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Photoinduced doping in heterostructures of graphene and boron nitride

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1. Determination of charge carrier mobilities and charge density fluctuations

To quantitatively study the effect of photo-doping on the electrical properties of the device we extracted the charge density fluctuation δn at the CNP, and the charge carrier mobility μ for each curve from Fig. 2a. Representative fits for these quantities are shown in Supplementary Fig. 1. For the μ of both carrier types we fit equation S1 on the electron and hole sides of the $G(n)$ curve.

$$G = \frac{W}{L}\left({\sigma_s}^{-1} + (n\, e\, \mu + \sigma_o)^{-1}\right)^{-1} \qquad \text{S1}^{1}$$

Here G is the conductance of graphene, W and L are the width and length of the graphene channel obtained from optical micrographs, n is the electrostatically induced carrier density that we acquire from the geometric capacitance between the graphene/h-BN and the silicon gate, e is the charge of an electron, μ is the carrier mobility, σ_o is the conductivity at the CNP, and σ_s is the charge density independent conductivity due to short-range scattering. The fits provide both μ and σ_s and were performed for Δn~10^{12} cm^{-2}as can be seen in Supplementary Fig. 1a. To extract the δn from our data we performed a Lorentzian fit of each $R(V_g)$ curve and acquired the full width at half maximum (FWHM). As shown in Supplementary Fig. 1b (black trace is the fit) we choose our starting and ending points at R~ 1kΩ.

2. Transport properties of graphene/BN device as a function of exposure time

The transport behavior of our devices has a strong dependence on the exposure time, as shown in Supplementary Fig. 2a. Here we measure $R(V_g)$ while exposing the device to a weak light at 500nm with V_g=-36V. The red trace corresponds to no exposure, yellow trace to one minute, green trace to 20 minutes and blue trace to 40 minutes of exposure to light. Notably, the $R(V_g)$ curves are distinct from one another. After one minute of exposure the $R(V_g)$ becomes much broader than before and the peak position shifts by ~-28V. With further exposure the $R(V_g)$ curve becomes sharper and the peak shifts closer to V_g=-36V. After 40 minutes of exposure $R(V_g)$ is stabilized and does not change significantly.

To gain insight into the effect of exposure time on the device transport properties we extract δn at the CNP, and μ from each curve in Supplementary Fig. 2a and plot these quantities as a function of photo-induced doping density in Supplementary Fig. 2b. Evidently, both quantities exhibit non-monotonic trends as a function of exposure time t.

This non-monotonic change results from a charge transfer relay between defect states close and far from graphene in the h-BN crystal, both of which are depicted in Supplementary Fig. 3. Charge can transfer from everywhere in BN into graphene due to the photo-doping effect that is explained in the main text. This charge transfer process is illustrated in Supplementary Fig. 3a. On the other hand, charge transfer can also occur between defects at different depths inside the h-BN flake, as shown in Supplementary Fig. 3b. The first process will dope graphene and impart a dramatic effect on its transport properties because some of the remaining charge defects are in close proximity to graphene. These charged defects are essentially scattering centers that degrade the transport properties[1]. This explains the shift of CNP and the degradation of transport properties as shown in the yellow curve in Supplementary Fig. 2. However, because of the second charge transfer process, charges from deeper defect states in h-BN will fill the empty states in the very first layer of h-BN; hence the charged scatterers migrate farther from graphene and deeper into the BN crystal. This internal charge transfer does not dope graphene, thus the CNP is not shifted. Finally, the charged defects form a distribution deep in the h-BN as shown in Supplementary Fig. 3c. These deeply embedded charged defects impart an insignificant effect[1] on the transport properties of graphene, which is evident by the similarity between the red and blue $R(V_g)$ curves. Interestingly, this buffer layer of neutralized defect states between the charged defect states is similar in spirit to modulation doping carefully implemented in semiconductor heterostructures.

3. Transport properties of graphene/BN device of different BN thickness

We find the thickness of the underlying BN does not affect the electrical transport properties of the graphene after it has been photo-doped. We show photo-doping behavior from two samples that have different BN thicknesses, ~20nm for Supplementary Fig. 4a and ~80 nm for Supplementary Fig. 4b. In Supplementary Fig. 4c-d we take the $R(V_g)$ curves from Supplementary Fig. 4a-b and shift them to overlay their charge neutrality points. Evidently, the curves overlay excellently with the initial non-photo doped curves, highlighting that photo-doping does not reduce sample quality in graphene/BN samples regardless of the BN thickness.

