We observe photocurrents induced in single layer graphene samples by illumination of the graphene edges with circularly polarized terahertz radiation at normal incidence. The photocurrent flows along the sample edges and forms a vortex. Its winding direction reverses by switching the light helicity from left- to right-handed. We demonstrate that the photocurrent stems from the sample edges, which reduce the spatial symmetry and result in an asymmetric scattering of carriers driven by the radiation electric field. The developed theory is in a good agreement with the experiment. We show that the edge photocurrents can be applied for determination of the conductivity type and the momentum scattering time of the charge carriers in the graphene edge vicinity.

PACS numbers: 73.50.Pz, 72.80.Vp, 81.05.ue, 78.67.Wj

The “bulk” transport properties of graphene have been studied intensively in recent years and yielded insight into the half-integer and fractional quantum Hall effect, phase-coherent effects or spin transport on the micrometer scale, to name a few examples [1, 2]. While the details of each of those effects depend crucially on the linear dispersion relation of graphene and its specific material properties, most of the transport phenomena have already been studied in other two-dimensional systems. Graphene edges, on the other hand, were predicted to show insulating or metallic, even magnetic behavior, depending on the crystallographic orientation and edge chemistry. In scanning tunneling experiments, an enhanced edge density of states was shown [3, 4] and Raman scattering experiments provided evidence for the dependence of scattering mechanisms on the edge orientation [5, 6]. In transport experiments edge effects are usually masked by bulk properties, nonetheless the graphene edges are expected to play a crucial role in the electronic properties of graphene-based nanoscale devices.

Here, we present an opto-electronic method to uniquely distinguish edge from bulk scattering by exploring edge photocurrents in graphene samples illuminated by terahertz (THz) radiation. For circularly polarized light the edge current is observed to form a vortex winding around the edges of the square-shaped samples. Its direction reverses upon switching the radiation helicity from left- to right-handed. Evidently, the photocurrent is caused by the local symmetry breaking at the sample edges resulting in an asymmetric scattering of carriers driven by the radiation electric field. It gives rise to a directed electric current along the sample boundary in a narrow stripe of width comparable to the mean free path. We show that the photocurrent measurements provide direct access to electron scattering at the graphene edges and allow to map the variation of scattering times along the edges.

We investigated two types of single-layer graphene samples: (i) large-area epitaxial graphene prepared by high-temperature Si sublimation of 4H and 6H polytypes of semi-insulating SiC substrates [7,8] and (ii) small area exfoliated graphene flakes [9] deposited on oxidized silicon wafers. Below, we report results on epitaxial graphene samples (labeled #1-4H, #2-4H, and #3-6H) and three samples prepared from exfoliated graphene. Hall measurements indicate that the epitaxial samples are n-doped (due to charge transfer from SiC) while the exfoliated samples are p-doped. The measured carrier density lies in the range $(2 \div 7) \times 10^{12} \text{cm}^{-2}$, the Fermi
energy $E_F$ ranges from 200 to 300 meV and the mobility is about 1000 cm$^2$/Vs at room temperature. Ohmic contacts were made at samples’ edges (see, e.g., inset of Fig. 1). Details on the material growth and characterization can be found in [10].

The experiments on edge photocurrents are performed applying alternating electric THz fields of a high power pulsed NH$_3$ laser operating at wavelengths $\lambda = 90.5$ µm, 148 µm or 280 µm (frequencies $f = 3.3$ THz, 2 THz and 1.1 THz, respectively). The radiation induces indirect (Drude-like) optical transitions, because the photon energies are much smaller than the carrier Fermi energy. The NH$_3$ laser generates single pulses with a duration of about 100 ns, peak power of $P \approx 10$ kW, and a repetition rate of 1 Hz. A typical spot diameter from 1 to 3 mm. The beam has an almost Gaussian form, which is measured by a pyroelectric camera [14].

All experiments are performed at normal incidence of light and at room temperature. Elliptically and, in particular, circularly polarized radiation is obtained applying $\lambda/4$ quartz plates. The resulting polarization state described by the Stokes parameters $S_1$, $S_2$, and $S_3 \equiv P_{\text{circ}}$ is directly related to the angle $\varphi$ between the initial linear polarization of the laser light along the $y$-axis and the plate optical axis. The experimental geometry is shown in Figs. 1 and 2. The current is measured via the voltage drop across a 50 Ω load resistor.

