Electro-Mechanical Sensing of Substrate Charge Hidden under Atomic 2D Crystals - Supporting Information

Nicholas. D. Kay[1], Benjamin. J. Robinson[1], Vladimir. I. Fal'ko[1], Konstantin. S. Novoselov[2], and Oleg. V. Kolosov[1]

[1]*Department of Physics, Lancaster University, Lancaster LA1 4YB, UK*

[2]*Department of Physics and Astronomy, Manchester University, Manchester M13 9PL, UK*

E-mail: o.kolosov@lancaster.ac.uk

Contents

1 Supporting Methods. Sample Preparation

The samples were exfoliated onto a highly doped Si substrate with 300 nm SiO_2 thermal oxide on the top where 150 to 200 nm wide trenches which were produced using optical edge lithography[1,2] providing high aspect ratio and close to vertical side walls. Prior to use the substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 mins each before being subjected to an Ar(2% O_2) plasma for three minutes to remove any remaining organic material. To prepare the samples, a small flake of bulk Kish Graphite was placed on (Gel-pak® 4x adhesion) cross-linked adhesive polymer film. After ensuring the flake was adhered to the film it was slowly peeled off leaving an area of thinner material. By sticking the two ends of the adhesive film together, one containing the flake residue, and repeatedly sticking them together, approximately 20 times, a good covering of material is achieved. The freshly cleaned substrate described above is then placed upon the exfoliated material and pushed gently for a few minutes before leaving the material for 15 minutes to establish good adhesion. This method produces a wide range of thicknesses from a few layers up to a few hundred nm with minimal surface contamination.

To prepare the sample for measurement through contact electrostatic force microscopy (contact EFM, or C-EFM), a single Cu wire was attached to the side of the Si chip where it was electrically contacted by the application of Ag paint, then secured in place with cyanoacrylate glue. For the purposes of studying the sample with ultrasonic force microscopy the sample was additionally mounted on PI Ceramics ultrasonic transducer (PZT PIC® 151) with a resonance frequency of approximately 4 MHz.

2 Supporting Note. Measurements of Electromechanical Response for non-contact EFM and C-EFM

To experimentally quantify the forces acting on the cantilever beam we applied a square waveform voltage interchanging between zero and V_{DC} at a frequency of 1.2 kHz, well below the cantilever resonance. The characteristic feedback time of the scanning probe system was reduced to approximately two orders below the period of the modulation, by reducing integral and proportional feedback gain. This allowed the direct measurement of the deflection signal and a reliable estimate of the total DC force acting on the cantilever as seen in Supporting Fig. 1.

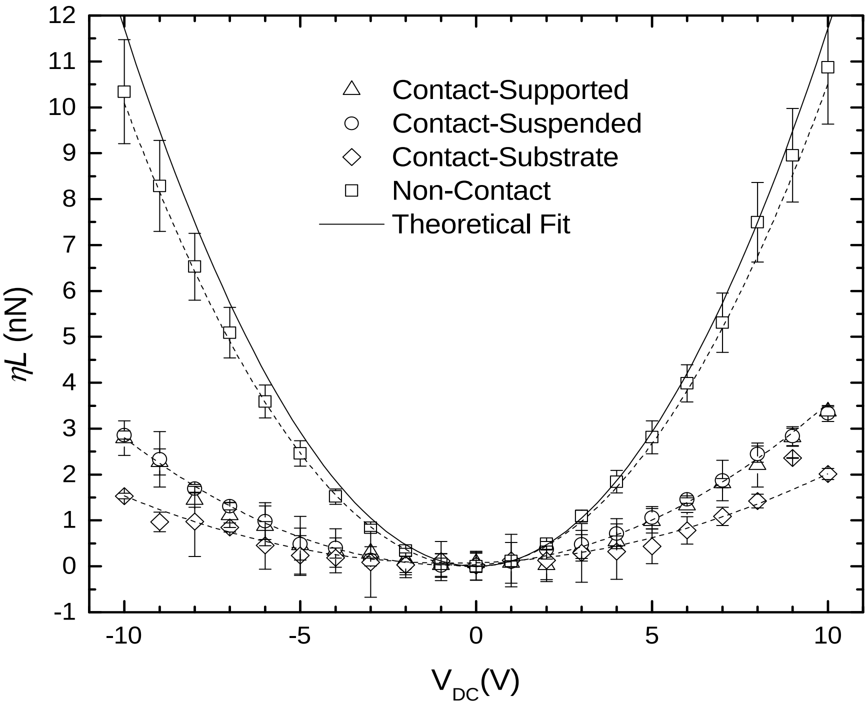

Figure S1: The total force acting on the cantilever in C-EFM when in contact with supported and suspended graphene (15 layers), as well as SiO_2 substrate. The force acting on the cantilever in NC-EFM when the tip is approximately 3 μm above the surface is provided as a reference.