4. Method for extracting the photo-doping rate

The doping density induced by light exposure in time interval Δt can be expressed as:

$$\Delta n = D\Delta t \frac{P}{A} \qquad \text{S2}$$

Where D is the photo-doping rate as we plot in Fig. 4 in the main text. $\frac{P}{A}$ is the light power density.

We measured Δn in the following manner: 1. Scan V_g to get $R(V_g)$ curve in absence of light (red curve in Supplementary Fig 5.a); 2. Set V_g to a negative (to measure donor like states) or a positive (acceptor like states) value; 3. Expose the sample to light for Δt; 4. Scan V_g to get $R(V_g)$ curve in absence of light (blue curve in Supplementary Fig 5.a). The shift of $R(V_g)$ curve after exposure ΔV_g can be readily obtained by making the two curves overlap with each other as can be seen in Supplementary Fig 5.b. $\Delta n = C\Delta V_g$ where C is the capacitance of the graphene FET device. Since Δn increases in a nonlinear fashion as a function of the exposure time as can be seen in Fig. 3a in the main text, we use very weak optical illumination so that the doping rate is measured within the linear region at the beginning of exposure. The doping is then erased by exposing the sample at V_g=0V before measuring the next photon energy. The same V_g set point is used for different photon energies. The error in determining ΔV_g is within +/- 0.2V, which defines the error bars in the inset of Fig. 3a in the maintext.

1. E. H. Hwang, S. Adam, S. Das Sarma, Carrier Transport in Two-Dimensional Graphene Layers. *Phys Rev Lett* **98**, 186806 (May 4, 2007).

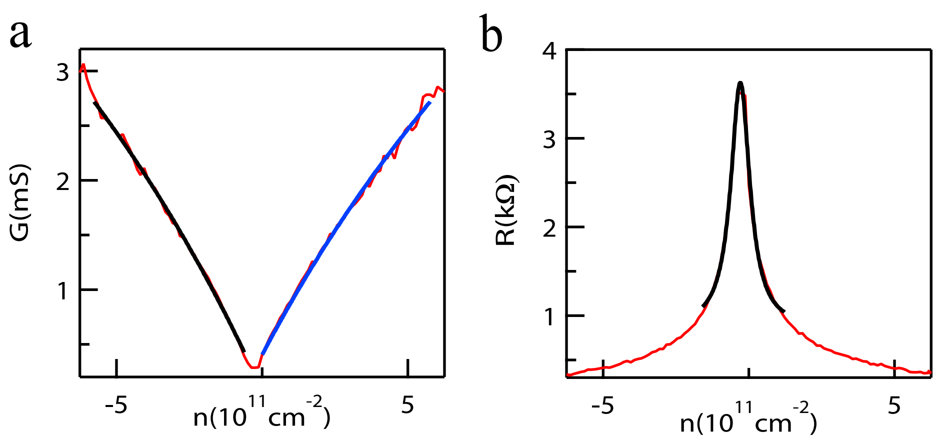
Supplementary Figure 1: Representative fits for μ and δn. (a) $G(n)$ trace in red and fits using eq. S1 for hole (blue) and electron (black) regimes. (b) $R(n)$ in red and fit using a Lorentzian function(black). The FWHM is extracted from the fit to acquire δn.

Supplementary Figure 2: Sequential electrical measurements of G/BN after exposure to light for varying durations of time. (a) $R(V_g)$ measurements where the red trace is taken before exposure to light, and the subsequent traces were acquired after exposure to light for different durations of time while V_g =-36V. Beginning with the yellow trace the different durations of time were: 1, 20, 40 minutes, respectively (right to left). The CNP shifts monotonically as a function of exposure time. (b) Charge carrier mobility μ and charge density fluctuations δn at CNP for electrons extracted from each trace in (a) using eq. S1, and plotted against the photo-induced doping density n_{PD}(left red axis) of each trace. As exposure time increases, μ decreases initially and then recovers while δn exhibits the opposite trend.