Illumination of the edge of unbiased large-area samples between any pair of contacts results in a photocurrent. By contrast, if the laser spot is moved toward the center the signal vanishes. The detected signal depends strongly on the radiation polarization, Fig. 1. The principal observation is that for right- ($\sigma_+$) and left-handed ($\sigma_-$) polarizations, respectively. Numbers indicate the photocurrent amplitude $J_A$ in microamperes.

FIG. 2: Photocurrent $J_A$ in sample #1-4H as a function of the laser spot position. The laser spot is scanned along $y$ and the current is picked up from two contact pairs at the top (red circles) or bottom (blue full circles) sample edges aligned along $x$ (see inset). Dashed lines represent the laser beam spatial distribution, which is measured by a pyroelectric camera, scaled to the current maximum. The bottom inset shows the scan for sample #3-6H.

FIG. 3: (a) Experimental geometry for the study of edge photocurrents. (b) Schematic illustration of the edge current generation. The electric field of circularly polarized radiation rotates clockwise or counterclockwise resulting in a circular motion of carriers, which is sketched by red and blue trajectories, respectively. Our theoretical model, see Eq. (7), shows that the circular edge current stems from carriers moving towards the edge. It is due to the second order $E$-field correction to the distribution function and involves the retardation of the electron motion with respect to the instantaneous electric field. Switching the radiation helicity reverses the motion direction and, consequently, the electric current. (c) and (d) photocurrent topology. Red and blue arrows show the current direction for $\sigma_+$ and $\sigma_-$ polarizations, respectively. Numbers indicate the photocurrent amplitude $J_A$ in microampere.
luminous behavior of the circular edge photocurrent: pairs are shown in Fig. 3b and 3c. The figures document \( \sigma \) respectively. Lines are fits to Eq. (7). The fitting parameters \( \tau/10^{-14} \text{s} \) for sample #1-4H and #2-4H are indicated by numbers. The inset shows the measured circular photocurrent \( J_A \) (open circles) together with the fit after Eq. (7). Data point measured at 2 THz for different \( \lambda \text{A} \) -axis. The signal was picked up independently recorded laser profile (dotted line) shows change of the system, in our case, due to the edges. Also note that the typical photon energy \( h\omega \sim 10 \text{eV} \) used in experiment is much smaller than the characteristic energy of carriers \( E_F \sim 100 \text{meV} \). Thus, the mechanism of current formation can be treated classically and should involve the action of the light’s electric field on free carriers in the vicinity of a graphene edge.

A microscopic process actuating the edge photocurrent generation is illustrated in Fig. 3b. It involves the time dependent motion of carriers under the action of the electric field of circularly polarized radiation and scattering at the sample edge. We note that this mechanism is similar to that of the surface photogalvanic effect observed in bulk materials [17, 18].

A microscopic theory of edge currents is developed in the framework of the Boltzmann kinetic equation. In this approach, the electron (hole) distribution is described by the function \( f(p, x, t) \). It depends on the carrier momentum \( p \), coordinate \( x \) (\( x \geq 0 \) for a semi-infinite layer), time \( t \), and obeys the equation

\[
\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + qE(t) \frac{\partial f}{\partial p} = Q\{f\},
\]

where \( E(t) = E_0 e^{-i\omega t} + E_0^* e^{+i\omega t} \) is the electric field of the radiation, \( v = vp/p \) is the electron velocity, \( v \approx 10^6 \text{m/s} \) is the effective speed, \( q \) is the carrier charge (\( q = +|e| \) for holes and \( -|e| \) for electrons), and \( Q\{f\} \) is the collision integral. The distribution function can be expanded in series of powers of the electric field,

\[
f(p, x, t) = f_0(\varepsilon_p) + [f_1(p, x)e^{-i\omega t} + \text{c.c.}] + f_2(p, x) + \ldots,
\]

where \( f_0(\varepsilon_p) \) is the equilibrium distribution function with \( \varepsilon_p = vp \) being the electron energy, \( f_1 \propto |E| \), and \( f_2 \propto |E|^2 \). The first order in \( E \) correction to the distribution function oscillates with frequency \( \omega \) and does not contribute to a dc current. The directed electric current along the structure edge is, therefore, determined by the second order \( E \)-field correction \( f_2 \) and given by

\[
J_y = 4q \int_0^\infty dz \sum_p f_2(p, x)v_y.
\]

