Carrier dynamics in photovoltaic nanostructures
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2.1 The Terahertz frequency

Spectroscopy is the detection and analysis of the interaction of light with atoms, molecules, and solid-state materials. Different types of resonances are associated with different regions of the electromagnetic spectrum. Fig. 2.1 summarizes the wavelength and frequency regions of the electromagnetic spectrum along with some specific excitations for each region. Typical timescales of the oscillation period of these different excited species are also given in Fig. 2.1. This schematic illustrates that THz light is very suitable to study rotational transitions of molecules and electronic motion in conducting materials. However, it was not until the late 1980’s that THz spectroscopy was established as a mature technology. This is primarily because of the difficulty of generation and detection of THz radiation. A frequency of 1 THz corresponds to a photon energy of 4 meV, which is much less than the electronic transitions of semiconductors that are usually used in sources or detectors of optical light.

![Figure 2.1](image-url) The electromagnetic spectrum from radiowaves to the x-ray region. Rotational, vibrational, and electronic transitions are shown along with electronic motion. The area accessible with THz spectroscopy is shown in shaded grey.
On the long wavelength side of the electromagnetic spectrum, GigaHertz and MegaHertz radiation can be easily generated with electronic devices. However, scaling GigaHertz electronics to operate in the THz region is limited by the frequency response of such devices. Because of the difficulty of generating and detecting light of THz frequencies, the spectral region between ‘electronics’ and ‘photonics’ has often been referred to as the ‘THz gap’. Spectroscopy in this THz region has become possible only after the realization of the generation and detection of single-cycle THz pulses by means of photoconductive antennas\(^1,2\) and optical rectification\(^4\). After this technological breakthrough, the technique has been used for time-resolved studies of polar and non-polar liquids\(^5-7\), biological media\(^8\), and solid-state materials like semiconductors\(^9-11\), conducting polymers\(^12,13\), and superconductors\(^14\). Most relevant for solar cell research is the ability of THz spectroscopy to study ultrafast carrier dynamics in various types of semiconductors. The oscillating THz field interacts strongly with charge carriers and the obtained frequency dependent response gives information on the nature of carrier conductivity in a material. As such, THz spectroscopy has been widely used to investigate the fundamental properties of a wide range of semiconductors used in photovoltaic applications, including bulk inorganic semiconductors\(^9,15\), mesoporous semiconducting films\(^16\), semiconducting polymers\(^12,13\) and QDs\(^15,17,18\). Also, charge separation dynamics and transport properties in nanostructured QD- and dye-sensitized solar cells can be studied using light of THz frequencies as a probe, as will be shown in this thesis. In this chapter, we will first describe the experimental setup and the characteristics of the THz light that we use as a probe. After discussing how the photoconductivity of a material can be extracted from the interaction of that material with the THz probe, we will discuss the THz response of three different types of charge carriers, i.e. free carriers in bulk semiconductors, confined carriers in QDs, and carriers in mesoporous semiconducting films.

### 2.2 TeraHertz time-domain spectroscopy (THz-TDS)

The goal of many of the THz experiments presented in this thesis is to determine the transient photoconductivity in a semiconducting material. For this purpose, we generate electrons in the conduction band by a visible pump pulse and we probe the carriers in the sample with a second pulse of THz frequencies. Hence, THz-TDS is a pump-probe technique. When delaying the probe pulse with respect to pump, the photoconductivity can be determined as a function of the pump-probe delay (the time in between arrival of the pump and the probe pulse). Since both the pump and the probe pulse have (sub)picosecond duration, the photoconductivity can be determined with ultrafast time-resolution. An additional advantage of THz-TDS is the contact-free nature of the experiment, since both
pump and probe are freely propagating optical pulses. This is especially advantageous when studying the photoconductivity in nanostructured materials, where it is difficult to apply electrical contacts directly.

2.2.1 The THz waveform

Fig. 2.2 shows a typical measurement of the THz electric field as measured by the THz spectrometer (see section 2.2.2). This waveform was measured in dry N\textsubscript{2} to avoid absorption of THz light arising from rotations of gas-phase water molecules, since these resonances are located in the THz frequency region\textsuperscript{19}. As can be seen in Fig. 2.2, the THz pulse is essentially a single oscillation of an electric field with a period of approximately 1 picosecond and a peak electric field of \( \sim 1 \text{ kV/cm} \). This field strength is sufficiently low to keep the system in the weak perturbation limit and, hence, the THz pulse acts as a true probe pulse. THz-TDS is special in the sense that both amplitude and phase of the probe pulse are recorded. This is in contrast to conventional Transient Absorption spectroscopy, where only the time-dependent spectral amplitude of the probe light is measured. Fourier transforming the time-domain THz trace into the frequency domain yields the power spectrum and the frequency-dependent phase of the THz pulse. As can be seen in Fig. 2.2, the THz pulse covers a wide spectral range from 0.2 – 2 THz. The advantage of detecting the amplitude \textit{and} the phase is that both the real \textit{and} imaginary components of the complex conductivity can be extracted simultaneously from the THz data (see section 2.3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.2.png}
\caption{Typical waveform of a THz pulse propagating through air \( E_{\text{air}}(t) \), measured by electro-optic sampling. Fourier-transforming the time-domain waveform yields the spectral amplitude and the phase of the THz electric field.}
\end{figure}

2.2.2 The THz-TDS spectrometer

The layout of the THz time-domain spectrometer is shown in Fig. 2.3. The light source used to operate the spectrometer is a pulsed laser system that is based on a Coherent Legend regenerative amplifier (Regen), seeded by a Coherent Verdi (790 nm central wavelength, 110 fs pulse duration FWHM, 80 MHz repetition rate, 500 mW output power). The Regen
is pumped by a Coherent Evolution system (527 nm central wavelength, 20 ns pulse duration FWHM, 1 kHz repetition rate, 23 W output power). The amplified output of the Regen is centered at 800 nm has a pulse duration of 110 fs FWHM and a repetition rate of 1 kHz. Of the 2.5 W output power of the Regen, ~900 mW is used to run the pump-probe THz-TDS setup.

