

SUPPORTING INFORMATION:

SURFACE POTENTIALS AND LAYER CHARGE DISTRIBUTIONS IN FEW LAYER GRAPHENE FILMS

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MATERIALS AND METHODS

Graphene Preparation

Graphene samples are synthesized using a mechanical exfoliation technique similar to that described in Ref. 1. We start with a highly-doped Si substrate with 300nm of thermally-grown SiO₂, cleaned with acetone and isopropyl alcohol. Adhesive scotch tape is used to extract and exfoliate a starting piece of bulk Kish graphite (Toshiba Ceramics, San Jose, CA). After the graphite has been sufficiently thinned, the tape is pressed against the SiO₂ surface and gently rubbed with the back of a tweezer for approximately 15s. The strength with which the tape is rubbed is varied across the sample surface, resulting in distinct FLG regions, some structurally pristine and others disordered. FLG regions of varying thickness are selected by visual inspection with an optical microscope.

Details of AFM and EFM measurements

Two different kinds of metal-coated SPM tips are used for AFM and EFM measurements: Ti-Pt tips (NSC18, Mikromasch) are characterized by force constant $k \sim 3.5\text{N/m}$, quality factor $Q \sim 250$, resonant frequency $\omega_0 \sim 75\text{kHz}$, tip curvature radius $\sim 40\text{nm}$; Cr-Au tips (NSC15, Mikromasch) are characterized by $k \sim 40\text{N/m}$, quality factor

$Q \sim 200$, resonant frequency $\omega_0 \sim 325\text{kHz}$, tip curvature radius $\sim 50\text{nm}$. AFM height measurements are done using intermittent contact mode.

Identification of Number of Layers

Previous experiments have indicated the possible presence of a “dead layer” between the FLG and the SiO_2 substrate that causes AFM measurements of the graphene thickness to be increased by up to several angstroms (1). If a dead layer were present, accurate identification of the number of layers in the FLG would be complicated. However, the number of layers present in a FLG region can be accurately measured by AFM if the film contains folds or wrinkles. AFM measurements of a folded FLG region prepared on the same chip as our samples indicate that the thickness of the dead layer, if there is one, is much smaller than the thickness of a single graphene layer (0.34 nm), so we are able to accurately determine the number of graphene layers in our FLG films. An example of this is shown in fig. S1.

EFM Measurements

By convention, the EFM phase shift $\Delta\Phi$ is measured with respect to the bare substrate (i.e. $\Delta\Phi = 0$ over a SiO_2/Si region with no deposited FLG). Each data point of fig. 3A (main text) represents the average of ~ 5 -10 different line scans over the same region (or the average of 10-20 line scans taken over two different regions of identical thickness – see the caption of Figure 3). As explained in detail in Ref. 2, conducting samples exhibit a negative phase shift, while insulating samples exhibit a positive phase shift that depends on the sample dielectric constant. For electrically floating conducting samples such as FLGs, changes in $\Phi(x,y)$ (given by equation 1 of the main text) result from changes in $C''(h)$, a geometric effect, or changes in the local sample surface electrostatic potential $V_s(x,y)$. Because the surface roughness of FLG bulk regions is of order 0.1 – 0.5 nm ($\sim 0.3\%$ of the tip radius (3)), $C''(h)$ is constant to an excellent approximation, and changes in $\Delta\Phi$ reflect changes in V_s (4).

We conducted multiple control experiments to verify the accuracy and reproducibility of the surface potential measurement. Height-dependent EFM measurements (fig. S2A) of $\Delta\Phi$ over the same FLG region at fixed V_{tip} have a power-law form $\Delta\Phi \sim h^{-1.6}$, characterized by an exponent between that expected for a cone-plane geometry ($C''(h) \sim h^{-1}$) and a sphere-plane geometry ($C''(h) \sim h^{-2}$), as seen by others (5). EFM measurements of the same FLG region were taken using two different lift heights, with the $\Delta\Phi - V_{tip}$ data shown in Fig S2B. The measured value of V_s is verified to be independent of the lift height h , as expected.

