Mapping nanomechanical phenomena in graphene nanostructures using force modulation and ultrasonic force microscopy

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ABSTRACT

Graphene is a novel nanomaterial that possesses outstanding electrical, thermal, and mechanical properties. Whereas its electronic properties are extensively studied, mechanical properties of graphene nanostructures are much less experimentally explored even for simple graphene structures [1]. At the same time, the nanoscale morphology of atomically thin graphene films, including rippling at various length scales and inter-layer force interaction are directly modified by the substrate and local environment that in turn changes of local nanoscale mechanical properties of a graphene nanostructure [2-4]. We use a combination of force sensitive scanning probe microscopies that combines low frequency and ultrasonic vibrations and enables mapping of wide dynamic range of stiffnesses from 0.02 to 2000 N/m with the lateral resolution of few nanometres. That allowed us to investigate results of residual stresses in supported graphene layers that revealed themselves as broken mechanical contact at the interface between graphene layer and the substrate, as well as to explore nanomechanical behaviour of suspended graphene film. We directly observed the transition of graphene layer deformation from plate to stretched membrane behaviour, and to create nanoscale maps of shell instability for few layer graphene sheets, providing insight to the stresses in the free standing graphene films.

Keywords: atomic force microscopy, nanomechanics, graphene, ultrasonic force microscopy, buckling.

1 METHODS AND MATERIALS

1.1 Nanomechanical mapping via force modulation and ultrasonic force microscopy

Few layer graphene (FLG) sheets were exfoliated from Kish graphite via traditional technique [1] on a dedicated plasma cleaned Si substrates. The substrate had 300 nm SiO_2 thermal oxide layer for easy identification of graphene film and narrow 180 nm trenches of 300 nm depth and sharp edges provided via recent edge lithography method with the sacrificial layer lift-off

A very large dynamic range of mechanical stiffness or dF/dz, that can be expected in graphene nanostructures results mainly from different mode of force loading. A bending deformation of a large cantilevered flake or a zero stress graphene plate over a large hole provide smallest stiffness values. Moderately stretched membrane or plate bridging narrow gap can have stiffness values several orders of magnitude higher. The highest stiffness corresponds to in-plane stretching of graphene film, in this mode it is one of the stiffest materials known in nature.

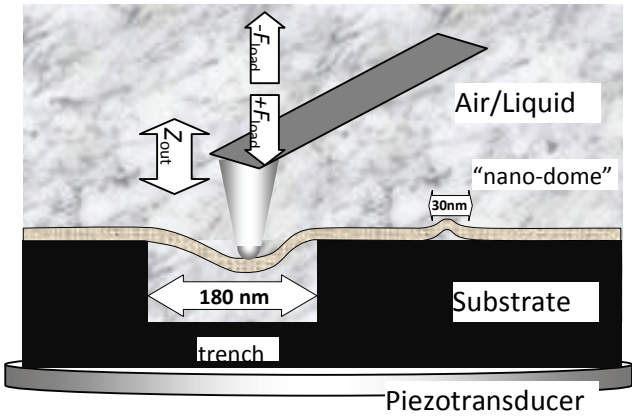

Figure 1: Schematic diagram of scanning probe experiment for mapping of graphene nano-mechanics. Few layer graphene (FLG) exfoliated sheets are deposited on the Si/SiO2 substrate with narrow nanoscale trenches, that is placed on the broadband piezo-transducer modulating vertical position of the substrate. Sharp tip with 10 nm radius of curvature mounted on the soft cantilever (k_c=0.2 N/m) is in contact with the FLG sheet, probing it bending stiffness in the force modulation mode (FMM) at modulation frequency f_{FMM}=2 kHz and in the ultrasonic force mode (UFM, f_{UFM}=4.1 MHz). FMM and UFM together allow to probe extremely wide range of contact stiffness of FLG nanostructures from 0.02 N/m through 2,000 N/m.