![Diagram of THz spectrometer](image)

**Figure 2.3** Schematic layout of the THz spectrometer. THz radiation is generated in a ZnTe crystal by means of optical rectification. The resulting divergent THz beam is collimated and focused on the sample using a pair of off-axis parabolic mirrors. Transmitted THz pulses are recollimated and focused on a second ZnTe crystal for detection via electro-optic sampling: the THz pulse induces birefringence in the ZnTe detection crystal and as a result, the polarization of the 800 nm sampling beam is changed from perfectly linear to slightly elliptical. By scanning the temporally short 800 nm sampling beam over the THz field using delay stage 1, the THz electric field can be recorded as a function of time $t$. In pump-probe experiments, a pump pulse is used to excite the sample and information on carrier dynamics is obtained by varying the pump-probe delay $\tau$ using delay stage 2.

For the THz generation and detection, 10% of the incoming laser beam is used (90 $\mu$J/pulse). THz radiation is generated in a phase-matched manner by optical rectification in a ZnTe crystal ($<110>$ orientation, 10x10x1 mm thickness, purchased from MaTeck). The ZnTe generation crystal is pumped with a slightly focused beam (~3 mm diameter) of 800 nm light (80 mW power). The THz light exits the ZnTe generation crystal slightly divergent and is first collimated and subsequently focused on the sample using a pair of off-axis parabolic mirrors. The sample can be mounted optionally in a closed cycle helium cryostat (Air Products) for temperature dependent measurements between 20 – 300 K.

The transmitted THz pulses are recollimated and focused on a second ZnTe detection crystal by another pair of parabolic mirrors, where they are imaged through electro-optical sampling. As a result of the strong electro-optical activity of ZnTe, the THz field induces a small birefringence in the detection crystal. This induced birefrigence can be probed
using 800 nm laser pulses with linear polarization as a sampling beam (< 1 μJ/pulse). Since the pulse duration of the sampling beam pulses (110 fs) is much shorter than THz pulse (several picoseconds), the sampling beam samples the quasi-instantaneous field strength at different times within the duration of the THz pulse. Upon passing through the birefringent ZnTe crystal, the initially linearly polarized sampling pulse becomes elliptically polarized. The s and p components of the elliptically polarized sampling pulse are separated by a second polarizer, which is a Wollaston prism, and the difference in intensity of the two polarization components is detected with balanced diodes. A quarter wave plate is used to ensure that the system is operating in the linear regime. Hence, the output signal is proportional to the magnitude and the sign of the field of the THz pulse at each point in time as defined by the arrival of the sampling pulse. By varying the delay (t) between the THz and the sampling pulse, one can reconstruct the temporal profile of the detected THz field, E(t). Since this detection scheme relies on ‘gating’ with 110 fs sampling pulses, the time-resolution is better than the duration of the THz pulse duration21, and transient photoconductivity in materials can be studied with subpicosecond time-resolution.

2.2.3 A typical THz experiment

The response of a material to the THz probe can be described in terms of the complex refractive index (n_{sample}). The real part of this complex parameter describes the refraction of THz light by the investigated material, whereas the imaginary part is associated with absorption of THz light by a material. The refractive index is related to the complex dielectric function (ε_{sample}) through:

\[ \varepsilon_{\text{sample}} = n_{\text{sample}}^2 \]  

Fig. 2.4(a) depicts the measurements of the THz field transmitted through air \( E_{\text{air}}^{\text{out}}(t) \) and transmitted through the unexcited sample \( E_{\text{sample}}^{\text{out}}(t) \), in this case a silicon wafer.

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**Figure 2.4** Measured waveforms in a typical THz-TDS experiment. (a) THz field transmitted through air (black line) and unexcited silicon (gray line). The scans contain both amplitude (absorption) and phase (refraction) information. (b) Transmitted THz fields through unexcited (gray solid line) and excited (black dashed line) silicon, required to extract the real and imaginary photoconductivity.
The refractive index of silicon at THz frequencies can be obtained from the delay of $E_{\text{out}}^\text{sample}(t)$ with respect to $E_{\text{out}}^\text{air}(t)$ in combination with knowledge of the sample thickness. The reduction of the amplitude of the THz field is related to reflection losses at the air-sample and sample-air interfaces and to absorption of THz radiation by the (unexcited) sample.