SUPPORTING TEXT

Outline of Thomas-Fermi Theory

The Thomas-Fermi (TF) theory describes the distribution of layer areal number densities $\sigma(z)$ that are in equilibrium with respect to fluctuations $\delta\sigma(z)$. The TF theory does not treat the effect of quantum coherence between the layers, and it applies in the controlled limit that the interlayer tunneling is tuned to zero. It is accurate when the variations of the interlayer potential or equivalently, when the local shift of the Fermi energies are large compared to the size of the interlayer hopping amplitudes.

For doped carriers described by the conical dispersion relation $E(k) = \hbar v_F k$, an excess areal carrier density contributes to the kinetic energy (per unit area) of each layer $K_i = 2\sqrt{\pi}\hbar v_F \sigma_i^{3/2} / 3$. The doped carriers in each layer also interact with a compensating density $-e\sigma_0$ in the substrate and with the charges in each layer. In the continuum limit, the grand potential for this system is

$$\Omega = \int_0^D \frac{dz}{d} \left(\gamma \sigma(z)^{3/2} - \mu \sigma(z) - 2\pi e^2 z \sigma_0 \sigma(z) \right) - \pi e^2 \int_0^D \frac{dz}{d} \frac{dz'}{d} \sigma(z) |z - z'| \sigma(z') \quad (S1)$$

where $\gamma = 2\sqrt{\pi}\hbar v_F / 3$ and μ is the chemical potential. Minimizing Ω and defining $f(z) = \sqrt{\sigma(z)}$ one finds

$$\frac{3\gamma}{2} f(z) = \mu + \beta z \sigma_0 + \frac{\beta}{d} \int_0^D dz' |z - z'| \sigma(z') \quad (S2)$$

and differentiating twice with respect to the observer coordinate z we obtain the equation quoted in the text

$$\frac{d^2 f}{dz^2} = \frac{2\tilde{\beta}}{d} f(z)^2 \quad (S3)$$

with $\tilde{\beta} = 4\pi e^2 / 3\gamma$. The boundary conditions can be determined by considering the behavior of the first derivative of eq. S2, along with the constraint of charge conservation

$$\begin{aligned}\left[\frac{df}{dz}\right]_{z=0} &= \tilde{\beta}\left(\sigma_0 - \int_0^D \frac{dz'}{d}\sigma(z')\right) = 2\tilde{\beta}\sigma_0 \\ \left[\frac{df}{dz}\right]_{z=D} &= \tilde{\beta}\left(\sigma_0 + \int_0^D \frac{dz'}{d}\sigma(z')\right) = 0\end{aligned}\tag{S4}$$

The solutions of eq. S3 are then obtained by using the conservation law

$$\frac{d}{dz}\left(\frac{1}{2}\left(\frac{df}{dz}\right)^2 - \frac{2\tilde{\beta}}{3d}f^3\right) = 0\tag{S5}$$

and then directly integrating df/dz to find $f(z)$. In terms of a dimensionless variable of integration $u = f(z)/f(0)$ we find

$$(1-r_D^3)^{1/6} \int_1^{r_D} \frac{du}{\sqrt{u^3 - r_D^3}} = 2\left(\frac{\tilde{\beta}\sigma_0 D^3}{3d}\right)^{1/3} = \Gamma\tag{S6}$$

where $r_D = f(D)/f(0)$. Equation (S6) provides a convenient relation between the dimensionless coupling parameter Γ and the screening parameter r_D .

