Photoconductivity of biased graphene

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Graphene is a promising candidate for optoelectronic applications such as photodetectors, terahertz imagers and plasmonic devices. The origin of the photoresponse in graphene junctions has been studied extensively and is attributed to either thermoelectric or photovoltaic effects. In addition, hot carrier transport and carrier multiplication are thought to play an important role. Here, we report the intrinsic photoresponse in biased but otherwise homogeneous graphene. In this classic photoconductivity experiment, the thermoelectric effects are insignificant. Instead, the photovoltaic and a photo-induced bolometric effect dominate the photoresponse. The measured photocurrent displays polarity reversal as it alternates between these two mechanisms in a backgate voltage sweep. Our analysis yields elevated electron and phonon temperatures, with the former an order higher than the latter, shedding light on the understanding of the hot electron-driven photoresponse in graphene and its energy loss pathway via phonons.
in Dirac point amounts to doping by the drain voltage. In the centre of the device this shift with drain voltage (Fig. 3a) is well understood as channel voltage. The systematic shift in the conduction minimum or Dirac change with gate voltage, and a single sign change with drain different as we will see below. It is composed of a twofold sign junction without source–drain bias9,10, but its origin is completely Fig. 3c is reminiscent of the situation in a dual-gated graphene p–n junction without source–drain bias9,10, but its origin is completely different as we will see below. It is composed of a twofold sign change with gate voltage, and a single sign change with drain voltage. The systematic shift in the conduction minimum or Dirac point with drain voltage (Fig. 3a) is well understood as channel doping by the drain voltage. In the centre of the device this shift in Dirac point amounts to $V_D/2$. It leads to a tilt in the near-vertical lines that separate positive and negative photocurrent regions in Fig. 3c, and it manifests itself in the shift in peak photocurrent position in Fig. 3d. The peak photocurrent is thus always associated with the Dirac point voltage. A short-circuit photocurrent on the order of 16 nA is visible near charge neutrality in the $V_D = 0$ V case (Fig. 3d). It also contributes at other drain voltages as a result of residual doping (electron–hole puddles) induced by the fixed laser beam in the centre of the device, which was necessary when sweeping both gate and drain voltages. The residual doping is not observed when the laser beam is continually scanned as in Figs 1 and 2, and we have corrected for this unintentional non-uniform doping in Fig. 3e, where we plot the peak photocurrents. The drain voltage dependence of the peak photocurrent is linear up to voltages on the order of 1 V, above which saturation sets in. Joule heating, which is negligible at $|V_D| = 1$ V, may play a role in the photocurrent saturation at high bias (Supplementary Section SIII).

Several processes of photocurrent generation contribute in biased graphene. The first is the thermoelectric Seebeck effect, in which the laser spot produces a temperature gradient in the device, which together with a doping asymmetry generates a thermoelectric current. Although unbiased homogeneous graphene is not expected to produce a thermoelectric current, the presence of an applied drain voltage renders the electrochemical potential spatially variable, and a thermoelectric effect should ensue even in homogeneous graphene. The second is the photovoltaic effect, where photoexcited electrons and holes are accelerated in opposite directions to produce a thermoelectric current, the presence of an applied laser spot produces a temperature gradient in the device, which together with a doping asymmetry generates a thermoelectric current. Although unbiased homogeneous graphene is not expected to produce a thermoelectric current, the presence of an applied drain voltage renders the electrochemical potential spatially variable, and a thermoelectric effect should ensue even in homogeneous graphene. The second is the photovoltaic effect, where photoexcited electrons and holes are accelerated in opposite directions by an electric field. The carriers produce a photocurrent either by reaching the contacts while still hot or by establishing a local photovoltage within the focal area that couples capacitively to the graphene FET.