To clarify the nature of the electromechanical response of the graphene film it was subjected to V_{DC} sweep at various normal forces (Supporting Fig. 2).

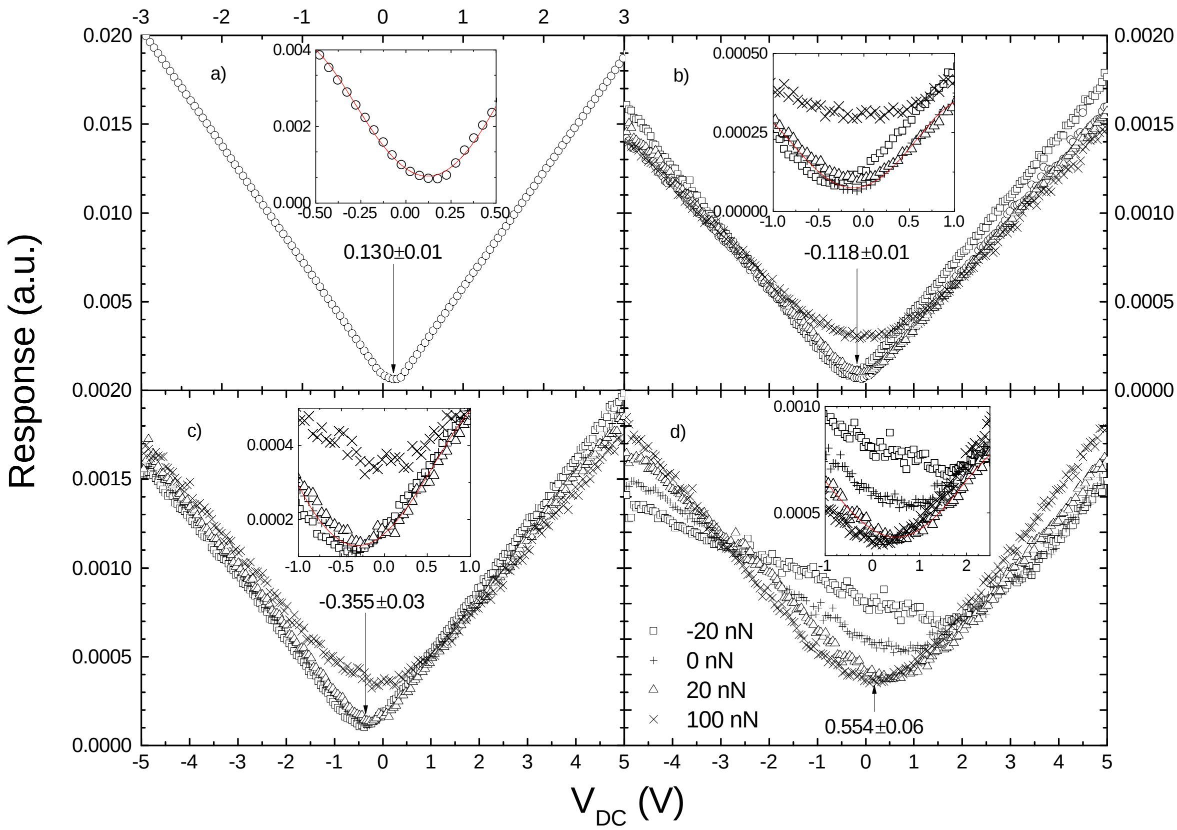

Figure S2: C-EFM response for fixed AC voltage $V_{AC} = 10\,V$ peak to peak and sweeping the gate voltage (V_{DC}) between -5 to +5 V. Set forces of -20 (square), 0 (plus), 20 (triangle) and 100 (cross) nN were used.

As Supporting Fig. 2 demonstrates, there is a significantly different behavior between the response of the suspended graphene and those of supported graphene and SiO_2. There is also the tendency for the responses of supported graphene and SiO_2 to become more rounded at higher set forces. This is believed to be due to the increased friction between the tip and surface which resists the bending moment produced by the electrostatic force. To further understand the effect of friction an additional study of the DC forces was done, similar to those in Supporting Fig. 1 except with the addition of an Ultrasonic force, see Supporting Fig. 3. By applying an ultrasonic vibration in the MHz range but modulated in amplitude at a frequency of 2.7 kHz (twice as high as the electrostatic actuation on the cantilever) it was possible to break the tip-surface contact thus removing any frictional forces[3].

