Charge carrier dynamics in photovoltaic materials

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4 DYNAMICS OF PHOTOEXCITED CARRIERS IN GRAPHENE

4.1 INTRODUCTION

Carbon was recently found to exist as a stable monolayer of conjugated atoms known as graphene [120]. Figure 4.1 shows the spatial structure and band structure of pristine monolayer graphene. The valence- and the conduction bands in graphene touch in a single point called the Dirac point, making it semi-metallic. At energies close to the Dirac point, the dispersion relation in this 2-dimensional material is linear, analogous to that of photons, only the velocity of light $c$ is replaced by the Fermi velocity $v_F \approx c/300$ [121]:

$$E = \hbar v_F |k|$$

(4.1)

Owing to the linear dispersion, charge carriers close to the Dirac point in

![Figure 4.1](image_url)

**Figure 4.1.** (a) Spatial structure of graphene, a one dimensional layer of carbon atoms. (b) Band structure of pristine graphene around the K-point in reciprocal space where the filled valence band (blue) and the empty conduction band (grey) meet in a single point called the Dirac point.
graphene can be described as massless relativistic Dirac fermions [122, 123]. The unique electronic structure gives graphene favorable conductive properties [124, 125], and exceptional charge carrier mobilities as high as 200,000 cm² V⁻¹ s⁻¹ have been observed in suspended single layer graphene at low temperature [126]. Graphene also possesses exceptional optical properties. As graphene has a bandgap energy of zero and a linear dispersion relation, pristine graphene displays a broad optical absorption ranging from the far infrared to the ultraviolet wavelength regime [129, 127], determined by the fundamental fine structure constant [130]. Owing to these remarkable properties, graphene has received much attention for use in optoelectronic applications [121, 131]. For these applications it is important to understand how light couples to the electronic system. For photovoltaics specifically, it is interesting to know how the optical energy absorbed in graphene over the wide spectral range is distributed: Whether it is retained in the electronic system from which it can potentially be extracted, or whether it is immediately lost to heat in the graphene lattice. Graphene is already considered a prime candidate for optical energy harvesting, and the photoresponse has been found to be dominated by energetic ‘hot’ charge carriers through the photothermoelectric effect where a light induced difference in electron temperature results in a thermoelectric voltage [132, 133].

With optical pump-THz probe spectroscopy, charge carriers can be optically excited, and their conductivity probed on sub ps timescales. This makes it possible to follow the evolution of the carrier population immediately after optical excitation with very high time resolution. The THz conductivity of intrinsic mobile carriers in doped, non-photoexcited graphene has been shown to exhibit a Drude-type response [134]. Early reports of optical pump-THz probe experiments performed on epitaxially grown multilayer (and thus undoped [135]) graphene samples showed that optically exciting graphene led to a decrease in the THz transmission [135, 136, 137]. This behavior could be explained by a Drude type conductivity with fixed scattering time, causing an increase in conductivity as carriers are photoexcited from the valence- to the conduction band. The increased conductivity in turn explains the decreased THz transmission. More recently, several groups have reported a photoinduced increase in THz transmission in CVD grown monolayer graphene, the cause of which is still under debate [63, 138, 139, 140].

We will show that the photoinduced increase in THz transmission can be explained by the transfer of energy from absorbed photons to multiple intrinsic

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*aFor graphene with intrinsic dopant carriers, the interband absorption in the near infrared region is reduced by Pauli blocking when the photon energy is smaller than 2|E_F| [127, 128].
dopant carriers in supported monolayer graphene, lowering the overall conductivity. By varying the excitation photon energies and -densities and measuring the resulting photoconductivity, we are able to quantify the efficiency of energy transfer from each photon to multiple dopant carriers in the graphene. We find a very efficient energy transfer. Thus graphene shows promise for optoelectronic and photovoltaic devices.

4.2 Samples

In this chapter we study single layer graphene grown by chemical vapor deposition (CVD). All data presented in subsection 4.3.1 were measured on a sample of graphene on quartz obtained from Graphenea, San Sebastián, and the data presented in the beginning of section 4.3 and in section 4.3.2 were measured on a similar sample obtained from Graphene Supermarket, Calverton, NY. The gated graphene sample used for the measurements presented in section 4.3.3 was fabricated by depositing a graphene monolayer grown by CVD on a conductive doped silicon substrate covered by an isolating SiO$_2$ layer. This configuration enabled the doped silicon substrate to function as a gating electrode. Electrical source and drain electrodes were also connected to the graphene layer.