The factor 4 accounts for the spin and valley degeneracy.
We solve Eq. (2) and calculate the current, Eq. (4), for the simple form of the collision integral,

\[ Q \{ f(p, x, t) \} = \frac{f(p, x, t) - f_0(\varepsilon_p)}{\tau}, \]

with \( \tau \) being the scattering time, and the boundary condition at \( x = 0 \),

\[ f(p_x > 0, p_y, 0, t) = -\int \frac{\nu'_y}{2p_f} f(p', 0, t) \delta(\varepsilon_p - \varepsilon_{p'}) \Theta(-\nu'_{y}) dp', \]

(6)

corresponding to diffusive scattering. In the case of a degenerate gas, the edge current takes the form (see [10] for details):

\[ J_y = -\frac{q^3 \tau^3 \nu^2}{2\pi \hbar^2[1 + (\omega \tau)^2]} \left[ \frac{10}{3} \frac{\omega \tau}{1 + (\omega \tau)^2} i[E_0 \times E_0^*]_z + \left( 1 + \frac{7}{6} \frac{1 - (\omega \tau)^2}{1 + (\omega \tau)^2} \right) \times (E_{0,x} E_{0,y}^* + E_{0,y} E_{0,x}^*) \right]. \]

(7)

The helicity-driven current is given by the first term because \( i[E_0 \times E_0^*]_z \equiv -P_{\text{circ}} \) for our geometry where the light propagates along \( -z \). The second term yields the current caused by linearly polarized radiation and vanishes for circular polarization. In the case of elliptically polarized light, \( E_{0,x} E_{0,y}^* + E_{0,y} E_{0,x}^* \propto (1/2) \sin 4\varphi = S_2 \). Both contributions are clearly detected in the experiment and correspond to the first (\( \propto J_A \)) and second (\( \propto J_B \)) terms in the empirical Eq. (1), see Fig. 1.

The helicity driven photocurrent described by Eq. (7) vanishes for zero frequency, has a maximum at \( \omega \tau \approx 0.6 \) and decreases rapidly at higher frequencies. Exactly this behavior is found in experiment (see inset of Fig. 4) as we explain in more detail below. The only free parameter in Eq. (7) is the scattering time \( \tau \). Corresponding data are shown in Fig. 3 where the photocurrent values measured at 2 THz for each of the contact pairs are plotted. These data points are first compared to calculated traces of \( J_A \) employing Eq. (7). Solid lines are calculated using the bulk values for the time \( \tau \) extracted from resistivity and carrier density for samples #1-4H (\( \tau = 2.0 \times 10^{-14} \) s) and #2-4H (\( \tau = 2.8 \times 10^{-14} \) s). The bulk scattering times used in Eq. (7) give for some of the contact pairs already perfect quantitative agreement. For other edge segments the current deviates significantly. This is a consequence of the strongly non-linear dependence of \( J_A \) on \( \tau \). Varying \( \tau \) by only \( \pm 15\% \) changes the current by \( \pm 50\% \). By fitting the photocurrent \( J_A \) we can extract the local scattering time \( \tau \) for every edge segment shown in Figs. 3c and d). The best fits are shown by dashed lines in Fig. 4 and constitute a map of scattering times along the edge. The average value of the circular edge current scales with the sample mobility. To check the frequency dependence predicted by Eq. (7) we show in the inset of Fig. 4 \( J_A \) vs. \( \omega \tau \) for one edge segment using the extracted \( \tau \). The data points are perfectly described by Eq. (7) and confirm the model.