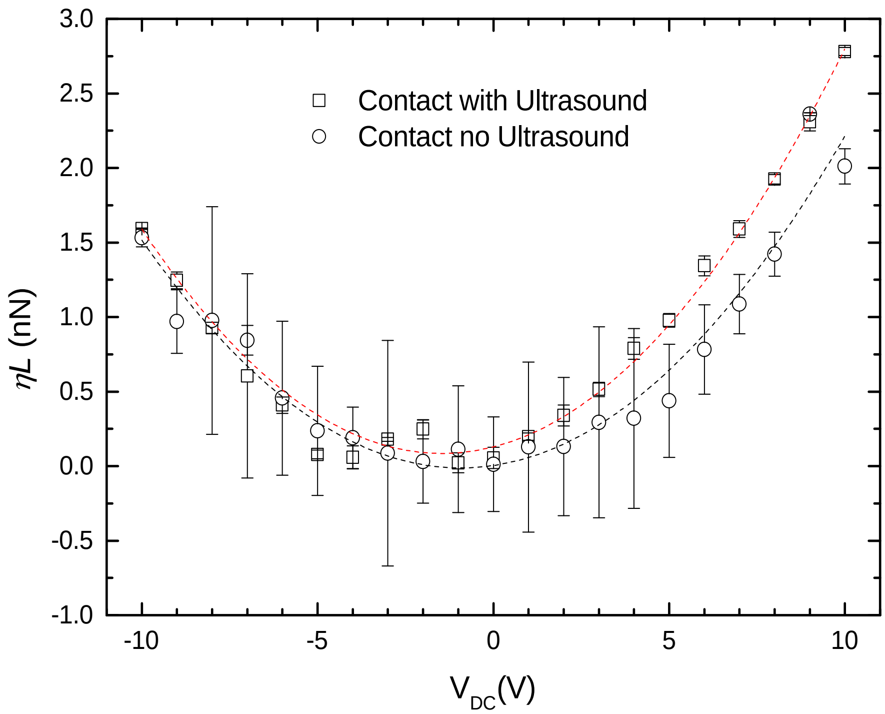

Figure S3: The total force acting on the cantilever in C-EFM when in contact with the SiO_2 substrate. The difference in apparent force is seen for when the tip periodically breaks contact with the surface due to ultrasound and C-EFM in constant contact.

Supporting Fig. 3 shows that, with an ultrasonic vibration periodically breaking the surface contact, the perceived forces acting on the cantilever are higher.

In C-EFM, the force acting between the cantilever and the sample F_E is distributed along the cantilever, and can be approximated as the force between two parallel capacitor plates, at the gate voltage $V = V_{DC} + V_{AC}\cos(\omega t)$ as

$$F_E = \frac{1}{2}\frac{dC}{dz}\left[(V_0 + V_{DC} + V_{AC}\sin(\omega t))^2\right] \tag{1}$$

where $C(z)$ represents the capacitance of the system, z the distance between the cantilever and the sample, and V_0 contact potential between the potential of the Si substrate and the driving voltage due to e.g. contact phenomena. Although possibly modifying the C-EFM contrast, the electrostatic forces which act directly on the tip can have only minor contribution as their bending moment is compensated by the equal and opposite bending moment of the sample reaction force. Similarly, for the non-contact EFM (NC-EFM) measurements in Fig. 2, the contribution of forces acting on the tip in our measurements can be neglected, albeit for another reason, as the tip-surface distance was approximately 3 μm, making the forces acting on the cantilever the dominating contribution. In general, the observed non-contact and contact EFM signals obeyed quadratic dependence as can be seen from the DC force measurements in the Supporting Fig. 2. In these measurements, the resulting amplitude of the AC force component at frequency ω can be derived from the Supporting Eq. 1 as

$$F_\omega = \frac{dC(z)}{dz} V_{AC} |V_{DC} - V_{dif}| \tag{2}$$

The response has a typical V-shaped dependence with a small $V_0 = 0.13 \pm 0.01\,V$, the latter arising most likely from the contact potential difference of the connection to the tip and doped Si substrate. In addition to observing an electromechanical response in graphene suspended over a trench as described in the paper, it was possible to observe this on graphene delaminations. These delaminations were caused, in most cases, by debris on the substrate prior to deposition resulting in the graphene being stretched over it, rather like a big top.

References

[1] Pumarol, M. E. *et al.* Direct nanoscale imaging of ballistic and diffusive thermal transport in graphene nanostructures. *Nano Letters* **12 (6)**, 29062911 (2012).

[2] Rosamond, M. C., Gallant, A. J., Petty, M. C., Kolosov, O. & Zeze, D. A. A versatile nanopatterning technique based on controlled undercutting and liftoff. *Advanced Materials* **23**, 5039–5044 (2011).

[3] Dinelli, F., Biswas, S., Briggs, G. & Kolosov, O. Ultrasound induced lubricity in microscopic contact. *Applied physics letters* **71**, 1177–1179 (1997).