracted directly. Further, if the effective mass $m^*$ is known, the carrier mobility $\mu(\omega)$ and the carrier density $N$ can be found from (2.13) and (2.15) respectively. The complex conductivity predicted by the Drude model is shown in Figure 2.8.

This model has been widely applied to describe the conductivity free charge carriers in bulk crystalline semiconductors and metals where the assumption of exclusively momentum randomizing scattering events, on either lattice defects or phonons, hold. Figure 2.9 from [70] shows frequency resolved photoconductivities measured on bulk GaAs and fitted to the Drude model. From these fits the carrier scattering rate $\gamma_s = \tau_s^{-1}$ and the sheet carrier density $N_s$ were found at various pump intensities and -delays.

In chapter 3 we apply the Drude model to extract the scattering time and carrier density in photoexcited InN in order to quantify the number of generated
Figure 2.9. Sheet photoconductivity versus ordinary frequency measured in GaAs at three pump delays and fitted to the Drude model. Markers show measured data and lines show Drude fits. From [70].

carriers per incident photon.

2.4.2 The Drude-Smith model

As mentioned in the previous section, the Drude model assumes that every carrier scattering event is completely momentum randomizing. However, in materials where for instance carrier scattering on boundaries of crystals or edges in 1-dimensional conducting molecules occurs, the assumption of completely momentum randomizing scattering is no longer valid, and the Drude model has been found poorly describe the conductive response. Instead a modified version called the Drude-Smith model, taking into account the possibility that a charge carrier scattering on for instance a boundary predominantly scatters in the backwards direction, has been successfully applied to describe the conductivity in for instance polymer samples [71, 72, 73].

\[
\sigma_{\text{Drude-Smith}}(\omega) = \frac{\omega^2 \mu_0 \epsilon_0 \tau_s}{1 - i\omega\tau_s} \cdot \left( 1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega\tau_s)^n} \right)
\] (2.17)

The Drude-Smith model was proposed by Smith [74] and it introduces the additional parameter \(c_n\) which denotes the probability that a carrier maintains its velocity in scattering event \(n\). It is common to assume that the persistence of velocity is retained only for the first scattering event so that only the first term of the sum in (2.17) is included. In this case the persistence of velocity is given by
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Figure 2.10. Drude-Smith conductivity versus angular frequency times scattering time for a few values of the backscattering parameter $c$. Increased backscattering reduces the real conductivity at low frequencies, and in the case of complete backscattering, the DC conductivity is zero. Additionally, the restoring force caused by the backscattering gives rise to a negative imaginary conductivity at low frequencies. In the case of complete backscattering ($c = -1$) the predicted behavior bears resemblance to the bound carriers described by the Lorentzian oscillator model.

the parameter $c$ so that $c = 0$ describes fully momentum randomizing scattering (and thus the model reduces to the classical Drude model) and $c = -1$ describes complete backscattering. Figure 2.10 shows the conductivity predicted by the Drude-Smith model including only one non-random scattering event for various values of the backscattering parameter $c$.

In chapter 5.3.1 the Drude-Smith model is used to describe the conductivity of two types of 1-dimensional graphene based conductors, graphene nanoribbons (GNRs) and carbon nanotubes (CNTs), oriented randomly so that scattering from the edges of the conductors is prominent in the THz conductivity experiment.

2.4.3 The Lorentz Oscillator Model

The Drude and Drude-Smith models presented above describe the conductivity of free charge carriers moving in a media with various scattering properties. Conductivity responses in the THz spectral range can also arise from charge carriers completely localized or ‘bound’ in excitons either by a confining environment or by strong electron-hole Coulomb attraction [49, 75, 76, 77]. The conductive response of such systems is most simply described as a Lorentzian oscillator with a resonance at a finite frequency. This model is a generalization
of the Drude model obtained by adding a restoring force term to (2.11). The conductivity predicted by the Lorentzian oscillator model is:

$$\sigma_{\text{Lorentz}}(\omega) = \frac{\omega_0^2 \epsilon_0 \tau_s}{1 - i \tau_s \omega + i \tau_s \omega_0^2 / \omega} \quad (2.18)$$

Where $\omega_0$ is the angular frequency of the oscillatory response so that $\nu_0 = \omega_0 / 2\pi$ is the resonance frequency. Thus the Drude expression in (2.16) is a special case of the Lorentzian oscillator centered at $\omega_0 = 0$. Figure 2.11 shows the conductivity predicted by the Lorentz oscillator model.

In excitons the energy of the resonance $\hbar \omega_0$ corresponds to the excitonic interband transitions. Exciton binding energies typically lie in the 1–100 meV range [42] and in most inorganic semiconductors excitons only exist well below room temperature [64]. However, in organic semiconductors where the dielectric screening between electrons and holes is low, excitons are observed at room temperature [71, 78, 79, 80]. For these excitons the interband transitions are typically much higher in energy than the THz photons, and no photon absorption occurs. These excitons therefore show no real conductivity. The THz photons do however polarize the excitons through a non-resonant interaction, and a negative imaginary conductivity is observed, see Figure 2.11. This is can also be seen from (2.18) by setting $\omega_0 \gg \omega$.

The condensation of carriers into excitons has important implications for the electronic properties of a material. Whereas free carriers can be accelerated by an electric field which induces a preferential drift and thus an electric current, electrons and holes bound in excitons have a net charge of zero and will not be
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Figure 2.12. Two processes that can cause the photoconductivity of mesoporous oxide films to deviate from bulk behavior. Scattering at the particle boundaries described by the Drude-Smith model, and depolarization fields in the dielectric oxide material, screening the probe field.

accelerated in a static electric field. As described in chapter 1, these properties have important consequences for the operating principles of photovoltaic devices based on materials with different levels of dielectric screening.

2.4.4 Effective medium theory

As seen in section 1.3 and 2.3, mesoporous oxide films are important electron acceptors in dye/QD sensitized solar cells. These films typically consist of 10–50 nm particles of TiO$_2$, SnO$_2$ or ZnO, sintered together to form percolated pathways for electron transport. Since the particle diameters in such films are larger than the Bohr radius for charge carriers, the individual oxide particles making up the film are expected to show bulk conducting character as described by the Drude model. However, the THz conductivity of mesoporous oxide films has been found to be poorly described by the Drude model [81, 82]. There are two possible reasons for this behavior, sketched in Figure 2.12. One is preferential backscattering at the boundaries of the oxide particles, which can be described by the Drude-Smith model introduced in section 2.4.2 [74, 81, 83, 84]. The other possible reason is the effect of depolarization fields [82, 85]. Because of the large contrast in dielectric constant between the oxide particles and the surrounding air phase, dipoles in the highly polarizable oxide phase will screen the electric field of the THz probe. The flux density is therefore larger in the air than inside the particles [82]. This means that the conductivity measured by the THz probe in the far field is different than the actual intrinsic conductivity of the oxide phase.

When the particles are significantly smaller than the probe wavelength, an
effective medium formalism can be applied where a single average dielectric function can be found for the air/particle system. The THz response of a TiO$_2$ mesoporous film has previous been explained using the analytical Maxwell-Garnett effective medium model [82].

In chapter 6 we apply the effective medium formalism combined with numerical calculations to gain further insight into the charge carrier dynamics in mesoporous TiO$_2$ networks.