Nano-Scale Movement Induced In Graphene Ripples by Multi-Probe Microscopy

Mona Alyobi[1,2],Chris Barnett[1], Richard Cobley[1]
[1]College of Engineering, Swansea University, Swansea, UK
[2]College of science, Taibah University, Medina, Kingdom of Saudi Arabia
609349@swansea.ac.uk

***Abstract*— An Omicron low temperature multi-probe technique is used for manipulation of mechanically exfoliated suspended and attached graphene sheets on SiO_2 substrates. Scanning electron microscopy (SEM) and Raman spectroscopy are used to detect the graphene sheets and determine their thicknesses and quality, respectively. The interaction of the etched tungsten tip with the graphene is used to lift and release the sheet and induce artificial ripples. Both suspended and attached sheets onto the substrates show different behaviour in response to bias voltage.**

***IndexTerms*: graphene,multi-probe microscopy, ripples.**

I. INTRODUCTION

Graphene is a two dimensional material consisting of carbon atoms arranged on a honeycomb structure, which has attracted extensive interest in the scientific community since its discovery in 2004 [1] and has become one of the most investigated materials to date. This is due to its very low mass density coupled with exceptional electronic and mechanical properties such as large conductivity and high intrinsic strength, which make it an ideal material for different applications such as force, charge or mass sensing [2].

This atomically thin material is intrinsically non flat and has quasiperiodic or random ripples at the nano scale [3, 4]. Given that this affects its mechanical and electronic properties, there is an increasing need to realise the graphene sheet with controlled ripples. Extrinsic ripples can be imparted to the graphene through the interaction with the underneath substrate, as the deposited graphene sheets tend to accommodate the roughness of the substrate surface through the van der Waals (vdW) coupling and thus ripples can be induced on the graphene [5]. These ripples often cause scattering of charge carriers and reduce the carrier mobility of the graphene [6, 7]. In order to maintain the high mobility required for nano-electronic devices, hexagonal boron nitride [8] and flat mica substrates [9] have been used in the last few years, which eliminate the surface roughness and lead to very flat morphology. Furthermore, suspending the graphene sheets over the trenches has been used extensively to reduce the effects of the substrate and investigate their intrinsic properties such as carrier mobility [10] and intrinsic tensile strength [11].

On the other hand, the rippled graphene can be an ideal candidate for sensing applications. Recently, simulations expect enhancement of the chemical activity in the rippled graphene [12, 13]. The summits and troughs of the graphene ripples create active locations for the chemisorption or adsorption of different particles. It was suggested that this can open an approach for regioselective, tunable functionalisation of the graphene [14].

Extrinsic rippling can be created in the graphene sheets via different ways, for example, by silica nanoparticles (NPs) [15] or depositing the graphene onto micro-corrugated substrates [16]. Recently, scanning tunnelling microscopy (STM) studies have revealed that the STM tip can be used to form permanent ripples by locally pulling the graphene sheets [2, 17, 18].

In this work, we illustrate the local electrostatic manipulation and measurements of the rippled few- and multi-layer suspended graphene sheets, as well as the layers of the same sheets attached onto silicon dioxide /silicon (SiO_2/Si) substrates using a multi-probe system at low temperature.

II. EXPERIMENT

A. Sample preparation

Electron beam lithography was used to pattern Si with an array of holes and then the defined patterns were transferred onto Si through dry etching. Following this, a 90 nm SiO_2 layer was grown via thermal oxidation.

The preparation of the graphene sheets was done by mechanical exfoliation onto the substrates using the Scotch tape method. The graphene samples were then soaked in an ultrasonic bath with acetone for an hour, and then rinsed with isopropanol and DI water to remove glue residue [1, 19].

B. Sample characterisation

Scanning electron microscopy (SEM) was used to locate thin sheets of the graphene that were suspended over the holes using a secondary electron detector (mixed signal of upper and lower detectors) at primary electron acceleration voltages of 2 kV and working distance of 10 mm [20]. The number of layers was then determined by Atomic force microscopy (AFM).