**Figure 1 | Photoconductivity (a.c.) of graphene with and without bias.** a, Schematic of the photoconductivity measurement set-up with a laser wavelength of $\lambda = 690$ nm, laser power of $P = 220 \mu W$, spot diameter of $d \approx 700$ nm, and chopping frequency of $f = 1.1$ kHz. b, Photocurrent (a.c.) at $V_D = 0$ V drain bias (short-circuit photocurrent) and $V_G = 5$ V gate bias (n-type regime). Left: the laser-scanning image shows the source and drain electrodes. The outline of the graphene sheet is indicated. Middle: amplitude $R$ of the photocurrent. Right: phase $\varphi$ of the photocurrent. A localized photocurrent is generated close to the contacts. The phases at source and drain contacts are $\varphi \approx 180^\circ$ (corresponding to negative $I_{ph}$) and $\varphi \approx 0^\circ$ (positive $I_{ph}$), respectively. c, Photocurrent (a.c.) under a drain bias of $V_D = -1$ V and gate voltage of $V_G = 5$ V. Laser scanning, amplitude and phase images are shown. The entire graphene channel is producing a photocurrent under applied bias, and the photocurrent is uniform in both amplitude ($R \approx 46$ nA) and phase ($\varphi \approx 180^\circ$) throughout the channel except for the contact regions. The small photocurrent generated next to the graphene channel is in response to a photovoltage at the Si/SiO$_2$ interface that couples capacitively to the graphene FET.
the rest of the device\textsuperscript{8}. The third is the bolometric effect, where the incident electromagnetic radiation raises the local temperature of the graphene, which alters the resistance of the device, producing a change in d.c. current under bias. Figure 4 summarizes the relative magnitude and signs of these effects in non-biased and biased graphene photodetectors. In the following we will discuss these effects in greater detail.

It is instructive to first review the thermoelectric effect in a p–n junction at zero bias\textsuperscript{6,8,10}. Figure 4a illustrates the experimental situation in a p–n junction, where the laser spot induces a temperature gradient $dT/dx$ and results in a net thermoelectric voltage across the graphene due to the Seebeck effect. The generated photocurrent is proportional to $(S_2 - S_1)dT/dx$, where $S_{1/2}$ is the Seebeck coefficient for the two sides of the junction. The sign of the thermoelectric photocurrent is the same as that of the photovoltaic effect, except for in some unipolar junction regimes such as $pp^+$ or $nn^-$, where the thermoelectric current can be reversed\textsuperscript{10}.

When the graphene doping is homogeneous, the photocurrent will be zero. However, the uniform doping can be rendered asymmetric under an applied drain bias, such that the effective doping along the graphene channel changes gradually. This doping asymmetry and the associated Seebeck effect are more prominent at low doping. Typical energy band profiles are illustrated in Fig. 4b,c together with the sign of the various photocurrents relevant in our experiments. Figure 4d illustrates the respective biasing conditions. Near the charge neutrality point, the thermoelectric effect registers a photocurrent opposite in sign to both the experimentally measured photocurrent and the expected photovoltaic current. This makes it possible to directly differentiate between the thermoelectric and photovoltaic effects near the Dirac point. Because the Seebeck coefficient $S$ is related to the electrical conductivity $\sigma$ via the Mott formula

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{1}{\sigma} \frac{d\sigma}{dE}$$

application of thermoelectric theory yields an estimate of a thermoelectric photocurrent of $\sim 4\, nA$ near the Dirac point (Supplementary Section SV), opposite and an order of magnitude smaller than the expected photovoltaic current.

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**Figure 2** | Photocurrent (a.c.) as a function of gate voltage. a, Spatial images of the photocurrent amplitude and phase as a function of gate voltage (drain voltage $V_D = -1\, V$; laser power $P = 370\, \mu W$). The photocurrent in the graphene channel switches sign twice from negative ($\phi = 180^\circ$) to positive ($\phi = 0^\circ$) and back to negative ($\phi = 180^\circ$). b, Photocurrent amplitude (red) and phase (blue) in the centre of the graphene channel as a function of gate voltage. The sign of the photocurrent is indicated. For comparison, the d.c. current flowing out of the source has positive sign for $V_D = -1\, V$. c, Photocurrent (red) corrected for the photo field effect (Supplementary Section SI) and source–drain current (black) as a function of gate voltage.
smaller than that observed in experiments. Away from the Dirac point, the thermoelectric effect is expected to be even less important because the electrochemical potential asymmetry is reduced with increasing Fermi level.