Whereas SPM was extensively used as a single point static force probe for flexural loads, for our study we required both real-time nanoscale resolution mapping of local stiffness combined with wide dynamic range. For the lower range of stiffness we used approach of force modulation microscopy (FMM) that is widely explored for

studies of polymeric materials. In FMM sample position zs is harmonically modulated with amplitude a_{FMM} at frequency f_{FMM} much lower than the resonance frequency of the cantilever fc such that $z_s = a_{FMM}\ cos(2\pi f F_{MM} t)$ If the contact stiffness kcont of the FLG graphene sheet contacted via SPM tip is $k_{cont}=k_{FLG}$ and cantilever spring constant is k_c, the resulting displacement of the cantilever $a_{FLG}= a_{FMM}\ cos(2\pi f_{FMM} t)\ k_{FLG}/[(k_{FLG}+k_c)]$. It is easy to see that if sample of stiffness is much higher than stiffness of cantilever ($k_{FLG}>> k_c$) the cantilever deflection amplitude is equal to the modulation amplitude of the sample, or $a_{FLG}= a_{FMM}$. As a result, FMM is sensitive to the range of contact stiffness kcont of the same order as cantilever stiffness k_c (in practice, $0.1k_c < k_{cont} < 10k_c$) and other SPM approaches are needed to map graphene nanostructures with higher stiffness. Substituting here values for the cantilever used in this study, we obtain 0.02 N/m$<k_{cont}<$2 N/m.

Such approach that is both capable in differentiating between high contact stiffness in SPM, as well is highly non-destructive is ultrasonic force microscopy (UFM) [5]. In UFM [2] a sample is vibrated at very high frequency $f_{UFM} >> f_c$ (typically between 2 - 60 MHz) and amplitude modulated at low (few kHz) frequency. Due to the high dynamic rigidity of the AFM tip-cantilever system, a nanoscale tip cannot move with the sample vibration, but instead elastically deform the sample at high frequency. If one assumes the concentrated mass and stiffness for the cantilever, its dynamic stiffness increases as $(f_{UFM}/f_c)^2$, whereas taking into account that cantilever mass and spring are distributed, dynamic stiffness of the cantilever can be approximated as $k_{dyn}=k_c\ (f_{UFM}/f_c)^{3/2}$. Substituting values for cantilever and UFM frequency and used in this study, we obtain $k_{dyn}\approx$1100 N/m, expanding range of stiffness accessible by FMM by three orders of magnitude [5].

The oscillating contact force is subsequently "rectified" owing to the extreme nonlinear force-vs-distance dependence of a tip-surface contact resulting in a net force at kHz modulation frequency that is easily detectable by the AFM cantilever. UFM was shown to have an excellent material contrast to semiconductor nanostructures ranging from quantum dots and superlattices to engineering ceramics and composites [6,7]. Another very useful feature of UFM is that it eliminates sample-tip friction as the solid-solid contact between SPM tip and the sample is broken for the part of oscillation period, thus allowing gentle imaging of the sample similar to the tapping mode.

1.2 Experimental setup of FMM and UFM

In order to realise both FMM and UFM in our studies of graphene nanomechanics, we have attached a sample on the piezoceramic ultrasonic transducer (PI Instruments) via thin layer of crystalline salol (melting point 42 ^{0}C). The piezotransducer was driven by an Agilent 33220A function generator. Modulation frequency of FMM was f_{FMM}=2 kHz and tested to be below resonance of the piezotube and the SPM setup used, whereas carrier frequency of UFM f_{UFM} was 4.1 MHz that was amplitude modulated using gated saw-tooth shape at frequency f_{AM}=1.7 kHz. Resulting cantilever deflection (at f_{FMM} or f_{AM} frequency for, correspondingly, FMM and UFM mode) was acquired via SRS-830 lock-in amplifier, with its output recorded by the auxiliary input of the Nanoscope III controller synchronously with the image scan. The sample stage and cantilever holder allowed operation in air as well as in liquid with measurements reported in this study performed in ambient air environment.

2 EXPERIMENTAL RESULTS

2.1 Mapping local stiffness of few layer graphene

Using FMM, we were able to map with nanoscale resolution a local bending stiffness of suspended FLG films for various values of normal load F_{load} (figure 2b,c). These maps clearly differentiate between the stiffness of 10 and 11 thick layer suspended FLG with spring constants of k_{11}2.22±0.23N/m and k_{10}=1.72±0.12N/m . These values may be compared to that of 5 layer thickness FLG where k_5=3.94±0.60N/m. It is believed that this unexpectedly large stiffness is due to a high tension in the film created upon deposition. These values were all observed under a 3.7nN contact force. In comparison, for supported FLG film, FMM provided no contrast within response very close to one of Si/SiO_2 substrate.