Once r_D is determined (S2) can be used to find the graphene contribution to the surface potential

$$V_D = \frac{3\gamma}{2}(3\tilde{\beta}d\sigma_0^2)^{1/3} \frac{1-r_D}{(1-r_D^3)^{1/3}} + V(0)\tag{S7}$$

The first term on the right hand side is the contribution to the surface potential from the charge distribution in the graphene. $V(0)$ is the potential at the graphene/silica interface and is offset from the potential deep in the silica because of the charge distribution in the charged acceptor layer. Setting the potential to zero in the silica bulk, we have

$$V(0) = \frac{3\gamma}{2}\tilde{\beta}\sigma_0 d_s = 2\pi e^2 \sigma_0 d_s\tag{S8}$$

for an areal acceptor density σ_0 within depth d_s of the interface.

SUPPORTING REFERENCES

1. K. S. Novoselov *et al.*, *Science* **306**, 666 (2004).
2. C. Staii, A. T. Johnson, N. J. Pinto, *Nano Letters* **4**, 859 (2004).
3. M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, E. D. Williams, *Nano Letters* **7**, 1643 (2007).
4. We note that because our measurements are performed under ambient laboratory conditions, the measured V_s is expected to be offset from the value measured under UHV. For example, although graphene is well known to be hydrophobic, we can not rule out the presence of a thin adsorbed water layer on the sample surface, or hydrogen bonded to the Si-OH silanol groups at the SiO₂. However, our investigations are of robust *changes* in the FLG surface electrostatic potential, and thus the slight offset introduced in our measurements by such effects does not affect our conclusions. Furthermore, we note that all the measurements presented are robust over a period of multiple weeks.
5. S. Belaidi *et al.*, *J. Appl. Phys.* **81**, 1023 (1997).