The main focus in many THz-TDS measurements is, however, to extract the THz response of a photo-excited sample in a pump-probe configuration. After photo-excitation of a material, the complex refractive index and dielectric function are described by $n_{\text{sample}} + \Delta n$ and $\varepsilon_{\text{sample}} + \Delta \varepsilon$, respectively, where $\Delta n$ and $\Delta \varepsilon$ are the photo-induced changes in the refractive index and dielectric function, respectively. The complex photoconductivity of the material can be related to $\Delta n$ (or, equivalently, to $\Delta \varepsilon$) by\(^6\):

$$\Delta \sigma(\omega) = -2i\omega\varepsilon_0 n_{\text{sample}} \Delta n$$  \hspace{1cm} (2.2)

where $\omega$ is the angular frequency and $\varepsilon_0$ is the vacuum permittivity. The unit of the photoconductivity is Siemens per meter (S/m, SI units). In a typical pump-probe measurement, the pump beam is chopped and $\Delta E(t)$ is measured, which is the difference between the THz field transmitted through an unexcited sample $E_{\text{out}}^\text{air}(t)$ and the transmission through the excited sample $E_{\text{out}}^\text{sample}(t)$. As can be seen in Fig. 2.4(b), $E_{\text{out}}^\text{sample}(t)$ has a smaller amplitude than $E_{\text{out}}^\text{air}(t)$ and is also delayed slightly. This THz response originates from the interaction of the THz field with the photo-generated carriers in the silicon wafer. Combining $\Delta E(t)$ with $E_{\text{out}}^\text{sample}(t)$ allows extracting the real and imaginary part of the photoconductivity $\sigma$ (see section 2.3). Throughout this thesis, $E_{\text{out}}^\text{air}(t)$ and $E_{\text{out}}^\text{sample}(t)$ are measured for determining the response of the unexcited sample (described by $n$ and $\varepsilon$), whereas $E_{\text{out}}^\text{sample}(t)$ and $E_{\text{out}}^\text{sample}(t)$ are used to extract $\Delta \sigma$, which is related to the modified THz response due to photo-excitation.

Depending on the material, the bandgap of a semiconductor varies between ~0.25 and 4 eV. In our setup, excitation wavelengths of 800 nm (1.55 eV), 400 nm (3.1 eV) and 266 nm (4.66 eV) are readily available from the fundamental laser beam and its higher harmonics. Conversion of the fundamental 800 nm laser beam into other excitation wavelengths from the UV to the IR was done by optical parametric generation and amplification in commercial OPA’s (TOPAS, Light Conversion Inc. and Opera, Coherent). In all pump-probe experiments, the beam size of the pump beam (~5 mm diameter) is larger than the THz beam size (~2 mm diameter) to ensure that a homogeneously excited region is probed. Optionally, the pump beam profile can be homogenized using diffusers in case an homogeneous excitation fluence is an absolute prerequisite for quantitative determination of the carrier density (see e.g. Chapter 5).
2.3 Determination of the complex parameters $n$, $\varepsilon$, and $\Delta\sigma$

In this paragraph, the general concepts of extracting the complex parameters $n$, $\varepsilon$, and $\Delta\sigma$ from the time-domain THz waveforms are discussed. In the case of an unexcited sample, the THz refractive index $n$ is obtained by comparing the THz electric field measured with $E_{\text{sample}}(t)$ and without $E_{\text{air}}(t)$ the sample. The formulation below is fully equivalent to the extraction of the complex dielectric function to characterize the material response (see equation 2.1). Fig. 2.5(a) illustrates schematically the transmission of a THz pulse through a sample -in this case a piece of semiconducting material- that is surrounded by air. A THz pulse with electric field $E_{\text{THz,in}}$ enters a sample of thickness $d$ at an angle of incidence $\theta$. The sample has a complex THz refractive index $n_2$ and at the first interface, the THz pulse experiences a reflection coefficient of $r_{12}$ and a transmission factor $t_{12}$ according to the Fresnel equations. The transmitted THz field then propagates through the sample and undergoes a change in amplitude by the complex factor $p_2$. Finally, the pulse leaves the sample through the second interface with an additional transmission factor of $t_{21}$. In the case of large refractive index mismatches and thin samples, multiple reflections at the interfaces also contribute to the emerging THz field, as is explained below.

**Figure 2.5** (a) schematic representation of the transmission of the THz field through a semiconducting sample that is surrounded by air ($n_1 = n_3 = 1$). The THz field enters the sample of refractive index $n_2$ and thickness $d$. The emerging THz field from the sample, $E_{\text{THz,out}}$, is related to the incoming THz field via the Fresnel factors, as described in the text. (b) Transmission of the THz field through a photo-excited sample. In many semiconductors, the penetration depth of optical light is small and a thin slab of material is photo-excited (inset: exponential excitation profile in slab). In case the slab is much thinner than the THz wavelength, the excitation density (and hence the refractive index) in the slab is approximated to be homogeneous. Taking multiple reflections within the slab into account, the emerging THz field is formed by constructive interference, as defined by the Fresnel factors described in the text.
Chapter 2: Experimental Techniques and Analysis

The emerging THz field, \( E_{THz, out}^{sample}(\omega) \) in Fig. 2.5a is given by:

\[
E_{THz, out}^{sample}(\omega) = \frac{p_{21}^{r, in} E_{p, in}}{1 - (p_{21}^{r, in})^2} E_{ref, out}^{sample}(\omega)
\]  

(2.3)