While the magnitude of the circular edge photocurrent agrees well with theory, the expected polarity of \( J_A \) for \( n \)-type graphene is opposite to the one observed. This, at first glance, surprising result agrees with results from spatially resolved Raman measurements demonstrating that edges of \( n \)-type graphene layers exhibit \( p \)-type conductivity [1-4]. This explains the sign of the photocurrent, which is generated in a narrow edge channel comparable to the mean free path (\( \approx 10 \div 20 \) nm) and has opposite sign for electrons and holes, see Eq. (4). Actually, the difference in the conductivity type can be also understood from the details of the sample fabrication. It is well established that epitaxial graphene on SiC(0001) is \( n \)-doped due to charge transfer from the interfacial buffer layer (see, e.g., [5, 6]), while so-called quasi-free-standing graphene, lacking such buffer layer and sitting on a hydrogen terminated SiC(0001) surface, is \( p \)-doped [19]. Therefore, it is reasonable that the edges of epitaxial graphene, exposed to the SiC substrate without the interfacial layer, can be \( p \)-doped. This assumption is corroborated by similar reports on the transition from \( n \)-to \( p \)-type of doping at the edges of graphene flakes on SiO\(_2\), which were attributed to the difference in the work functions of graphene and the substrate [21].

To summarize, our observations clearly demonstrate that illuminating monolayer graphene edges with polarized terahertz radiation at normal incidence results in a directed electric edge current. The effect is directly coupled to electron scattering at the graphene edge and vanishes in bulk graphene. Our results suggest that circular the photocurrents can be effectively used to study edge transport in graphene even at room temperature.

We thank K. S. Novoselov, V. Lechner, S. Heydrich and V. V. Bel’kov for fruitful discussions. Support from DFG (SPP 1459 and GRK 1570), EU-ConceptGraphene, Linkage Grant of IB of BMBF at DLR, RFBR, Russian Ministry of Education and Sciences, and “Dynasty” Foundation–ICFPM is acknowledged.
SUPPLEMENTAL MATERIAL

S1. Details of the Samples

We investigated three epitaxial samples grown on SiC. Samples #1-4H and #2-4H were grown by the Linköping group on a Si-terminated surface of a 4H-SiC(0001) semi-insulating substrate (Cree Inc.) [8]. The reaction kinetics on the Si-terminated surface is slower than on the C-face because of the higher surface energy, which fosters homogeneous and well controlled graphene formation [2]. Graphene was grown at a temperature of 2000°C and 1 atm Ar gas pressure resulting in monolayers of graphene atomically uniform over more than 1000 μm², as shown by low-energy electron microscopy [21]. Eight contacts were produced by depositing 3 nm of Ti and 100 nm of Au. The quadratic sample size of 5 × 5 mm² was achieved by oxygen plasma etching of all four edges. Hall measurements indicate that the large area samples are n-doped due to charge transfer from SiC [7, 8, 22–25]. The measured carrier concentration is between 3 × 10¹² cm⁻² and 7 × 10¹² cm⁻², the Fermi energy $E_F$ ranges from 200 to 300 meV and the mobility is about 1000 cm²/Vs at room temperature. In these samples, as well as in other large-area samples, the resistance at room temperature is about 2 to 5 kΩ.

The third epitaxial graphene sample #3-6H, was grown by the Erlangen group on 6H-SiC(0001) wafers (II-VI Inc.). Graphene growth was performed using sublimation growth in Ar atmosphere [2, 3]. First, polishing damage was removed by etching the substrate in 1 bar hydrogen at 1550°C for 15 min. Second, graphene was grown by annealing the sample in 1 bar Ar at a temperature of 1650°C for 15 min. The graphene coverage was determined by x-ray photoelectron spectroscopy (XPS). The square-shaped sample size of 4 × 4 mm² was achieved by mechanical cutting the edges. Both, carrier density and mobility in the n-type sample #3-6H are very similar to those of the Linköping samples.

For all epitaxial graphene samples, low-temperature quantum Hall measurements reveal the high quality and homogeneity.