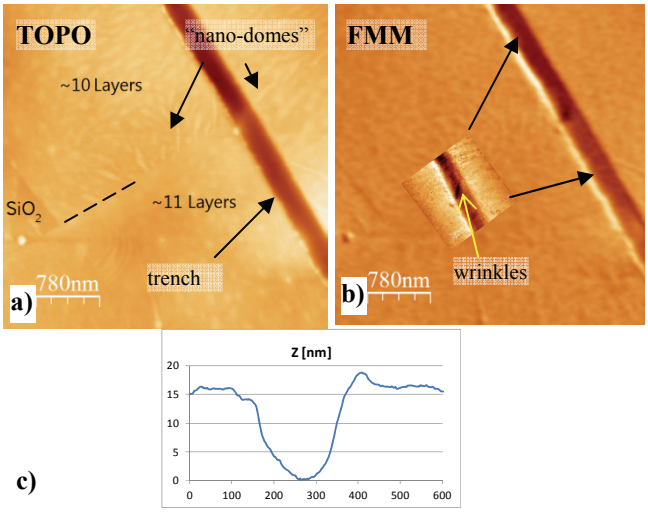

Figure 2: a) Wide area topography image of FLG sheet (10 and 11 layers, or ~ 3.5 nm thick) deposited by exfoliation on the Si/SiO2 substrate that has 180 nm wide, 300 nm deep trenches; dotted line shows the boundary between two sheets with one graphene layer thickness difference; typical topography profile across the trench is shown in c). b) Force modulation microscopy (FMM) stiffness map of the same area; lower brightness corresponds to softer areas. Inset in b) - enhanced contrast showing "wrinkles" modulating the bending stiffness of the FLG sheet.

For positive loads, bending stiffness of suspended FLG film (as observed in FMM) varied across the trench, with stiffness consistently decreasing towards the middle of the suspended area (figure 3 c). In the vicinity of trench edges, especially close to edge irregularities, local FLG stiffness varied locally at distances on the order of 10-20 nm. We also noted presence of elongated areas within the trench ("wrinkles" visible only in FMM images, inset in figure 2b) of lower stiffness.In UFM the suspended part of FLG layer represented continuous low stiffness zone, with practically no UFM signal. In contrast, areas of FLG resting on substrate showed rich morphology in UFM images (figure 3 b) with lower signal areas corresponding to shallow few nm high bulges in topography ("nano-domes", figure 3 b) that were more abundant in the thinner FLG layer. These "nano-domes" are often created during exfoliation process of graphene preparation and can be interpreted as delaminations where mechanical contact between substrate and graphene film is lost. In 10-11 layer FLG sample these were shallow bulges of approximately 2 nm in height and 30-50 nm width and sometime extended over several hundreds of nm (figures 2, 3).

Stiffness of a FLG layer suspended over trench or within "nano-domes" is a combination of shear stress contribution similar to ones of a bent plate (that should be dominant at zero or low loads) and stiffness of a stretched membrane due to in-plane stresses in the film (this component increases with the increased tension in the film). Wrinkles in the suspended area of FLG locally modify stress in the suspended graphene layer, and therefore influence FLG layer stiffness. Interesting to note that these stresses cannot be directly observed in the topographical images, and it is stiffness mapping by FMM that allowed their direct observation.

2.2 Mapping local stiffness of stiff graphene layer on substrate – enters UFM

As we will analyse below, the bending stiffness of both plate and membrane rapidly increases with the decrease of characteristic width of the suspended area, as a result, stiffness of "nano-domes" is much higher than stiffness of suspended area of membrane. In our experiment we used cantilever with stiffness k_c=0.2 N/m that limited FMM sensitivity to k_{cont} by 0.02 $N/m < k_{cont} < 2$ N/m, and it is apparent that contact stiffness for Si, FLG resting on the support as well as FLG within "nano-dome" delaminations was clearly much higher than 2 N/m, making FMM inefficient for such studies.