Supplementary Figure 3: Dynamics of photo-induced doping and charged defects migration. (a) Charge transfer from h-BN to graphene. Orange '+' circles represent charged defects and black '-' represent electrons. (b) Charge transfer from deep bulk in h-BN to top layer of h-BN. (c) Distribution of charged defects after both charge transfer processes finish.

Supplementary Figure 4: Transport properties of photo-doped GBN with different BN thickness. (a) The red trace shows the behavior of a pristine sample on a BN flake ~20nm thick. The other traces were acquired after photo-doping where the graphene CNP has been set at V_g=-17, -36 and-53V, respectively (from right to left). (b) The red trace shows the behavior of a pristine sample on a BN flake ~80nm thick. The other traces were acquired after photo-doping where the graphene CNP has been set at V_g=-10, -20, -30, -40 and-50V. (c)&(d) represent $R(V_g)$ curves from (a)&(b) respectively where their charge neutrality points are overlaid by a shift of V_g.

Supplementary Figure 5: Determination of photo-induced doping density. $G(V_g)$ trace in red and blue depicts before and after light exposure, respectively, for 10 minutes at very low light intensity. The dashed green trace is the blue trace shifted by a translation of ΔV_g to overlap with the red trace. We control the exposure dosage so that the ΔV_g is linearly proportional to the exposure time and the shape of $G(V_g)$ before and after exposure is not modified significantly.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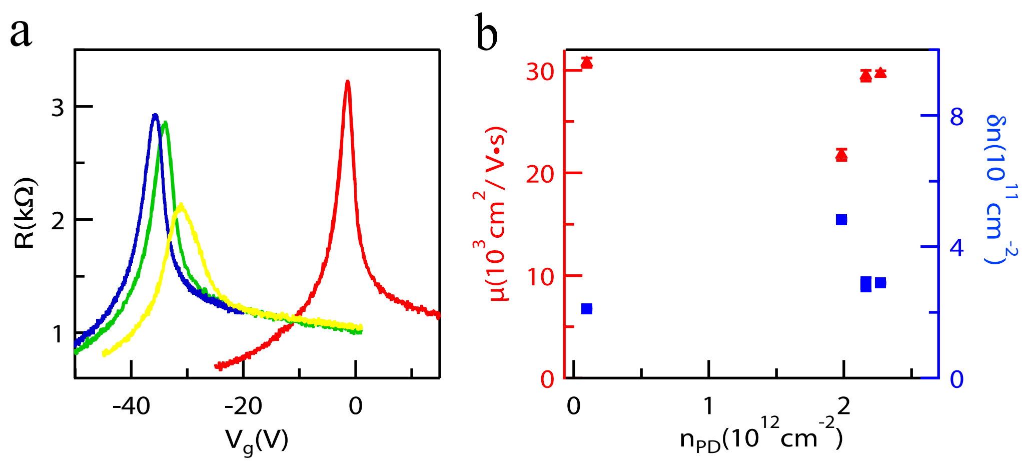
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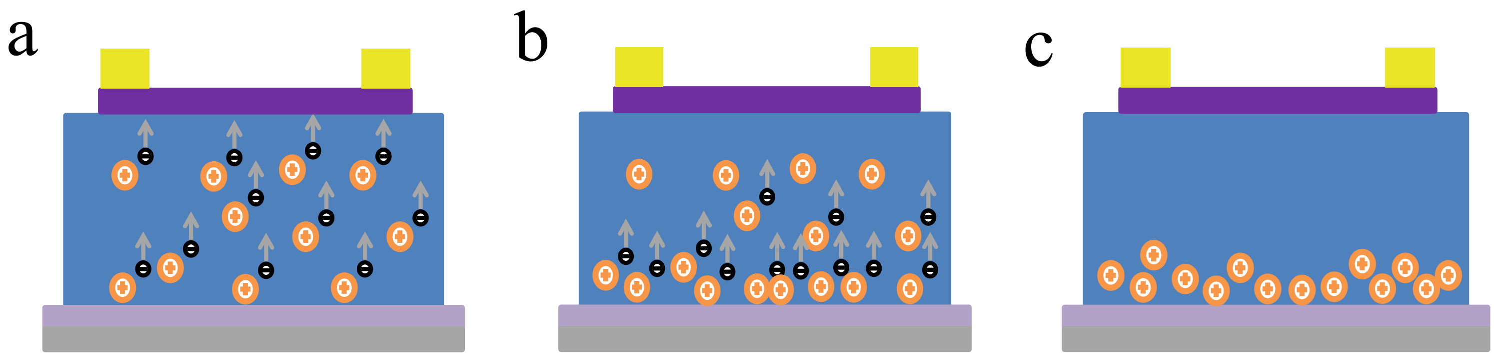