Equation 2.3 is written in the frequency domain as a function of the angular frequency \( \omega \). The numerator in this equation accounts for directly transmitted THz radiation, whereas the \((p_{21}^{r, in})^2\)-term in the denominator accounts for multiple reflections. These reflections have to be taken into account when \( 2n_\parallel d/c \), i.e. the propagation time of the reflected THz pulse through the sample (where \( c \) is the speed of light) is comparable to, or smaller than, the typical THz pulse duration. For such samples, it is assumed that the contributions to \( E_{THz, out}^{sample}(\omega) \) from multiple reflections overlap spatially and add coherently. The contribution of multiple reflections can be neglected in case of relatively thick samples, where the directly propagated THz pulse is temporally separated from the contributions associated with reflections at the interfaces. For the case of normal incidence, the Fresnel factors in equation 2.3 are given by:

\[
t_{21}^{r, in} = \frac{4n_\parallel n_\perp}{(n_\parallel + n_\perp)^2}, r_{21}^{r, in} = \frac{n_\parallel - n_\perp}{n_\parallel + n_\perp}, \text{ and } p_{21} = \exp\left(-\frac{2n_\parallel n_\perp d}{c}\right)
\]  

(2.4)

In an additional measurement, the THz transmission is determined without the sample. In this situation, \( E_{THz, out}^{air}(\omega) \) also obeys equation 2.3 but the refractive index of the sample is substituted by that of air. When knowing the sample thickness \( d \), the refractive index of the sample can be obtained from a comparison of the measured waveforms \( E_{THz, out}^{sample}(\omega) \) and \( E_{THz, out}^{sample}(\omega) \).

In the majority of the experiments presented in this thesis, the behavior of the photo-excited sample is investigated. This situation is represented in Fig. 2.5(b), where the photo-excited region is denoted as a thin slab. The excitation profile within the sample usually obeys the Lambert-Beer equation and the excitation density decreases exponentially with distance (see inset Fig. 2.5(b)). In many semiconductors, the penetration depth of the pump beam at optical excitation wavelengths is much smaller than the typical wavelength of THz radiation (at 1 THz, \( \lambda = 300 \mu m \)). In this limit, the photo-excited region in the sample can be approximated as a slab with homogeneous excitation density, because different parts of the THz pulse always experience the same excitation density, when scanning the THz-pulse in the time-domain. The opposite limit occurs when the absorption is very weak and most of the pump light is transmitted through the sample. In this case, the excitation density is approximately constant as a function of the distance in the sample and all material in the sample is homogeneously excited.
In these extreme limits, the photoconductivity, or equivalently the photo-induced refractive index $\Delta n_2$, can be extracted from an adapted version of equation 2.3:

$$E_{\text{sample}}^\text{out}(\omega) + \Delta E_{\text{sample}}^\text{out}(\omega) = \frac{p_{21}^2E_{\text{in}}(\omega)}{1 - (p_{21}^2)^2} E_{\text{ref, in}}(\omega)$$

(2.5)

where the asterisks indicate that the Fresnel factors now describe the response to the photo-excited sample. Usually, the changes in the THz waveform as a result of photo-excitation, $\Delta E_{\text{sample}}^\text{out}(\omega)$, are at most a few percent, indicating that we are operating in the regime of weak perturbation. Hence, the Fresnel factors can be linearized for small changes and the change in the refractive index can be inferred from the changes in the transmitted THz pulses through:

$$\Delta n_2 = \left[ \frac{i\omega \cdot d_i}{c} - \frac{n - n_i}{n(n + n_i)} + MR \right]^{-1} \frac{\Delta E_{\text{sample}}^\text{out}(\omega)}{E_{\text{sample}}^\text{out}(\omega)}$$

(2.6)

Applying this equation to the situation of strong absorption, $\Delta n_2$ corresponds to the change of the refractive index in the excited slab, of which the thickness is defined by the penetration depth $d_i$ (which is much smaller than the sample thickness $d$). In case of homogeneously excited samples, $\Delta n_2$ corresponds to the change of the refractive index over the full thickness of the sample (in this situation, $d_i$ in equation 2.6 is equal to $d$). In a typical photo-excitation experiment, $E_{\text{sample}}^\text{out}(\omega)$ is recorded by chopping the THz generation beam, whereas $\Delta E_{\text{sample}}^\text{out}(\omega)$ is recorded while the pump beam is chopped. The term in the bracket in equation 2.6 describes that the transmitted THz field is affected by pump-induced changes via modification of propagation losses, changes in surface reflections, and a contribution from multiple reflections, respectively. The latter contribution is given by:

$$MR = \frac{2(p_{21}r_{21})^2}{1 - (p_{21}r_{21})^2} \left\{ \frac{i\omega \cdot d_i}{c} - \frac{2n_i}{(n_i^2 - n^2)} \right\}$$

(2.7)

Throughout this thesis, the response of a photo-excited material to the THz field is given by the photoconductivity. This quantity is related to $\Delta n_2$ through:

$$\Delta \sigma = -2i\omega \varepsilon_0 n_2 \Delta n_2$$

(2.8)
2.4 Interaction of THz radiation with carriers

The behavior of charge carriers in semiconductors (determining the type of photoconductivity) depends on the semiconductor material, the morphology, and the temperature. Three different types of conductivities in the THz window are discussed below. The discussed models are representative for several systems that are investigated in this thesis.