AFM measurements were carried out under ambient condition in contact mode. The thickness of the graphene samples was determined from the step-height between the graphene sheets and the SiO_2 [1, 21]. The AFM images of graphene were analysed using the free Gwyddion software.

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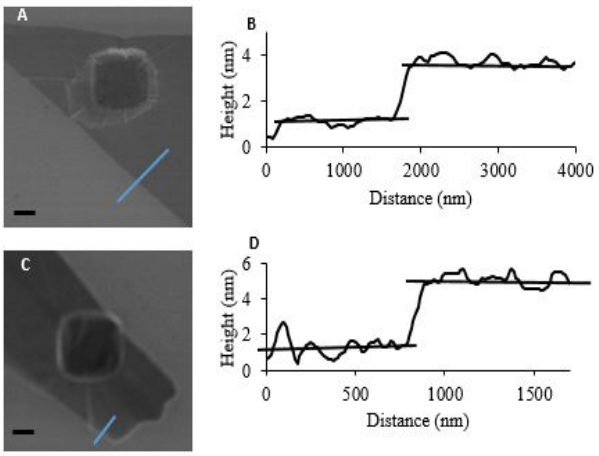


Fig. 1: Identification of the graphene samples. (A) SEM image of few-layer graphene (the scale 1 um), (B) Height profile measured by AFM along the blue line shown in A, (C) SEM image of multi-layer graphene (the scale 1 um), (D) Height profile measured by AFM along the blue line shown in C.

C. Multi-probe measurements

For multi-probe experiments, an Omicron LT multi-probe system in ultra-high vacuum (UHV) guided under SEM was used at 81.6 K in a base pressure of $1x10^{-10}$Torr. Two tungsten tips were used to perform manipulation and displacement measurements of the graphene sheets locally. These tips were fabricated by electrochemical etching of polycrystalline tungsten (W) wire and then annealed in UHV to remove probe oxide contamination [22]. The graphene samples were annealed in UHV at 200 ^{0}C for an hour.

Most research investigating graphene on a technologically relevant insulating substrates such as SiO_2/Si require the formation of contacts to the graphene to provide electrical contacts. However, these processing steps can cause change or damage to the sheet [23, 24]. Using a multi-probe system is critical because it allows process-free electrical contact to be made to the graphene by placing the probes on specific positions, which eliminates potential sources of contamination that arise when electrodes are made using conventional lithography. In our experiments, we used one tip to contact the sheet and provide ground, while another tip was used to perform the manipulation experiments with fixed voltages of +2, -2, +0.2, and -0.2 V. This tip was approached to graphene sheets until the current was detected and then retracted.

III. RESULTS AND DISCUSSION

A. Sample characterisation

SEM images of few- and multi-layer graphene are shown in Fig. 1a and Fig. 1c. These images can give estimation of the thickness of the layers. It is clear that thicker sheets appear darker as a result of the decreased intensity of the emitted secondary electrons with increased graphene thickness. The edge effects also appear much stronger as the thickness increases, which are indicated by a high brightness making clear white lines along the boundary of each sheet [25].

The number of the layers was determined using AFM. Figures 1b and 1d show AFM height profiles through the blue lines evident in the SEM images of few- and multi-layer graphene in Fig. 1a and Fig. 1c, respectively. The average height differences of the few-layer graphene and the multi-layer graphene are ~ 2.5 nm and ~ 3.6 nm and the estimated number of the graphene layers in the samples are 4 and 6 layers, respectively. These results were obtained according to the AFM results reported on few-layer graphene, where the height difference of single layer graphene is around 1 nm [1, 21], most probably due to different attraction forces between the tips and graphene films as compared to SiO_2 surface and the distance gap between SiO_2 surface and graphene.

B. Multi-probe experiments

We used multi-probe techniques to manipulate the graphene sheets and measure the local displacements of induced ripples through their interaction with the biased tip. When the tip is approached to the compliant sheets, it induces remarkable deformations. The acting forces between the graphene and the tip are intermolecular vdW and electrostatic forces, which could be either repulsive or attractive [2]. Graphene sheets also generate restoring forces when they are released.