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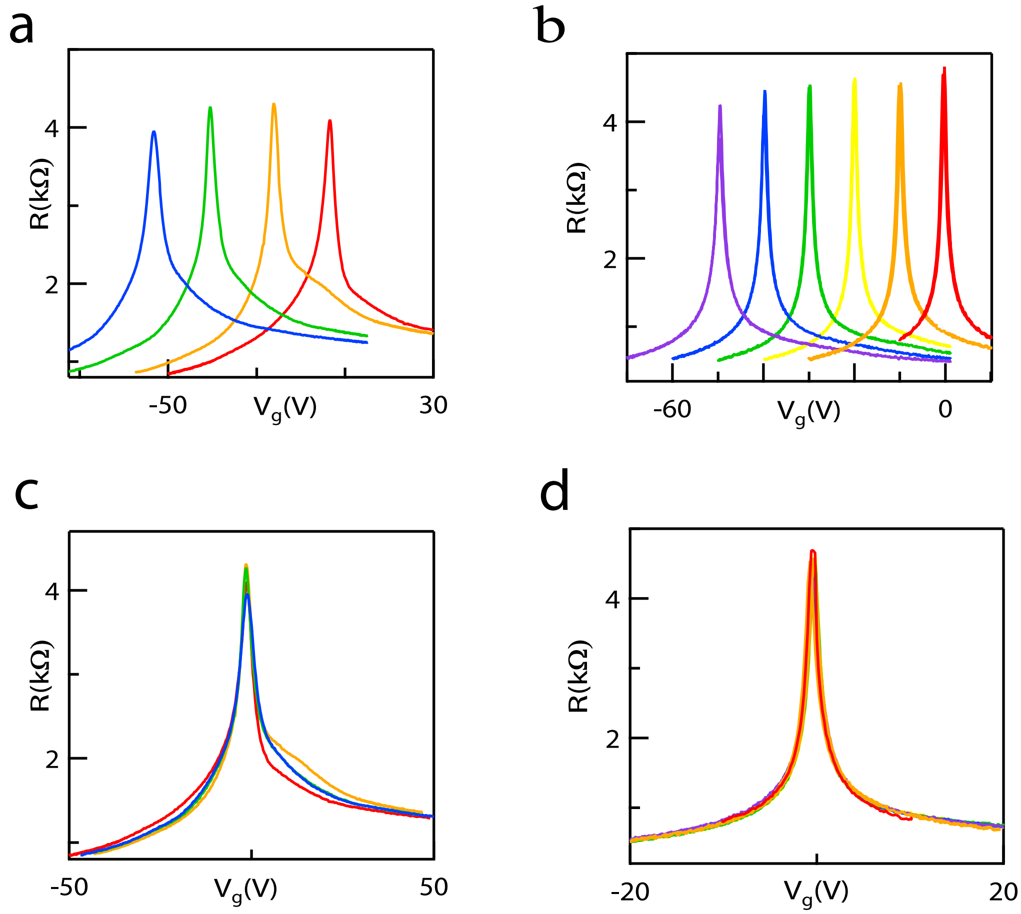
c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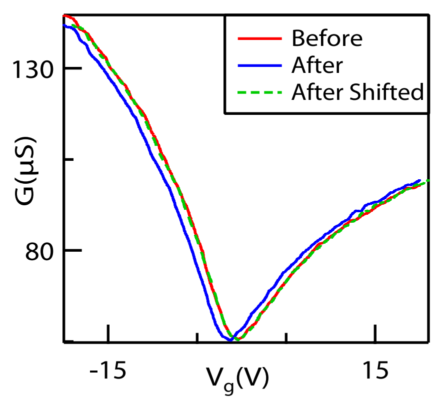
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After
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Vg(V)