The exfoliated graphene samples (small-area graphene samples 4, 5, and 6) has been prepared from natural graphite using the mechanical exfoliation technique [1] on an oxidized silicon wafer. The oxide thickness of 300 nm allowed to locate graphene flakes in an optical microscope and to assess their thickness. We checked the reliability of this method using Raman spectroscopy and low-temperature quantum Hall measurements on similar samples [26]. The single layer graphene flakes obtained by this method were typically p-doped by adsorbed contaminants with carrier concentrations $p \leq 2 \times 10^{12}$ cm⁻². The Fermi energies were $E_F \leq 165$ meV and the mobilities at room temperature of the order of 2.5 × 10³ cm²/Vs. The flakes included in this study were all single layer with the flakes size of the order of 10 to 30 micrometers. The sample morphology was characterized by atomic force microscopy measurements under ambient conditions with the microscope in intermittent contact mode with standard silicon tips [27]. After recording the position of the flakes with respect to predefined markers, we contacted them by electron beam lithography and thermal evaporation of 60 nm Pd electrodes. The resistance of graphene measured between various contacts was about 1 to 3 kΩ.

S2. Laser beam parameters

In addition to the pulsed THz laser described in the main text, we also used a continuous-wave (cw) CH₃OH laser ($\lambda = 118$ μm) with a power of $P \approx 20$ mW. In the experiments applying the CH₃OH laser, the cw radiation was modulated at chopper frequencies in the range from 120 to 600 Hz. The sign of the signal is defined as a relative phase with respect to the lock-in reference signal, which was kept the same for all measurements.

Elliptically and, in particular, circularly polarized radiation has been obtained by transmitting the laser beam, which is initially linearly polarized along the y-direction for the pulsed laser and along the x-direction for the cw laser, through $\lambda/4$ crystal quartz plates. The resulting polarization state is directly related to the angle $\varphi$ between the initial linear polarization of the laser light and the optical axis of the plate. It is described by the Stokes parameters $S_1, S_2, S_3$ [15]. In particular, the dependence of the circular polarization degree, given by $S_3$, on the angle $\varphi$ in our experimental geometry has the form

$$P_{\text{circ}} \equiv S_3(\varphi) = \sin 2 \varphi.$$  (8)

The parameters $S_1$ and $S_2$ are given by the bilinear combinations of the polarization vector components,

$$S_1(\varphi) \equiv |e_x|^2 - |e_y|^2 = - \cos^2 2 \varphi,$$

$$S_2(\varphi) \equiv e_x e_y^* + e_y e_x^* = \frac{1}{2} \sin 4 \varphi.$$  (9)

The parameters $S_1$ and $S_2$ describe the degree of linear polarization in the coordinate axes $x, y$ and in the coordinate frame rotated about an angle of 45°, respectively [15]. Note that radiation is incident along $-z$ axis. The resulting polarization ellipses for the cw THz laser for some angles $\varphi$ are sketched on top of Fig. 5. Further details on the experimental technique can be found in Ref. [28].

S3. Photocurrents in small-area samples

Helicity driven photocurrents excited at normal incidence have also been observed in small-area graphene...
with the boundary condition (6) has the form
\[ f_1(p, x) = -\frac{q\tau f_0}{1 - i\omega\tau} \left[ E_0 \cdot v - \left( E_0 \cdot v + \frac{\pi i}{4} E_{0,x} v \right) \exp \left( -\frac{1 - i\omega\tau}{v_x \tau} \right) \right] \Theta (v_x), \]
where \( f_0 = df_0(x)/dx \). The equation for the second-order correction \( f_2(p, x) \) is given by
\[ v_x \frac{\partial f_2(p, x)}{\partial x} + 2q\Re \left[ E_0 \frac{\partial f_1(p, x)}{\partial p} \right] = -\frac{f_2(p, x)}{\tau}, \]
which yields
\[ \int_0^\infty f_2(p, x) dx = v_x \tau \left[ f_2(k, 0) - f_2(k, \infty) \right] - 2q \int_0^\infty \Re \left[ E_0 \frac{f_1(p, x)}{d^p} \right] dx. \]
By using Eq. (4) for the edge electric current and Eq. (10) we derive
\[ J_y = -8q^3 \tau^3 \sum_p \Re \left\{ \frac{v_y v_x E_0^*_x d[E_0 \cdot v]}{1 - i\omega\tau} \right\} \Theta (v_x), \]
where the above two contributions to the current stem from the first and second terms on the right-hand side of Eq. (13), respectively. Finally, taking into account that the electron energy and velocity in graphene are given by \( \varepsilon_p = v|p| \) and \( v = v p/p \), respectively, and assuming that the electron gas is degenerate and \( \tau \) is independent of \( \varepsilon_p \), we obtain Eq. (7) of the main text.