4.3 Results and Discussion

Upon photoexcitation of graphene with visible photons we observe an increase in the transmitted THz field, see Figure 4.2 (a). Recently, several optical pump - THz probe studies on monolayer graphene have similarly shown a photoinduced increase in THz transmission [63, 138, 139, 140]. One group saw a strong dependence on environmental conditions on the magnitude and even the sign of the photoconductivity [138]. Based on these and other observations, the authors concluded that physisorption of gaseous molecules cause the opening of a small bandgap in the graphene, which enables stimulated emission of THz radiation. This emission can then explain the observed increase in THz transmission upon photoexcitation. However, THz gain was not observed [138]. Others did not observe any influence of the ambient environment [140], and the negative photoconductivity has been explained by a decrease in the mean carrier scattering time upon photoexcitation, leading to a lower conductivity [63, 140]. It is known that CVD grown graphene deposited on a supporting substrate is intrinsically doped [135, 134], and the mobile dopant carriers cause an intrinsic conductivity in unexcited graphene samples. The observed photoinduced increase in THz
transmission can therefore be explained by a reduction in the conductivity of the dopant carriers as the carrier population is heated by the energy of the optical excitation, after initial electron-hole pair generation [135, 139].

These two interpretations, THz emission vs. photoinduced reduction in the intrinsic conductivity, have very different implications for the behavior of the THz transmission at increasing photon fluences: In the case of a photoinduced reduction in conductivity ‘bleaching’ the THz absorption, the upper limit of the absorption change would be the initial absorption in the unexcited sample, while in the case of THz amplification in the graphene, the transmission change could exceed this value. From Figure 4.2 (b) we see that upon photoexcitation, the THz transmission approaches, but does not exceed, that of the empty substrate. This observation indicates that THz emission is not the cause of the observed
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Figure 4.3. Optical pump - THz probe dynamics of graphene measured with 3.10 eV excitation.

photoinduced increase in THz transmission. THz emission appears to be either absent or not detected in our experiment.

4.3.1 Multiple hot carrier generation

A typical optical pump-THz probe trace for graphene is shown in Figure 4.3. Here we plot the actual value of $\Delta T/T$ (recorded on the THz peak) which is positive, corresponding to a negative real photoconductivity $\Delta \sigma$, see equation (2.10). The imaginary photoconductivity in graphene is found to be close to zero. The sample is photoexcited at zero pump-probe delay, and a very fast rise in the negative conductivity is seen upon excitation, followed by a slower decay. These observations can be explained as follows: As argued in [139] and the discussion below, the energy of an optically excited high energy electron-hole pair in graphene is quickly dissipated via one of the processes shown schematically in Figure 4.4: It can be transferred to secondary electron-hole pairs through carrier-carrier scattering, exciting them above the Fermi level, Figure 4.4 (a), or the it can be immediately dissipated via phonon emission as shown in Figure 4.4 (b). The heating of the intrinsic dopant population during the thermalization of the primary photogenerated charge carriers gives rise to a reduction in overall conductivity as described in [139] and the associated supporting information. This explains the rapid decrease in conductivity seen as the rising negative photoconductivity in Figure 4.3. The observed fast negative rise in conductivity is consistent with reported carrier-carrier scattering times which are well below 100 fs [135, 141]. The competing phonon mediated cooling of the optically excited carriers occurs through emission of optical phonons [141] on
timescales of hundreds of femtoseconds [137]. The conductivity change in Figure 4.3 peaks at time $\tau_{\text{peak}} \approx 200$ fs, when the initial photoexcited carriers have completely thermalized with the other carriers, and the system has reached a thermalized ‘hot’ state with an elevated carrier temperature. At this stage the carriers are in thermal equilibrium with each other, but out of equilibrium with the graphene lattice. After $t_{\text{peak}}$, the energy is dissipated as the carriers revert to thermal equilibrium with the lattice. As the energy of the thermalized hot carriers is below the optical phonon energy of $\sim 200$ meV [142], energy dissipation via optical phonon emission is not possible [143]. The energy transfer from the carrier population to the lattice then occurs via acoustic phonon emission, which is slower than carrier-carrier thermalization and optical phonon relaxation [144, 145]. It has been proposed [142, 146] that the electron-to-acoustic phonon energy transfer can occur through a process called supercollisions. Here the momentum conservation restrictions that limit the energy of the emitted acoustic phonons to low values ($\lesssim 4$ meV) [146] is relaxed via disorder scattering [142]. We find that the process of acoustic cooling occurs with a characteristic decay time of $\sim 1.4$ ps, similar to the dynamics observed in other studies of graphene [63, 135, 147].