UFM, at the same time, is perfectly suited for mapping of high contact stiffnesses and therefore was able to easily differentiate between areas of "nano-domes" and graphene resting on the substrate. It should also be noted that as long as graphene-substrate separation is above the characteristic length for interactomic forces (~1 Å), the UFM will be sensitive to the details of such intimate contact [6]. That unique UFM capability may prove essential for the development and monitoring of graphene nano-devices (Figure 3).

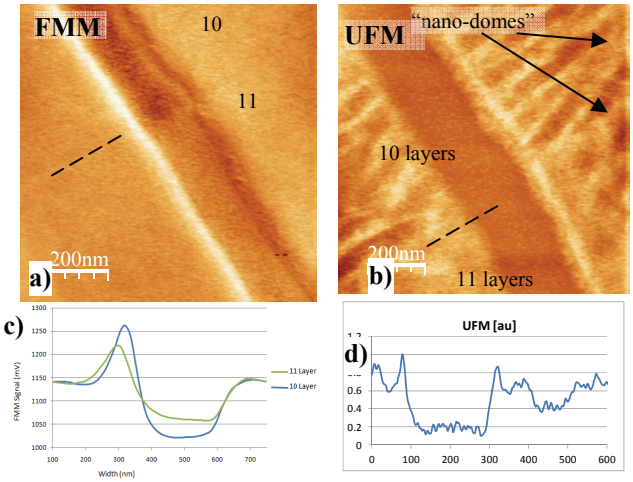

Figure 3: a) Force Modulation (FMM) and Ultrasonic Force Microscopy (UFM) images of the same area as inset (figure 2 b). In both FMM and UFM lower brightness corresponds to softer areas. c, d) FMM and UFM profiles.
"Nano-domes" that are much stiffer than the trench cannot be observed in FMM, but easily observed in UFM images and corresponding profile d).
Cantilever stiffness k_c=0.2 N/m, nominal tip radius 10 nm, FMM modulation frequency f_{FMM}=2 kHz and amplitude 1.4nm, UFM frequency f_{UFM}=4.3 MHz, ultrasonic amplitude ~ 1 nm.

3. REAL TIME AND REAL SPACE MAPPING OF BUCKLING INSTABILITY OF GRAPHENE

Even more surprising was the behaviour of the stiffness of FLG graphene film at negative loads. Negative loads were possible due to sufficiently strong adhesive forces present between graphene layer and the SPM tip in teh ambient environment. Stable imaging at negative (pulling) loads up to -10 nN was routinely achieved. As one can see from figure 4a, at negative load (Fload=-9 nN) the 5 layer FLG efficiently bends upwards and create a convex profile as the tip is scanned across the trench as in figure 4c. At the same time, bending stiffness of the FLG sheet kFLG was surprisingly flat across the trench with exception of narrow ~10 nm zone near the trench edges where drop in stiffness was always observed (figure 4d). Both membrane and plate bending regimes would suggest significant increase of the stiffness in the vicinity of the edges – so perhaps another phenomenon is present here.

First of all one has to take into account that the profile seen in the picture 4 c) does not represent a stationary profile of FLG sheet under negative load, but rather is a result of dynamic deformation of suspended graphene area as the tip is scanned across at the constant pulling force. A schematic

representation of graphene layer bending in this case is given in the figure 4e. Near trench edges FLG film clearly adheres to the trench walls due to van-der-Waals and hydration forces, but as the tip moves away from the wall (to the characteristic distance we can estimate of 10-15 nm), graphene sheet bends upwards creating wave of deformation that follows the tip.