SUPPORTING FIGURES

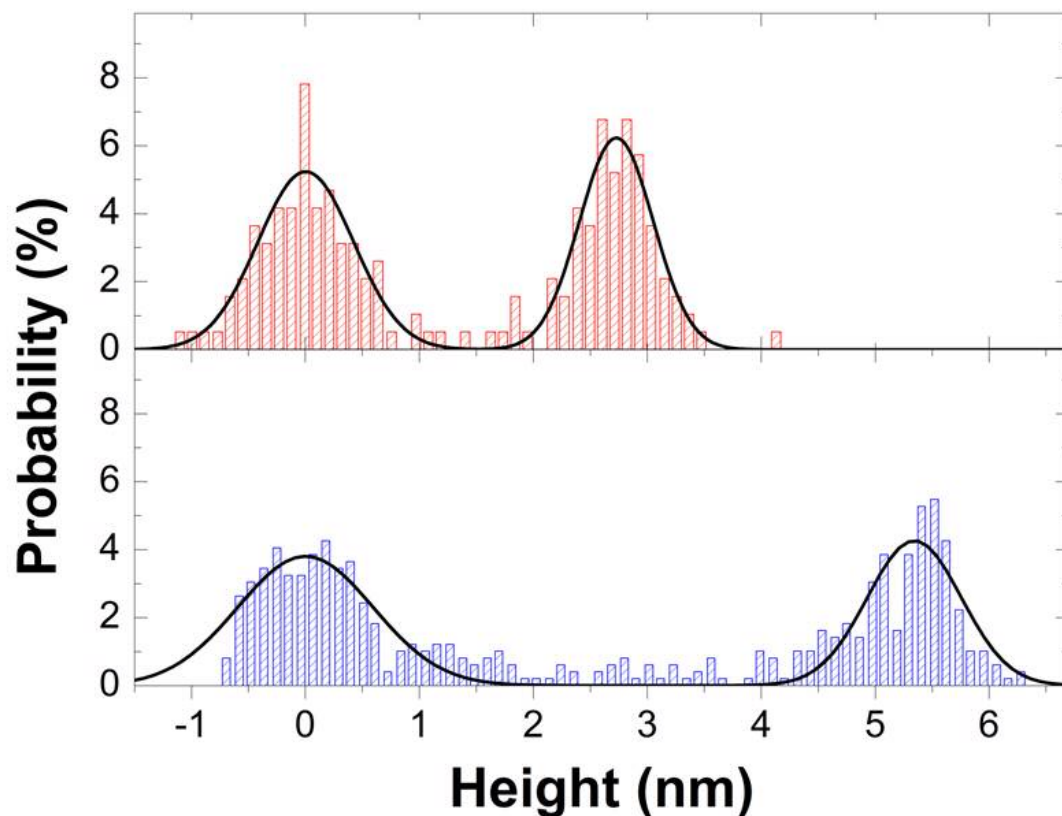


Figure S1. AFM across FLG fold. Height histograms acquired across an unfolded FLG/substrate edge (top) and a folded FLG/substrate edge (bottom), for neighboring pristine regions of the sample shown in figure 4 of the main text. The height difference between the bulk region and the SiO₂ is ~ 2.73 nm, while the height difference between the folded region and the SiO₂ is ~ 5.3 nm, almost exactly twice as large. We thus conclude that the unfolded region consists of 8 layers (~ 2.73 nm / 0.34 nm, 0.34 nm being the thickness of a single graphene layer), and that the thickness of the “dead layer” (if any) in this experiment is negligible compared to the interlayer spacing.

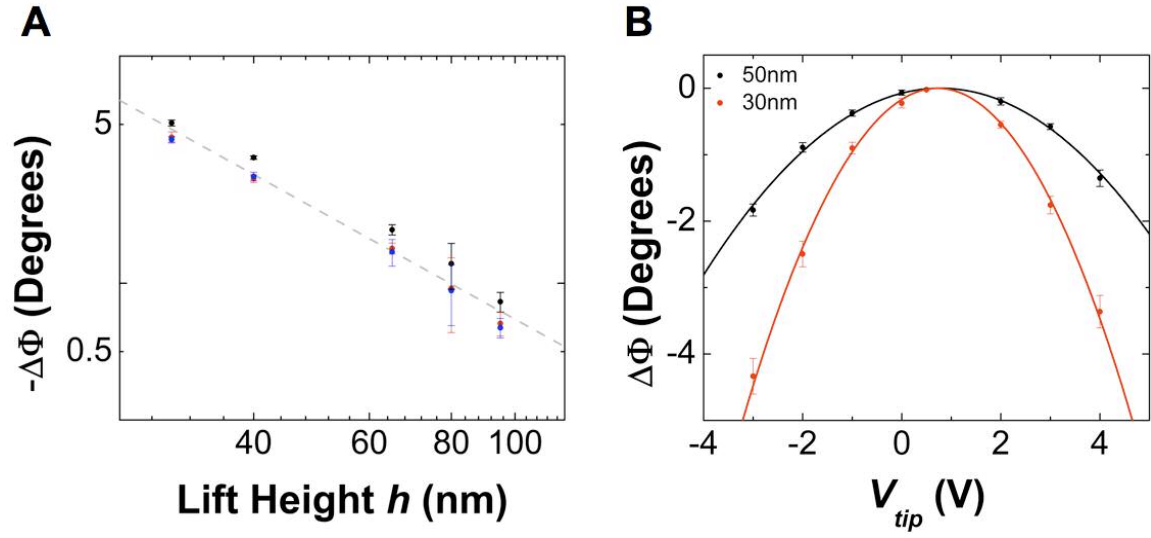


Figure S2. Results of EFM control experiments. (A) Negative of EFM phase shift ($-\Delta\Phi$) measured as a function of the lift height h , over three different FLG regions (different colors). The dashed line indicates the functional form $-\Delta\Phi \sim h^{-1.6}$. (B) $\Delta\Phi$ versus tip voltage V_{tip} for the same FLG region of height ~ 6.1 nm (18 layers), for lift heights $h = 30$ nm and 50 nm. The measured $\Delta V_s = V_s - V_s^{\max} = 0.02 \pm 0.06$ V agrees well with data in figure 3 of the main text, and confirms that the measured value of V_s is not sensitive to the lift height h .