We next consider the bolometric response of the graphene photodetector, which can only be observed in biased devices and was therefore absent in previous short-circuit measurements on graphene contacts or junctions\textsuperscript{2–10}. The bolometric effect can be determined by measurement of the temperature dependence of the transport current. Figure 5a shows the change in transport current \( T \) around room temperature\textsuperscript{21–23}. A similar measurement around our lowest temperature of \( 205 \text{ K} \) yields the other curve for the temperature coefficient in Fig. 5b. The negative values of \( \beta(V_{G}) \) in single-layer graphene are due to electron–acoustic phonon scattering and electron–remote phonon scattering of surface polar phonons in the \( \text{SiO}_2 \) underlayer, both of which are enhanced at elevated temperatures\textsuperscript{24}. For comparison, Fig. 5c shows the experimental photocurrents at room temperature and \( T_0 = 205 \text{ K} \). The similar shapes of the curves in Fig. 5b,c are striking. In particular, both the bolometric coefficient and the photocurrent are largest (and negative) at high doping and the electron–hole asymmetry of the temperature coefficient is reproduced in the photocurrent measurement. Although the bolometric effect can explain these general features of the gate voltage dependence of the photocurrent, it cannot explain the positive photocurrent in the direction of the d.c. current under conditions of low doping.

The photovoltaic effect is the only known mechanism that is consistent with the positive photoresponse near the Dirac point seen experimentally. Under light excitation, the hot carriers with separated electron and hole chemical potentials are formed on a timescale of the order of \( 100 \text{ fs} \), followed by a slow picosecond carrier recombination and cooling\textsuperscript{11–15,17}. At steady state, the photo-induced carrier density \( n_e^* \) depends on its non-equilibrium carrier temperature \( T_e \) and the chemical potential and has to be determined by imposing charge conservation, that is, \( n_e^* = n_h^* \). In addition, \( T_e \) has its maximum at the focal spot and is proportional to \( QL/k_\text{B} \), where \( Q \) is the laser power, \( L \) is the device length, and \( k_\text{B} \) is the electronic thermal conductivity (related to the electronic conductivity through the Wiedemann–Franz relation). Making use of the above facts allows us to compute the gate-dependent photo-induced carrier densities \( n_e^* \) (Supplementary Section SVI). The photovoltaic current can then be estimated from \( qn_e^*eF \), where \( e \) is the electric field and \( \mu \approx 2,700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) is the carrier mobility of our device. In general, the non-equilibrium \( n_e^* \) values decrease with increasing equilibrium doping, consistent with electron–electron scattering, which increases with doping. Hence, the modelled photovoltaic current as shown in Fig. 5c decreases gradually with increasing bias away from the charge neutrality point. Near the Dirac point, the elevated electron temperatures of \( T_e = T_h - T_0 \approx 8 \text{ K} \) and \( 12 \text{ K} \) at initial temperatures \( T_0 = 300 \text{ K} \).
and 200 K, respectively, as shown in Fig. 5d; these also decrease with increasing equilibrium doping. The estimated electronic temperatures are lower bounds, because we neglect the small thermoelectric component of the photocurrent, which points in the opposite direction.

We next subtract the estimated photovoltaic current component from our experimentally measured photocurrent to obtain the purely bolometric contribution \( I_{\text{BOL}} \). The elevated lattice temperature \( T_1 = T_\text{ph} - T_\text{e} \) can then be determined from the ratio \( I_{\text{BOL}}/\beta \), where \( \beta \) is the experimentally determined bolometric coefficient (Fig. 5b) discussed earlier. As shown in Fig. 5d, \( T_1 \) is of the order of 1 K and is weakly dependent on doping. Both \( T_1 \) and \( T_2 \) are enhanced at lower temperatures as a result of less efficient heat flow. Although electron–electron interactions result in energy equilibration of the electronic system, they do not lead to a net energy loss. The dominant energy loss pathways are due to phonons. Intrinsic energy loss channels due to acoustic/optical phonons are known to be inefficient energy loss pathways and have a power density of only \( Q_0 \approx 10^2 - 10^4 \text{ W m}^{-2} \) for \( T_1 - T_0 \approx 10 \text{ K} \) (Supplementary Section SVII)\(^{13,24} \). However, with a typical graphene–substrate thermal resistance of \( r_{\text{tg}} \approx 1 \times 10^{-7} \text{ km}^2 \text{ W}^{-1} \) (refs 25,26), our measured lattice temperature suggests a lattice heating power density of the order of \( Q_0 = T_1/r_{\text{tg}} \approx 1 \times 10^6 \text{ W m}^{-2} \) or somewhat lower, because of the uncertainty in the temperature at the Si/SiO\(_2\) interface after photoexcitation. The inferred larger power density in experiments may indicate the presence of more efficient electron energy loss pathways in graphene devices. Electron–remote phonon scattering of surface polar phonons in the SiO\(_2\) underlayer\(^{27-30} \), and extrinsically enhanced graphene phonon-scattering processes mediated by ionized impurity and random strain-induced gauge fields\(^{31} \), may provide these additional decay pathways. More systematic studies in this regard are needed to clearly identify the energy dissipation mechanisms in graphene, but it is clear from our measurements, that lattice heating is more efficient than expected from refs 9,10, even though electrons are a factor of 10 hotter than the lattice.

