Supporting Information

Nanoscale control of rewriteable doping patterns in pristine graphene/boron nitride heterostructures

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1. Determination of $\tilde{V}_g$ for light–induced doping

Light-induced doping modifies both the global charge density and the local charge density profile. To focus on the latter, we carefully choose $\tilde{V}_g$ to eliminate the former. This is done in the following manner: First, $dI/dV$ spectra are measured at the same location in all maps in order to track the charge neutrality point (CNP) after each light exposure treatment; next, this information is used to tune the gate voltage (prior to taking a map) to account for the CNP shift. This gate voltage is $\tilde{V}_g$. By using this procedure and applying the same sample bias voltage, the $dI/dV$ maps in Figs 2c-e of the main text are configured to the same global charge density. This ensures differences seen between these maps arise primarily from changes in the local charge density profile.

2. Converting $dI/dV$ intensity to charge density fluctuations after light-induced doping

The $dI/dV$ maps in Figs 2c-e of the main text can be converted to charge density. In order to do this, we performed $dI/dV$ measurements (with the STM feedback loop closed, $V_s = -0.25 \text{ V, } I = 0.2 \text{ nA}$) as a function of back-gate voltage $V_g$, an example of which is displayed in Fig. S1.

Here the conversion of $dI/dV$ to charge density is relatively straightforward because the charge inhomogeneity $\delta n$ induced by light exposure is small. Using Fig. S1 as a conversion tool, values of $dI/dV$ in the line trace were matched to appropriate values of $V_g$. Finally, the line trace was converted to charge density through $|e|\delta n = C \delta V_g$, where $C$ is capacitance per unit area calculated using a total SiO$_2$ and BN thickness of 360 nm (BN thickness measured by atomic force microscope).

3. Tip-doping $dI/dV$ spectra with $V_g > 0 \text{ V}$
Figure S3 shows four \( dI/dV \) spectra obtained on our graphene/BN heterostructure. Each spectrum was taken at \( \bar{V}_g = 0 \) V and after an STM tip voltage pulse was applied while \( V_g \) was set to different positive values (in contrast to Fig. 3a of the main text, which shows the case for \( V_g < 0 \) V). All the measurements were taken at the same location that the tip pulses were applied. The red curve is the original \( dI/dV \) spectrum obtained before tip pulsing. The graphene Dirac point (DP), which is denoted by the black arrow, shifts to greater positive \( V_s \) values with each successive voltage pulse (\( V_g = +10 \) V, +20 V, +30 V for the yellow, green, and blue traces, respectively). This indicates that the sample becomes more p-doped after each pulse with \( V_g > 0 \) V. We note that it is the value of \( V_g \) during a tip pulse that determines the amount of tip-doping (i.e. each sufficiently long tip pulse (\( \Delta t > 30 \) sec. – see Supporting Information Section 5) acts as an independent excitation unaffected by the previous tip-doping history).

4. Converting \( dI/dV \) intensity to charge density after tip-doping

Figure 3c of the main text can be converted to charge density through a similar method. The procedure for converting \( dI/dV \) to charge density is more complex here, however, because the charge density variation is not small and \( dI/dV \) is not monotonic with \( V_g \) over the range of interest. We summarize our conversion algorithm here (in more technical language, we use a combination of dynamic time warping with a Euclidean metric and locally weighted linear regression). First, Fig. 3c of the main text was radially averaged (the top right corner is the center point) to reduce the influence of the moiré superlattice and dot defects on the conversion algorithm. The radially averaged \( dI/dV \) was then matched to \( V_g \) values using a \( dI/dV(V_g) \) curve, ensuring that \( V_g(r) \) is a continuous function of the radial distance \( r \). The \( V_g \) values were then converted to charge density through \( |e|\Delta n = C \Delta V_g \). We performed this algorithm on \( dI/dV \) maps.
taken at the same location at different $V_g$ set points, and the resulting charge density curves are in good agreement (with a constant offset corresponding to the different $V_g$ set point). Figure S2a shows the result of this $dI/dV$-to-charge-density conversion. Applying the conversion algorithm to $dI/dV$ maps with different $V_s$ set points yields slight discrepancies ($\sim 10\%$), which we attribute to tip-induced band bending.

We can also apply this algorithm without radially averaging a $dI/dV$ map (in this case we first smooth the map using linear interpolation to remove the moiré lattice). This yields a charge density map as shown in Fig. S2b. The charge density map shows only small deviations from circular symmetry, justifying the radial average used to construct the charge density profile in Fig. S2a.

5. Tip pulsing procedure

Here we present the procedure for creating a graphene pn junction through a tip pulse:

1. Set $-1 \leq V_s \leq 1$ V and $V_g = V_g^*$ under closed loop conditions, where $V_g^*$ is the desired shift of the local charge neutrality point.

2. Open the STM feedback loop.

3. Withdraw the STM tip by $0.5 \leq \Delta z \leq 2.5$ nm. This tip pulse procedure also works in the tunneling regime (i.e. $\Delta z = 0$ nm), but can potentially damage the graphene or tip at such close distances.