![Diagram](image)

**Figure 4.4.** Charge carriers in doped graphene following photoexcitation. The high energy electron-hole pair generated via optical excitation can thermalize in two ways: (a) The energy of the initial electron-hole pair can be transferred to the population of intrinsic dopant carriers via the process called multiple hot carrier generation, or (b) the energy can be lost via phonon emission.

Similar to the experiments presented in section 3, we can use the photoinduced (negative) THz conductivity to quantify the efficiency of energy trans-
fer from the primary excited electron-hole pairs to secondary charge carrier in graphene. We use the term *multiple hot carrier generation* to denote the process where energy is transferred to the intrinsic carriers in order to distinguish it from the *carrier multiplication* process studied in chapter 3, where secondary carriers are excited across the bandgap of a semiconducting material as opposed to being ‘heated’ above the Fermi level. Still, in the present process the energy is retained in the electronic system from which it can potentially be extracted in an external circuit, for instance in a photovoltaic application as suggested in [133].

The value of the negative conductivity at the peak in the pump-probe measurements $t_{\text{peak}}$, corresponding to the thermalized hot carrier population, can be taken as a measure of the energy transferred to the intrinsic dopant carriers during the thermalization of the initial photoexcited carriers, before the energy is lost to the lattice. By measuring the magnitude of the negative photoconductivity at $t_{\text{peak}}$ versus the density of absorbed photons, we can quantify the conductivity change per photon of a certain energy. This conductivity change is proportional to the amount of heat absorbed in the electronic system, and therefore to the hot carrier density, see supporting info of [139]. The peak conductivity versus excitation density was measured at increasing photon energies in order to find the excitation efficiency, that is, the fraction of energy transferred to the intrinsic carriers per photon, as a function of the original photon energy. Figure 4.5 (a) shows the peak $\Delta T/T$ values versus absorbed photon density measured at various photon energies. In the fluence regime employed here, the THz conductivity signal scales linearly with photon density, meaning that each photoexcited carrier acts independently of other photoexcited carriers. Each photoexcited carrier thus gives rise to a constant change in conductivity, depending only on the energy of the absorbed photon. It is clear from Figure 4.5 (a) that for a given absorbed photon density, the magnitude of the conductivity change increases with increasing photon energy. This is because a higher energy photon leads to more electron-electron scattering events, and therefore a hotter carrier distribution. The number of hot carrier per photon is given by the slopes of the lines in Figure 4.5 (a), that is, the measured conductivity change per absorbed photon. These slopes are plotted versus the photon energy in Figure 4.5 (b). The scaled conductivity signal rises almost linearly with photon energy. Qualitatively, this can be taken as an indication of efficient energy transfer from an absorbed photon into multiple secondary carriers: As the photon energy is increased, causing an initial electron-hole pair of higher energy, more electron-electron scattering events can take place, and
more energy is transferred to the secondary carriers. This causes an almost proportional increase in (negative) photoconductivity with photon energy. Energy loss via the emission of optical phonons becomes visible at higher photon energies where the carrier-carrier energy transfer cascade takes more time, and electron-phonon scattering start playing a role. However, this effect seems to be rather modest for the photon energies studied here. The observation that the photoconductivity per amount of energy initially put into the sample stays almost constant means that almost all the absorbed photon energy is converted into heated carriers. If energy relaxation via phonon emission would dominate, the normalized conductivity signals should be independent of photon energy [139, 141]. More quantitatively, it was shown in [139] that the deviation from linearity of the values plotted in Figure 4.5 (b) can be used to directly extract the coupling constant $\gamma_{\text{el-ph}}$ between electrons and optical phonons, competing with the carrier-carrier transfer process during the rise of the THz signal in Figure 4.3. From $\gamma_{\text{el-ph}}$ extracted from the data in Figure 4.5 (b) the authors of [139] could calculate the branching ratio - the ratio between the rate constants - between the two energy relaxation processes carrier-carrier scattering and carrier-phonon scattering as function of photon energy. From the branching ratio the efficiency of energy transfer from an optically excited carrier to the population of intrinsic dopant carriers was found to be 75 % and higher for photon energies in the visible spectrum [139].

\[ \Delta T_{\text{peak}} / T \text{ scaled to } N \text{ (a. u.)} \]

\[ \text{Photon energy (eV)} \]

Figure 4.5. (a) THz signal at $t_{\text{peak}}$ vs. absorbed photon density at various photon energies. Lines show linear fits. (b) THz peak signal normalized to photon density vs. photon energy. Error bars show the standard deviation of the $\Delta T_{\text{peak}} / T$ over $N$ values, and the line is a guide to the eye.