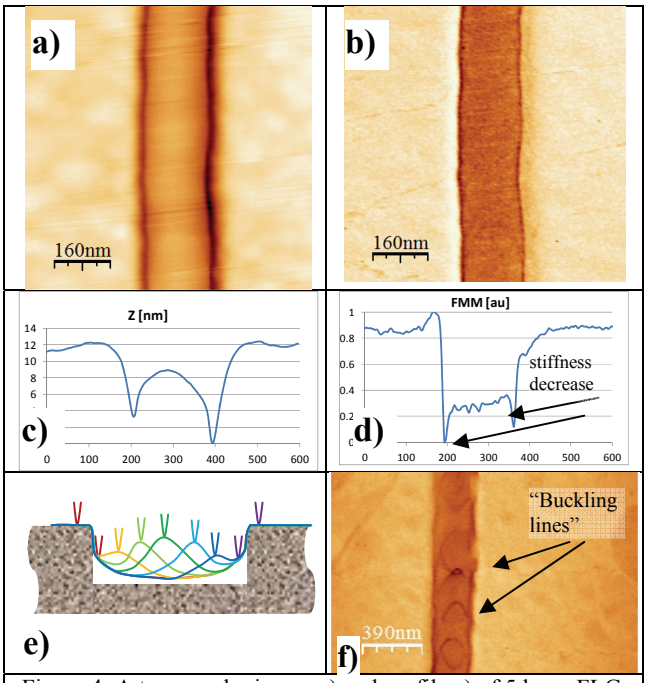

Figure 4: A topography image a) and profile c) of 5 layer FLG imaged at negative (pulling) loads of -9 nN. B, d) A simultaneously acquired stiffness map b) and stiffness profile d) of graphene sheet. e) Schematic representation of formation of topographical image - graphene layer bends upwards creating a convex profile with inflection lines parallel to the trench axis as the tip is scanned across the trench. f) "Buckling lines" where bending stiffness rapidly drops with FMM acquired at load closer to zero.

Such deformation shape would create inflection lines parallel to the trench axis of zero stress, with bending stiffness very different from the point loaded plate or membrane and therefore leading to the practically constant bending stiffness as measured with the FMM (figure 4b,d). From the stability of shells theory it is known that when shell zero curvature "buckling" is created, its stiffness strongly decreases. In view of this, one could expect that at negative forces such stiffness decrease would appear when SPM tip is near trench edges – the place where the buckling would initially start. And this is precisely the position where we have observed stiffness drop in the FMM images (figure 4b) and profiles (figure 4b). It should be noted here that for positive loads (c.f. figure 2f) no such drop was observed.

Finally, what would happen if FLG stiffness is mapped at loads closer to the zero net force? In full support of our model and analysis, the "buckling" now happens more in the central part of graphene sheet as seen in figure 4f. The shape of these lines suggest quite inhomogeneous distribution of the stress in the suspended exfoliated graphene layer, that is quite consistent with our observation of the formation of "nano-domes" as seen via UFM imaging.

3 CONCLUSIONS

In summary, we have mapped bending stiffness of few layer graphene sheets (5 to 10 layers thick) in contact with the substrate as well as suspended over 180 nm wide narrow trench by using combination of force modulation (FMM) and ultrasonic force microscopy (UFM) approaches. For supported areas UFM provided nanoscale resolution maps of zones of imperfect contact between graphene layer and the substrate, whereas FMM allowed measurements and exploration of nano-mechanical behaviour of suspended graphene films. We have directly observed the transition of graphene layer deformation from plate bending where shear forces are dominant to stretched membrane where in-plane tension is prevailing. Moreover, reversible shell instability of graphene layer was mapped with the nanoscale resolution for the first time, providing insight to the stresses in the free standing graphene films.

REFERENCES

[1] Novoselov, K. S.. Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Science 2004, 306, (5696), 666-669.

[2] Gass, M. H. et al. Free-standing graphene at atomic resolution. Nature Nanotechnology 3, 676-681, doi:10.1038/nnano.2008.280 (2008).

[3] Scarpa, F., Adhikari, S., Gil, A. J. & Remillat, C. The bending of single layer graphene sheets: the lattice versus continuum approach. Nanotechnology 21, doi:10.1088/0957-4484/21/12/125702 (2010).

[4] Lee, C., Wei, X. D., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 321, 385-388, doi:10.1126/science.1157996 (2008).

[5] Kolosov, O. V. & Yamanaka, K. Nonlinear detection of ultrasonic vibrations in an atomic force microscope. Japanese Journal of Applied Physics Part 2-Letters 32, L1095-L1098 (1993).

[6] Dinelli, F., Biswas, S. K., Briggs, G. A. D. & Kolosov, O. V. Measurements of stiff-material compliance on the nanoscale using ultrasonic force microscopy. Physical Review B 61, 13995-14006 (2000).

[7] Andrew Briggs and Oleg Kolosov, Acoustic Microscopy, 2nd ed,. Oxford University Press, (2009).