The current Eq. (7) of the main text is consistent with the point-group symmetry \( C_s \) containing the mirror plane \((x, z)\). It should be noted that for elliptical polarization, in some experiments the photocurrent described by Eq. (7) is superimposed with an additional contribution proportional to \( \cos^2 \theta \) [see the third term in Eq. (10)]. This term can be attributed to a lowering of the system symmetry to \( C_1 \) showing the non-equivalence of \( y \) and \(-y\) directions, e.g., due to (i) inhomogeneous photoexcitation, (ii) macroscopic roughness of the investigated edges, (iii) non-equivalence of contacts, etc. The symmetry reduction hinders the edge photogalvanic currents under study and complicates their analysis. However, the obstacle can be easily overcome applying circularly polarized radiation, like used in the present work. Indeed, as addressed above the edge currents driven by circularly polarized light change their signs upon variation of the radiation helicity. By contrast, other current contributions caused by the additional symmetry lowering are insensitive to the radiation helicity and vanish for circularly polarized radiation.

S4. Theory

Equation (7) of the main text is obtained by expanding the distribution function \( f(p, x, t) \) in series of the electric field. To first order in the electric field, solution of Eq. (2)
[1] K. S. Novoselov et al., Science 306, 666 (2004).
[2] S. Das Sarma et al., Rev. Mod. Phys. 83, 407 (2011).
[3] Y. Nimi, et al. Phys. Rev. B 73, 085421 (2006).
[4] K. A. Ritter and J. W. Lyding Nature Mat. 8, 235 (2009).
[5] C. Casiraghi et al., Nano Lett. 9, 1433 (2009).
[6] S. Heydrich et al., Appl. Phys. Lett. 97, 043113 (2010).
[7] K. V. Emtesev et al., Nature Mat. 8, 203 (2009).
[8] A. Tzalenchuk et al., Nature Nanotech. 5, 186 (2010).
[9] M. Ostler et al., Phys. Stat. Sol. B 247, 2924 (2010).
[10] See Supplemental Material.
[11] S. D. Ganichev, S. A. Emel’yanov, and I. D. Yaroshetskii, JETP Lett. 35, 368 (1982).
[12] S. D. Ganichev et al., Phys. Rev. Lett. 80, 2409 (1998).
[13] S. D. Ganichev and W. Prettl, Intense Terahertz Excitation of Semiconductors (Oxford Univ. Press, 2006).
[14] E. Ziemann et al., J. Appl. Phys. 87, 3843 (2000).
[15] B. E. A. Saleh and M. C. Teich, Fundamentals of Photonics (John Wiley & Sons, Inc., 2007).
[16] J. Karch et al., Phys. Rev. Lett. 97, 182107 (2010).
[17] L. I. Magarill and M. V. Entin, Phys. Solid State 21, 743 (1979).
[18] V. L. Alperovich et al., JETP Lett. 31, 547 (1980).
[19] F. Speck et al., arXiv:1103.399v1.
[20] E. J. H Lee et al., Nature Nano. 3, 486 (2008).
[21] C. Virojanadara et al., Phys. Rev. B 78, 245403 (2008).
[22] A. Bostwick et al., Nature Phys. 3, 36 (2007).
[23] T. Ohta et al., Phys. Rev. Lett. 98, 206802 (2007).
[24] K. V. Emtelev et al., Phys. Rev. B. 77, 155303 (2008).
[25] S. Kopylov et al., Appl. Phys. Lett. 97, 112109 (2010).
[26] J. Eroms and D. Weiss, New J. Phys. 11, 095021 (2009).
[27] U. Stöberl et al., Appl. Phys. Lett. 93, 051906 (2008).
[28] W. Weber et al., Phys. Rev. B 77, 245304 (2008).