It has been demonstrated [132, 133, 148], that by employing particular device geometries to achieve a difference in thermopower or Seebeck coefficient across
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A graphene sample, a photovoltage can be achieved via the photothermoelectric effect, meaning that photoexcited electrons and holes can be separated. The high photon-to-electron energy conversion efficiency in graphene found above is thus a positive result for prospective graphene based optoelectronic applications. Particularly, the efficient generation of multiple hot carriers from a single photon can potentially boost the photocurrent of a PV device, and thereby increase the energy conversion efficiency as suggested in section 1.4.

4.3.2 Carrier dynamics at high pump intensities

In the section above, the photoinduced conductivity change was used to quantify the energy transfer efficiency from photons to dopant carriers in the limit of low fluence where the photoconductivity scales linearly with excitation density. Here we explore the photoinduced THz transmission in the region of high excitation fluence in order to confirm the role of the intrinsic dopant carriers in the observed negative photoconductive behavior.

Figure 4.6 (a) shows the photoinduced $\Delta T/T$ value (proportional to the negative real conductivity) measured at $t_{\text{peak}}$ versus absorbed fluence for two photon energies measured on a fluence range much larger than the data in Figure 4.5. We see a clear saturation behavior at high fluences, and the photoinduced THz transmission at both photon energies tends towards the same value. The saturation of the THz transmission observed at high excitation fluence can be explained by a quenching of the conductivity of the intrinsic dopant population. When the intrinsic population of mobile carriers gradually becomes hotter, showing gradually less conductivity, less photoinduced conductivity change occurs for each additional absorbed photon.

From Figure 4.6 (a) we also see that saturation occurs for a lower fluence of 3.10 eV photons than 1.55 eV photons. This is consistent with our previous findings that a high energy photon causes more carriers to be heated via the process of multiple hot carrier generation, and therefore gives rise to a bigger conductivity change than a low energy photon. In Figure 4.6 (b) we plot the photoinduced THz transmission versus absorbed energy rather than number of absorbed photons. We observe a very similar behavior for the two photon energies employed here, confirming the efficient transfer of energy from high energy photons into the electronic system in graphene found in section 4.3.1. As the energy from either 1.55 eV or 3.10 eV photons is efficiently transferred to the electronic system in graphene, it is the total energy of the absorbed photons that determines the change in carrier temperature and therefore the change in conductivity.
We fitted the data in Figure 4.6 (a) to a simple saturation model [149]

\[
\frac{\Delta T}{T_{\text{peak}}} = \frac{A}{1 + F_{\text{sat}}/F}
\]

(4.2)

Where \( F \) is the fluence, \( A \) is the end level of transmission for fluence going to infinity, and \( F_{\text{sat}} \) is the saturation fluence - a measure of the fluence at which saturation becomes significant. The fits are shown together with the data in Figure 4.6. In order to obtain more statistical data, we repeated the measurements presented in Figure 4.6 and extracted the fit parameters and standard deviations. Taking the data for 1.55 eV and 3.10 eV excitation together, we find an end level transmission of \( A = 4.8 \pm 0.8 \) %. This value is comparable to, but smaller than the total THz absorption of the unexcited graphene caused by the intrinsic dopant population, which was found to be 5.4 %. The saturation fluences were extracted separately for the two excitation photon energies, and we found \( F_{\text{sat}} = 6.0 \pm 0.3 \cdot 10^{15} \text{ m}^{-2} \) for 1.55 eV, and \( F_{\text{sat}} = 3.5 \pm 0.5 \cdot 10^{15} \text{ m}^{-2} \) for 3.10 eV. As the THz measurements were performed on various spots on the sample, the standard deviations in the extracted values of \( A \) and \( F_{\text{sat}} \) might arise from spatial variations in the dopant density.

We employed Raman spectroscopy to study the level of intrinsic doping in the graphene. Figure 4.7 shows a Raman spectrum obtained on our CVD graphene-on-quartz sample. By monitoring the G peak in the Raman spectrum positioned at 1580 cm\(^{-1}\) in pristine undoped graphene, one can recover the
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Figure 4.7. Raman spectrum of graphene on quartz showing the G peak close to 1580 cm$^{-1}$. Raman excitation wavelength was 488 nm.