The responsivity of our graphene photodetector (on the order of \( 2.5 \times 10^{-4} \text{ A W}^{-1} \) for 1 V bias) is on par with those reported for graphene p–n junctions\(^{5-10} \). However, because the entire graphene channel is photosensitive, our device offers real-world advantages. In addition, several techniques to enhance graphene photodetection have been reported within the last year. First, photodetection in single-layer graphene is mainly limited by the small light absorption coefficient of a few percent. However, plasmonic structures can greatly enhance the absorption coefficient, approaching total light absorption\(^{32} \). Indeed, advances in this direction have recently been demonstrated\(^{33,34} \). Second, single-layer graphene has a limited temperature dependence due to the vanishing bandgap. The temperature sensitivity can be enhanced by either opening a bandgap in bilayer graphene, or by utilizing superconducting contacts that act as tunnel junctions. Two papers detailing these approaches have just been posted\(^ {19,20} \). These recent developments clearly demonstrate the rapid advancement in the optoelectronics device technology arena and the potentials for significant device improvements.

In conclusion, our measurement and theory of the intrinsic photoconductivity of biased graphene show that both bolometric and photovoltaic effects are relevant, and we have demonstrated in detail that operating conditions determine which photocurrent generation mechanism becomes dominant in graphene. The polarity and magnitude of the photocurrent can be modulated by electrostatic doping, which upon examination allows us to probe the non-equilibrium hot carrier and phonon characteristics. Our work therefore opens up the possibility of engineering the hot carrier photoresponse, which plays an essential role in applications such as bolometers, calorimeters and photodetectors.
Methods

Graphene FETs were fabricated by mechanical exfoliation from graphite. Electron-beam lithography and evaporation of 15 nm of titanium/gold were used to create the contacts. A second electron-beam lithography step and plasma etching defined rectangular graphene sheets (length, 6 μm; width, 1 μm). Single-layer graphene was identified by its optical contrast on the 90 nm SiO2 dielectric. We used a highly doped (n-type) silicon substrate to avoid an excessive photo field effect, annealing and laser scanning with a green laser for an hour. After this treatment, the as-prepared samples behaved in a p-type manner. To render them intrinsic, enhance mobility and reduce hysteresis, the samples were evacuated for a few days before the measurements and subjected to a combination of current annealing and laser scanning with a green laser for an hour. The laser spot diameter on the sample was d ≈ 690 nm. The laser power values are given in the figure captions. Considering the electric-field enhancement due to the gate stack, we estimate that 2.5% of the incident light was absorbed in the graphene. The photocurrent amplitudes reported in this Article are due to the gate stack, we estimate that 2.5% of the incident light was absorbed in the graphene. The photocurrent amplitudes reported in this Article are

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Figure 5 | Magnitude of bolometric and photovoltaic effects and determination of the hot electron and lattice temperatures. a. Temperature-dependent change in current from its room temperature (T0 = 299 K) value as a function of gate voltage. Inset: gate voltage characteristic as a function of temperature when cooling down from room temperature. b. Bolometric coefficient β(VG) = ΔIG/ΔVG of the transport current as a function of gate voltage at two different ambient temperatures T0. c. Experimental photocurrent (PC, corrected for the photo field effect) and modelled photovoltage component of the photocurrent. The photovoltaic (PV) component is important only near charge neutrality where it determines the sign of the overall photocurrent. Away from the Dirac point, the bolometric effect (b) dominates. d. Electron (Te) and lattice (TL) temperatures extracted from the data as detailed in the text.
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Author contributions
All authors discussed the results and commented on the manuscript.

Additional information
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Competing financial interests
The authors declare no competing financial interests.