2.4.1 THz response to free carriers (Drude model)

The conductivity of charge carriers in bulk semiconductors is usually described by the Drude model. In this model, carriers are treated as an ideal gas of free particles, interacting with the crystal lattice (i.e. impurities or phonons) only through momentum-changing collisions. In the absence of an electric field, the movement of charge carriers has no preferential direction but exhibits a random walk throughout the lattice, characterized by the mean free path in between collisions, \( l_0 \). In the presence of an externally applied electric field, the carriers are accelerated along the direction of the applied field. In a quantum mechanical picture, electrons and holes are pictured as waves that can propagate through the oscillating potential of the perfect crystal lattice. In a perfect lattice at cryogenic temperatures, the acceleration of the carriers is not damped by interaction with the lattice. In reality, however, each material contains a certain amount of defect centers (of structural or chemical nature) and carriers will scatter from these impurities. At low temperatures, scattering from impurities is the dominating scattering mechanism. At elevated temperatures, carriers will predominantly scatter with phonons. Scattering from impurities and phonons are the dominant processes that are damping the drift motion of free carriers.

As a consequence, the carrier motion can be characterized by a scattering time \( \tau_r \) (the average time in-between scattering events) and a net drift velocity \( v_d \), which is much smaller (typically \( \sim 10^{-3} \text{ m/s} \)) than the thermal velocity of the carriers (typically \( \sim 10^5 \text{ m/s} \)).

The motion of a carrier that is accelerated by a time-varying electric field and damped by scattering from impurities or phonons can be described by a first order differential equation\textsuperscript{23}. In the case of applying an sinusoidal electric field, \( E(t) = E_e e^{i\omega t} \), the solution of this differential equation yields the drift velocity as a function of time\textsuperscript{23,24}:

\[
v_d(t) = -\frac{e\tau_r}{m} \frac{1}{1 - i\omega\tau_r} E_e e^{i\omega t}
\]

where \( m^* \) is the carrier effective mass and \( e \) is the electron charge. The carrier mobility \( \mu(\omega) \) is the proportionality factor between \( E(t) \) and \( v_d \) and is defined as:

\[
\mu(\omega) = \frac{e\tau_r}{m^*} \frac{1}{1 - i\omega\tau_r}
\]

(2.10)
The magnitude of $\mu(\omega)$ indicates how easy carriers can move through a material. From equation 2.10, it follows that mobility is largely determined by the carrier effective mass and the scattering time: the former quantity is a material property whereas the latter is determined by the quality of the sample (amount of defects per unit volume), the temperature (availability of phonons), and the carrier density (carrier-carrier interactions). The macroscopic electrical properties of a material depend on the carrier mobility and the carrier density, $N$. Therefore, the conductivity of a macroscopic material is defined as:

$$\sigma(\omega) = Ne\mu(\omega)$$  \hspace{1cm} (2.11)

which is equivalent to:

$$\sigma(\omega) = \frac{\varepsilon_0 \omega_p^2 \tau_r}{1 - i \omega \tau_r} \text{ where } \omega_p^2 = \frac{e^2 N}{\varepsilon_0 m^*}$$  \hspace{1cm} (2.12)

This relationship is called the Drude equation, in which $\omega_p$ is the plasma frequency and $\varepsilon_0$ is the vacuum permittivity. Figure 2.6(a) plots the real and imaginary part of the conductivity. The resonance for absorption of electromagnetic light by free carriers (peak of the real conductivity) is positioned at $\omega = 0$. In many types of harmonic motion, like vibrations and rotations of molecules, the resonance is positioned at $\omega > 0$. The position of the resonance is determined by the force constant, which is the proportionality factor between the displacement of the particle and its restoring force. For free carriers, the force constant is zero, giving rise to a linear damping of the electronic motion and explaining why the resonance in the Drude model is positioned at $\omega = 0$. Figure 2.6(b) shows the conductivity of free carriers in germanium in the frequency window of our THz spectrometer. The sample was excited with 400 nm pulses and the conductivity was

**Figure 2.6** a) plot of the Drude equation as a function of the angular frequency. The resonance of free carriers is positioned at $\omega = 0$ and the frequency at which the real and imaginary conductivity cross, is determined by the scattering time: $\tau_r = 1/2\pi \omega_{cross}$. b) Measured conductivity of free carriers in germanium (grey dots), after excitation with 400 nm pulses. Fitting the data (spheres) with the Drude equation (solid line) yields values for $\omega_p$ and $\tau_r$. 

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measured at a pump-probe delay of 50 ps. Clearly, the real part of the conductivity continuously increases towards lower frequencies, which is indicative of the free carrier resonance at $\omega = 0$. The frequency at which the real and imaginary conductivity cross, defines the scattering time ($\tau = 1/2\pi\omega_{\text{cross}}$). The data can be fitted accurately with the Drude model (solid line in Fig. 2.6b), yielding $\omega_p$ and $\tau$. The strength of THz-TDS is illustrated clearly by Fig. 2.6(b): the fits of the two traces (real and imaginary photoconductivity) using the Drude equation describe the offset, the curvature and the amplitude of the two curves surprisingly well, using only two global parameters, $\omega_p$ and $\tau$. Hence, THz-TDS measurements are excellently suited for determining the two key parameters of the photoconductivity, $\omega_p$ and $\tau$, in a bulk semiconductor like germanium.