Fermi energy and in turn the level of intrinsic doping [128]. The position of the Fermi level relative to the Dirac point can be found from the G peak center frequency $\nu_G$ through [128]

$$|E_F| = \frac{\nu_G - 1580 \text{ cm}^{-1}}{42 \text{ cm}^{-1} \text{ eV}^{-1}}$$  \hspace{1cm} (4.3)

Figure 4.8. Spatially resolved Raman image showing the center position of the G peak $\nu_G$ measured on an area of 1 by 1 mm with 100 $\mu$m steps. Red color indicates areas where reliable spectra were not obtained.

Figure 4.8 shows a spatially resolved map of $\nu_G$ measured on a 1 by 1 mm area with 100 $\mu$m steps. This step size corresponds roughly to the diameter of the THz probe beam, although the spot probed by Raman is significantly smaller. From the data in Figure 4.8 we find the average G peak position for the whole area to be 1588.7 cm$^{-1}$ with a standard deviation of
2.6 cm\(^{-1}\). Both quantities correspond well with other reported values obtained on supported monolayer graphene [150, 151]. We obtain a mean Fermi level of 0.21 eV ± 0.06 eV. From this we can find the density of intrinsic dopant carriers \(n_i\). Using \(|k_F| = \sqrt{n_i \pi}\) [125] in (4.1), we obtain

\[
n_i = \frac{E_F^2}{\hbar^2 v_F^2 \pi}
\]  

(4.4)

where \(v_F = 1.1 \cdot 10^6\) m/s is the Fermi velocity [123]. We obtain an average dopant density of \(n_i = 2.7 \cdot 10^{16}\) m\(^{-2}\).

In order to compare the saturation fluences found above to the intrinsic carrier density, we calculate the corresponding number of carriers excited to higher energy levels through the multiple hot carrier generation process. The average number of electron-hole pairs \(\langle N \rangle\) heated through carrier-carrier scattering by a photon of energy \(E_{\text{ph}}\) can be approximated by [141]:

\[
\langle N \rangle = 0.55 \cdot E_{\text{ph}}/E_F
\]  

(4.5)

Using the value \(E_F = 0.21\) eV from the Raman measurement, we find a theoretical multiplication factor of 4 for 1.55 eV excitation and 8 for 3.10 eV excitation. For comparison we calculate the ratio between the intrinsic dopant density \(n_i\) and the saturation fluences \(F_{\text{sat}}\) to find the experimental multiplication factor corresponding to a photoinduced excitation of all dopant carriers. We find a value of 4.5 for 1.55 eV excitation and 7.7 for 3.10 eV. These values are very close to the theoretical multiplication factors, indicating that the saturation in photoconductivity is indeed associated with a quenching of the conductivity of the intrinsic dopant states. These observations thus corroborate our interpretation that efficient energy transfer occurs from photons to the dopant carriers through the process of multiple hot carrier generation.

Another possible explanation for the leveling off of the photoconductivity at high photon fluences is saturation of the interband optical absorption due to Pauli blocking. However, it has been shown [152, 153, 154] that this process occurs at excitation densities of about \(5 \cdot 10^{17}\) m\(^{-2}\), much higher than the absorbed photon densities for which we observe saturation of the THz photoconductivity. We would therefore not expect this process to contribute significantly to the saturation of the conductivity that we observe.

4.3.3 ELECTRICALLY GATED GRAPHENE

The dependence of the THz photoconductivity on the dopant population in graphene can be further studied by performing photoconductivity measurements
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Figure 4.9. Gated graphene sample: a monolayer of graphene is deposited on a doped silicon substrate which acts as a gating electrode. The graphene is electrically isolated from the silicon electrode by a SiO₂ layer. Source and drain electrodes are also attached to the graphene for DC current measurements.

at varying dopant densities. To this purpose we used a sample consisting of a monolayer of graphene deposited on a conducting silicon substrate, electrically isolated from the silicon by a thin layer of SiO₂, see Figure 4.9. A static voltage was applied to the Si substrate which then worked as a back-gate, allowing control over the Fermi level relative to the energy bands in the graphene band diagram. This allowed us to change the density of conductive dopant charge carriers in the graphene by shifting the Fermi level closer to- or further away from the Dirac point. The graphene was also contacted with source and drain electrodes which allowed us to measure the DC conductivity.