4. Increase $V_s$ to +5 V.

5. Wait $\Delta t$ seconds. The wait-time $\Delta t$ depends on the tip geometry and tip-sample distance, but needs to be significantly long to fully shift the local Dirac point $E_D$ at $V_g = V_g^*$ to
ED(Vg = 0 V). Usually, Δt = 30 sec. is sufficient for Δz = 1 nm (although Δt can be significantly shorter for Δz < 1 nm and longer for Δz > 1 nm).

6. Decrease Vt, back to the original value.

7. Close the STM feedback loop.

8. Set Vg = 0 V. The Dirac point at Vg = 0 V is now at ED(Vg = -Vg*) before the tip pulse procedure.

6. G(Vg) before and after tip-doping

G(Vg) measurements of a two-terminal device were acquired before and after tip-doping in order to explore the electronic functionality of our doping technique. These measurements were performed at ~77 K in our STM and are plotted in Fig. S4. The response of the device prior to tip-doping is shown as the red trace. Here a single dip in G(Vg) can be seen at Vg ~ -22 V, which marks the CNP. We then set Vg = 15 V and performed tip pulses using our STM tip at 12 different locations within a 200 nm radius on the sample (see Supporting Information Section 5 for tip-doping procedure). The approximate location of the tip-doping array is depicted by the red “x” on the graphene flake in the inset of Fig. S4. The G(Vg) curve measured after the tip-doping is shown as the blue trace. Here we see a new, additional dip in G(Vg) located at Vg ~ 15 V. The existence of these two dips in G(Vg) indicates that a graphene pn junction was created using our tip-doping technique (such signatures have been observed in previous transport measurements of graphene pn junctions1,2).

7. Nature of BN defects
For the high-purity single-crystal BN used in our study (synthesized by T. Taniguchi and K. Watanabe\textsuperscript{3}), secondary ion mass spectroscopy identified oxygen and carbon impurities as prominent defect types\textsuperscript{4}. Additionally, a comparison between recent optoelectronic experiments on BN crystals\textsuperscript{5,6} with theoretical work\textsuperscript{7} shows that the nature of defects in these crystals is consistent with nitrogen vacancies and carbon impurities. Existence of the carbon impurities was further supported by recent STM studies on graphene/BN heterostructures\textsuperscript{8}. Using the measured impurity density for bulk BN crystals from Taniguchi \textit{et al.} \textsuperscript{4}, we estimate a defect density of $\sim 10^{15}$ cm$^{-2}$ for a 100 nm thick BN flake (distributed through the entire thickness).
Figure Captions:

**Figure S1**: d$I$/d$V(V_g)$ curve used for converting d$I$/d$V$ to charge density. This d$I$/d$V(V_g)$ curve was taken after a short light exposure was imparted on the sample (20 seconds), while holding $V_g = -15$ V. Changes seen in d$I$/d$V$ amplitude from Fig. 2d can be converted to charge density fluctuation by using the above measured d$I$/d$V(V_g)$ curve and $|e|\delta n = C \delta V_g$, in which $C$ is capacitance per unit area.

**Figure S2**: Charge carrier density map obtained from a d$I$/d$V$ map after an STM tip pulse. (a) Radially averaged $n(r)$ obtained from Fig. 3c of the main text using the procedure outlined in Supporting Information Section 3. (b) $n(x,y)$ is obtained by a similar procedure as (a). The map depicts a nanoscale pn junction that was created by an STM tip pulse.

**Figure S3**: Nanoscale doping controlled with an STM tip voltage pulse. (a) d$I$/d$V$ spectroscopy of a pristine surface before a tip pulse (red) and after a tip pulse ($V_s = 5$ V, 30 sec.) for $V_g = 10$ V (yellow), 20 V (green), and 30 V (blue). Initial tunneling parameters: $I = 0.4$ nA, $V_s = -0.5$ V, $\tilde{V}_g = 0$. The curves are vertically offset for clarity.

**Figure S4**: Tip-doped device transport data before and after tip-doping. Inset: Optical micrograph of device consisting of graphene (outlined by dashed lines) on an ~80nm thick BN flake (green) that is contacted by Cr/Au electrodes (yellow). Scale bar, 5 μm. G($V_g$) curves obtained at ~77 K before tip-doping (red) and after tip-doping (blue). Tip-doping was performed at 12 different locations on an evenly spaced grid over a 4μm x 4μm area approximately centered at the red “x” seen in the inset (tip-doping parameters: $V_s = 5$ V, 20 secs, $V_g = 15$ V). The red
curve shows a single CNP before tip-doping at $V_g = -22V$. After tip-doping two CNPs are clearly seen ($V_g = -22V$ and $V_g = 16V$), indicating the presence of a pn junction after the tip-doping treatment. All data were acquired from a device with a 6 μm width and 8 μm source-drain separation.
References:


Figure S1
Figure S2

(a) Radial distance from center of p-n junction (nm)

(b) $n(x,y) \times 10^{11} \text{ cm}^{-2}$
Figure S3

Tip-doping $dI/dV$ spectra

$\tilde{V}_g = 0 \text{ V}$