The Drude model as discussed above is a simple model that describes the electrical properties of many materials surprisingly well. However, the model is based on a number of drastic simplifications that makes it not generally applicable. First of all, the interaction of carriers with the lattice is only incorporated by scattering processes, and Coulomb interactions are neglected. For highly polarizable materials, the Coulomb interaction of charge carriers with the charged lattice should be taken into account. For very strong carrier-lattice interactions, the carriers may become self-trapped and transport occurs by a hopping process. Secondly, holes and electrons are treated as an ideal classical gas, i.e. interactions between them are neglected. It has been demonstrated, however, that carrier-carrier interactions are significant at high carrier densities (especially in materials with low dielectric constants)\(^{25}\). In this situation, the Drude model (including only scattering with phonons) does not correctly describe the conductivity anymore, but has to be extended with carrier-carrier interactions. And finally, all carriers are treated as equivalent particles, whereas in reality, there is a distribution of electron velocities and scattering times. These three simplifications make the Drude model inappropriate for describing the conductivity in certain situations, e.g. when the carrier density is high and carrier-carrier interactions cannot be neglected. However, in many situations, the Drude model is a very suitable description to describe the electrical behavior of carriers in a macroscopic sample.

2.4.2 THz response to excitons

Electrons and holes in photo-excited semiconductors are not always present as free carriers. In some cases, they form bound electron-hole pairs that are referred to as excitons. There can be different reasons for the formation of excitons instead of free carriers. In low dielectric function materials, charge screening is relatively weak and the Coulombic attraction energy can be higher than the thermal energies of electrons and holes, especially at low temperatures. The low-temperature formation of excitons in materials like silicon and GaAs has been studied extensively with THz-TDS\(^{11,26-28}\).
More relevant within the scope of this thesis is the existence of excitons in nanostructured materials like quantum dots. As explained in chapter 1, the dominating contribution to the exciton energy comes from the confinement energy, rather than from Coulombic attractions. Because of quantum-confinement, excitons are formed in QDs also at room temperature and their response to THz radiation is similar to that of excitons in bulk materials at low temperature. In contrast to free carriers, an electron (hole) within the exciton cannot be displaced significantly by an applied THz field, because the oppositely charged hole (electron) provides a restoring force by means of Coulombic attraction. As a result, the characteristic exciton resonance is different from the free carrier Drude response (resonance positioned at zero frequency). Rather, the excitonic resonance originates from intraband transitions of holes and electrons (see Fig. 1.1). The energy associated with these resonances is determined by the spacing between the energy levels: the relative position of these energy levels (and hence the associated spacing between the levels) is determined by the QD radius and the carrier effective masses (see Eq. 1.3). Fig. 2.7(a) shows a schematic representation of the conductivity of the lowest-energetic intraband transition. In most materials, the effective mass of holes is significantly larger than that of electrons\(^\text{29}\), resulting in typical energy spacings between valence levels of 40-100 meV and spacings between conduction levels of 300-600 meV\(^\text{30,31}\). Since the spectrum of our THz probe lies between \(~0.2 – 2\ THz \ (~1–8\ meV)\), the energy of the THz probe is insufficient to excite intraband transitions in QDs directly. Therefore, the THz light is not absorbed by excitons in QDs (no real photoconductivity), but the THz pulse experiences a phase-shift as a result of the polarization of excitonic wavefunctions. THz data of InAs QDs after excitation with 800 nm light in Fig. 2.7(b) is in agreement with the expected excitonic THz response. Clearly,

**Figure 2.7** THz conductivity for excitons. (a) Schematic of the lowest-energetic excitonic resonance, which is positioned at finite frequency (in contrast to the zero frequency Drude conductivity). The interaction of THz light with excitons originates from intraband electronic transitions. (b) Conductivity of 4.4 nm InAs QDs (grey dots) in the frequency window of the THz spectrometer, after excitation with 800 nm light. The real conductivity is zero (no absorption) and the imaginary conductivity is negative and decreasing with frequency, in agreement with the theoretical excitonic conductivity depicted in (a). The solid line in (b) is a fit of the data with equation 2.21.
the real conductivity is zero and the imaginary conductivity is negative and decreasing with frequency, corresponding to the photo-induced phase shift of the THz pulse.

To describe the THz response in Fig. 2.7(b) quantitatively, the QDs can be treated as polarizable spheres on a macroscopic and a microscopic level. For a macroscopic sample, the total electric dipole moment \( P \) is given by\(^{32}\):

\[
P = \chi E
\]  
\[(2.13)\]

where \( E \) is the external electric field and \( \chi \) is the dielectric susceptibility, which is related to the dielectric constant by \( \varepsilon = 1 + 4\pi\chi \). In a microscopic description, the polarization induced in a single QD is a result of the internal electric field, \( E' \), which is different from the external electric field because of the dielectric screening of the field by the QD. The internal electric field inside the (spherical) particle is given by\(^{32}\):

\[
E' = E + \frac{4\pi}{3} P
\]  
\[(2.14)\]

For a single QD, the electric dipole moment \( p \) is defined as:

\[
p = \alpha \cdot E'
\]  
\[(2.15)\]

where \( \alpha \) is the polarizability of the QD. The microscopic dipole moment \( p \) is connected to the macroscopic total dipole moment \( P \) by:

\[
P = N \cdot p = N \cdot \alpha \cdot E'
\]  
\[(2.16)\]

On eliminating \( E' \) from the above equations, one finds the Lorentz-Lorenz formula that relates the microscopic polarizability \( \alpha \) with the macroscopic dielectric constant \( \varepsilon \):

\[
\alpha = \frac{3}{4\pi N} \frac{\varepsilon - 1}{\varepsilon + 2} = R \cdot \frac{\varepsilon - 1}{\varepsilon + 2}
\]  
\[(2.17)\]