Figure 4.10 (a) shows the conductivity of the graphene layer measured with the source and drain electrodes as function of gate voltage. We observe a clear decrease in conductivity when sweeping the gate voltage ($V_g$) to positive values, signifying that the Fermi level is shifted closer to the Dirac point, and the density of dopant carriers is reduced. When going to negative gate voltages, the doping level is increased and the conductivity increases.

Figure 4.10 (b) shows optical pump-THz probe dynamics for the graphene-on-silicon sample for two different back-gate voltages corresponding to a relatively low- and a relatively high level of doping. At the high doping level at $V_g = -50$ V, corresponding to the high conductivity in Figure 4.10 (a), we observe an initial negative photoconductivity with a fast rise and decay. This is attributed to the photoconductivity of the graphene. At longer pump-probe delay the positive signal of the silicon rises and dominates the photoconductivity. Interestingly, at $V_g = 0$ V the graphene photoconductivity is not noticeable. This is more clearly seen in Figure 4.10 (d) which shows the pump-probe traces for graphene on silicon with the signal from pure silicon subtracted.

Figure 4.10 (c) shows the photoinduced THz conductivity measured at the pump delay corresponding to the peak of the graphene photoconductivity as
Figure 4.10. Conductivity measurements on back-gated graphene (Figure 4.9) performed with electrical contacts and optical pump-THz probe measurements. (a) DC conductivity between source and drain vs. back-gate voltage. (b) THz photoconductivity vs. pump-probe delay at two gate voltages, excitation photon energy 3.10 eV. (c) THz photoconductivity recorded at a pump-probe delay corresponding to the peak of the graphene signal versus gate voltage. (d) THz photoconductivity of graphene-on-silicon minus the photoconductivity of bare silicon at two gate voltages, photon energy 3.10 eV.
a function of gate voltage. Here the transition from the negative graphene photoconductivity to the positive silicon response is clearly seen.

Thus, by reducing the dopant carrier density we are able to reduce the absolute magnitude of the negative photoconductivity. These observations clearly show that the characteristic negative photoconductivity of graphene is related to the intrinsic dopant population.

4.4 Conclusions

Using THz spectroscopy we have investigated the electronic processes taking place immediately after photoexcitation of supported single layer graphene. We found that photoexcitation of the graphene causes an increase in the THz transmission, corresponding to a photoinduced decrease in the conductivity. This observation is consistent with a photoinduced heating of the intrinsic dopant carrier population, reducing the overall conductivity. After photoexcitation of a high energy electron-hole pair, its energy is quickly dissipated either via energy transfer to the dopant carrier population or via emission of phonons.

As the magnitude of the negative photoconductivity scales linearly with the amount of energy deposited in the population of intrinsic conductive carriers ([139] and associated supporting information), we were able to study the energy transfer from an optically excited electron-hole pair to the dopant carriers by changing the excitation photon density and -energy. We found that the negative photoconductivity per absorbed photon, measured after thermalization of the carriers, increases with photon energy. This indicates that a high energy photon leads to a larger number of dopant carriers being heated than a lower energy photon. The energy transfer occurs via a process we refer to as multiple hot carrier generation. In this process the energy of a single photon, initially absorbed in one electron-hole pair, is transferred to multiple charge carriers near the Fermi level through a series of electron-electron scattering events. We observe that the negative photoconductivity scales nearly linearly with photon energy, indicating efficient conversion of energy from each initially photoexcited charge carrier into multiple carriers. Detailed calculations show a very high energy conversion efficiencies in excess of 75%.

At increased excitation densities we observed a saturation of the photoconductivity, indicating a quenching in the conductivity of the intrinsic dopant carriers. The photoinduced THz bleaching at high excitation densities is comparable to the total THz absorption of the unexcited sample. We also found that saturation occurs at a lower photon density when the photon energy is
high, consistent with our finding of efficient transfer of the photon energy into multiple hot carriers. Additionally, we found that the number of carriers excited at the fluence where the signal saturates corresponds well with the number of dopant carriers. By tuning the Fermi level with a back-gate electrode, we were able to change the population of intrinsic conducting carriers. This resulted in a change not only in the DC conductivity of the graphene as measured with physical electrodes, but also in the THz photoconductivity. The results confirm that the observed negative photoconductivity is caused by the heating of intrinsic conducting carriers in doped graphene.