The polarizability \( \alpha \) of an excited QD consists of a contribution from valence electrons (reflected by the ground state dielectric constant \( \varepsilon \)) and a contribution from the polarizable exciton (reflected by the photo-induced change in the dielectric constant \( \Delta\varepsilon \)). Combining equations 2.1, 2.2, and 2.17, one finds the expression that relates the exciton conductivity \( \sigma_0 \) to the exciton polarizability \( \alpha_{exc} \):

\[
\frac{(\varepsilon - 1) + i\sigma_0(\omega) / \omega\varepsilon_0}{(\varepsilon + 2) + i\sigma_0(\omega) / \omega\varepsilon_0} = \frac{\varepsilon - 1}{\varepsilon + 2} + \frac{\alpha_{exc}(\omega)N_{exc}}{3}
\]  
\[(2.18)\]
where $N_{\text{exc}}$ is the exciton density. Analogous to the hydrogen atom, the polarizability of a transition dipole of an intraband resonance is characterized by a Lorentzian lineshape given by:

$$\alpha_{\text{exc}}(\omega) = \alpha_{0,\text{exc}} \frac{\omega_0^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$  \hspace{1cm} (2.19)

where $\alpha_0$ is the static (DC) polarizability associated with a specific intraband transition, $\omega_0$ is the intraband transition energy defined by the spacing between energy levels, and $\gamma$ is the linewidth of the absorption. Rearranging equation 2.18 gives the expression that defines $\sigma_0$ as a function of $\alpha_{\text{exc}}$:

$$\sigma_0(\omega) = \frac{-i\omega\epsilon_0(\epsilon + 2)^2 \alpha_{\text{exc}}(\omega)N}{(9 - (\epsilon + 2)\alpha_{\text{exc}}(\omega)N)}$$  \hspace{1cm} (2.20)

Typically, $\alpha_{\text{exc}}N < 1$ and equation 2.20 can be reduced to

$$\sigma_0(\omega) = -\frac{(1/9)i\omega\epsilon_0(\epsilon + 2)^2 \alpha_{\text{exc}}(\omega)N}{\alpha_{\text{exc}}(\omega)N}$$  \hspace{1cm} (2.21)

Fitting the data in Fig 2.7(b) with equation 2.21 yields $\omega_0$ and $\gamma$. In the fitting procedure, a value for $\alpha_0$ of 15,000 Å$^3$ was used, which was determined from THz-TDS measurements in Chapter 3. In this thesis, the excitonic response at THz frequencies was used to investigate exciton dynamics in colloidal QDs (see Chapters 3 and 4).

### 2.4.3 THz response to nanostructured semiconductors

Nanocrystalline semiconductor films are widely used in dye-sensitized solar cells, because of the large surface area per unit volume$^{33}$. Most commonly, the films are 1 – 10 µm thick and consist of sintered TiO$_2$ particles of 10 – 50 nm size. Such TiO$_2$ films are also candidates as supporting material for QD-sensitized solar cells, as explained in paragraph 1.5. The THz response of carriers within TiO$_2$ nano-films is vastly different from bulk semiconductors$^{16,23,34,35}$, even though the constituent TiO$_2$ particles have bulk properties since their size is much larger than the exciton Bohr radius of TiO$_2$ (~ 1 nm). The reason is the large dielectric contrast between nano-particles and the surrounding medium, typically air or an organic solvent. Microscopically, the applied electric field that causes acceleration of free carriers is screened by the highly polarizable TiO$_2$ particles ($\epsilon_p \sim 120$)$^{23}$. As a result, the internal electric field is reduced compared to the field experienced in a homogeneous sample of the bulk material.

To calculate the conductivity of nanocrystalline films, it is necessary to define an effective dielectric function for a material consisting of two phases (e.g. TiO$_2$ and air). A commonly used approach is the Maxwell-Garnett effective medium theory$^{23,36}$ that relates
the dielectric function of the polarizable particles, \( \varepsilon_p \), and of the surrounding medium, \( \varepsilon_m \), to the effective dielectric function \( \varepsilon \) of the composite by:

\[
\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} = f \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}
\]

where \( f \) is the filling fraction of the polarizable particles. For example, a film of TiO\(_2\) particles (\( \varepsilon_p = 120 \)) in air (\( \varepsilon_p = 1 \)) with \( f = 0.4 \) results in \( \varepsilon = 2.9 \) according to equation 2.21.

The photo-conductivity of carriers in a nanoporous medium can be obtained by combining the Drude model (\( \sigma = -i\varepsilon \omega \varepsilon_p \)) with equation 2.22:

\[
\frac{\varepsilon + i\sigma/\omega \varepsilon_m}{\varepsilon + i\sigma/\omega \varepsilon_p} = f \frac{\varepsilon_p + i\sigma/\omega \varepsilon_m}{\varepsilon_p + i\sigma/\omega \varepsilon_m}
\]

Figure 2.8(b) gives the complex conductivity of a 2 \( \mu \)m nanocrystalline TiO\(_2\) film in air. The film consists of sintered anatase TiO\(_2\) particles of 15 nm in diameter (see Fig. 2.8(a) for a scanning electron microscope image) and is directly excited with 266 nm pulses. The solid line in Fig. 2.8 is a fit to the Maxwell-Garnett effective medium theory (equation 2.23). Clearly, the combination of the Drude equation with effective medium theory is consistent with two characteristic features of the conductivity in nanocrystalline semiconductors, i.e. the fact that the conductivity becomes zero for \( \omega \to 0 \) and the fact that the imaginary conductivity is negative. Both features are inconsistent with the ‘normal’ Drude model, but can be accounted for by incorporating local field effects.

![Figure 2.8](image-url)

**Figure 2.8** (a) SEM image of a nanostructured TiO\(_2\) film. (b) THz conductivity of a nanostructured TiO\(_2\) film (grey dots), measured after direct excitation with 266 nm light. The solid line is a fit to the Maxwell-Garnett effective medium theory (see text).
2.5 Transient Absorption

Transient Absorption (TA) is one of the most common techniques for the investigation of ultrafast excited state dynamics in QDs\textsuperscript{37-40} and dyes\textsuperscript{41}. Like THz-TDS, it is a pump-probe technique using ultrashort pulses of ~ 50 – 150 fs. The main difference with THz-TDS is that TA makes use of a probe pulse of visible or infrared (IR) frequencies. While a probe at THz frequencies is ideally suited for investigating the carrier mobility and conductivity in (nano-structured) semiconductors via the complex refractive index, TA gives information on the dynamics of electronic and vibrational excitations by tuning the probe light to the transition of interest in for instance molecules and QDs. In this thesis, TA is used to obtain information about the population of electronic excitations in QDs. The choice between visible and IR probe light is dictated by the QD material: CdSe QDs have interband transitions at visible frequencies\textsuperscript{42}, whereas the transitions in InAs\textsuperscript{43} and PbSe\textsuperscript{44} QDs are located in the IR region (see chapter 3 and 6).

In a typical TA experiment, a QD sample is irradiated with a visible pump pulse resulting in photo-excitation of electrons into ‘conduction’ energy levels (see Fig. 1.1). Subsequently, a probe pulse is transmitted through the sample having a photon energy equal to the interband transition. QDs in the excited state absorb less probe light compared to unexcited QDs, since fewer electronic transitions are available due to the population of electrons in conduction levels. Measuring the difference in absorption of the probe light between the excited and unexcited sample, $\Delta \alpha$, gives information about the population of QDs in the excited state. As in THz-TDS, the dynamics of the excited state population can be detected on a picosecond timescale by varying the delay between the pump and the probe pulse.

![Figure 2.9 Dynamics of a TA measurement on 4.4 nm InAs QDs. The dynamics were determined using a pump intensity of 1.1 $\mu$J/mm$^2$ (excitation at 800 nm). The inset shows the absorption spectrum for 4.4 nm core-shell InAs QDs. The 1S population was probed with 1200 nm light to ensure that only dynamics of the 1S transition (positioned at 1100 nm) are probed.](image-url)
Typical TA data is shown in Fig. 2.9. An experiment was performed where 4.4 nm core-shell InAs QDs were excited with 800 nm pulses and the population of electrons in the 1S\textsubscript{e} level was probed with 1200 nm light. The bandgap of 4.4 nm InAs QDs is positioned at 1100 nm (1.13 eV, see inset Fig. 2.9) and by probing at 1200 nm we ensure that only the dynamics of the 1S transition, and not the higher-lying 1P transition, are probed. In the experiment presented in Fig. 2.9, the 800 nm excitation fluence is chosen sufficiently low that no more than one exciton per quantum dot is generated. Absorption of an 800 nm photon will excite electrons into hot conduction levels. The initial rise of the signal in Fig. 2.9 can be attributed to relaxation of hot electrons to the 1S\textsubscript{e} level, with a time constant of \approx 0.8 ps, as obtained from fitting the data with a two-level model (solid line, see Chapter 3 for details fitting procedure).

The schematic layout of the TA setup is given in Figure 2.10. Similar to the THz spectrometer, the TA setup is based on ultrashort 800 nm pulses with a pulse duration of \approx 110 fs FWHM and a repetition rate of 1 KHz. Part of this beam is used to pump the sample with 400 or 800 nm pulses and the remainder is used to generate the probe light. For InAs or PbSe QDs, the probe light is tuned to the QD bandgap at IR frequencies by an Optical Parametric Amplifier (OPA, Coherent). CdSe QDs are probed with a white light continuum that is generated by irradiating a sapphire plate with 400 nm pulses. The transmitted probe light through the sample is spectrally dispersed by a grating and detected on a diode array. In a TA experiment, only the intensity of the probe light is detected and not the phase, which is a major difference with THz-TDS.

![Figure 2.10 Schematic layout of the TA setup. The sample is excited with a pump pulse of visible frequencies (400 or 800 nm) and subsequently probed with visible or IR light pulses, depending on the QD material. The IR light is tuned to the QD bandgap by an Optical Parametric Amplifier (OPA, Coherent). When probing at visible frequencies, a white light continuum is made by pumping a sapphire plate with 400 nm pulses (not shown in figure). The transmitted probe light is spectrally separated by a grating and subsequently detected on a diode array.](image)
References

(23) Hendry, E. Charge Dynamics in Novel Semiconductors, University of Amsterdam, 2005.
(33) Grätzel, M. Progress in Photovoltaics: Research and Applications 2006, 14, 429-442.