The schematics in Fig. 2 summarise our multi-probe experiments. In (a), the tip starts at Z0 and approaches to the sample. At Z1 (b), it interacts with the sheets and the current increases until it reaches the pre-amp current limit. As the tip retracts (c), it pulls all the sheets until, at Z2 (d), the sheets have been released and the current returns to zero. The local electrostatic manipulations and measurements were done on few- and multi-layer suspended graphene sheets, as well as the layers of the same sheets attached onto the SiO_2/Si substrates.

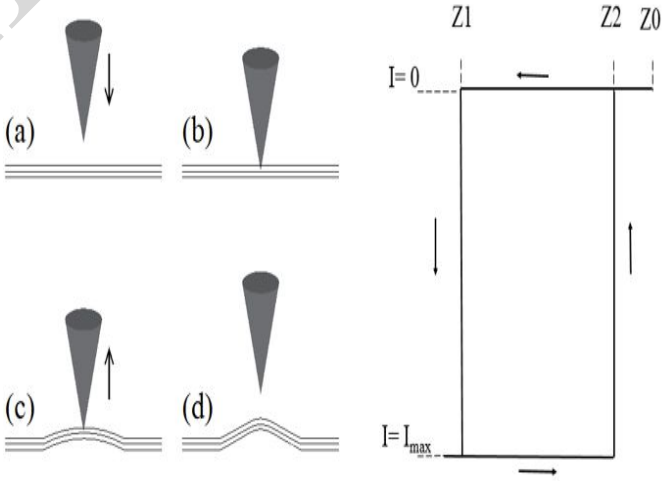


Fig. 2: Schematics summarise the multi-probe experiments through illustration the movements of the graphene with the tip.

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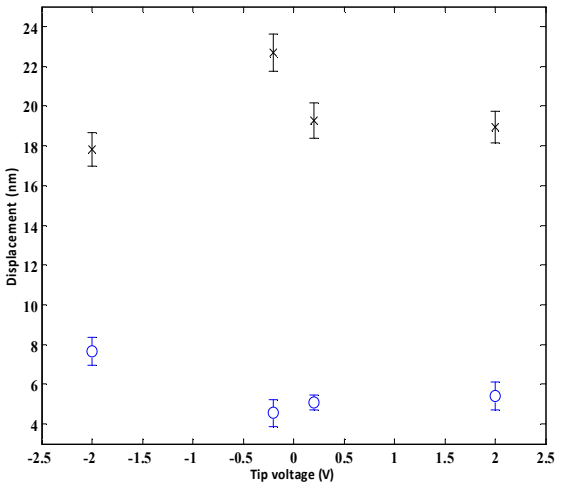


Fig. 3: Displacements of the ripples versus tip voltage in few-layer graphene, black crosses are for suspended graphene and blue circles are for attached graphene onto the substrate.The error bars show the standard error of ten repeated measurements taken at the same position.

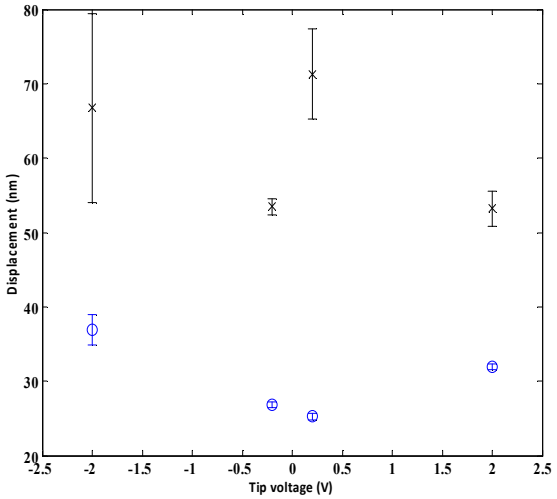


Fig. 4: Displacements of the ripples versus tip voltage in multi-layer graphene, black crosses are for suspended graphene and blue circles are for attached graphene onto the substrate. The error bars show the standard error of ten repeated measurements taken at the same position.

Both thicknesses of graphene sheets (suspended or attached to the substrates) show a hysteretic deflection in response to the tip bias as shown on the right in Fig. 2. The averaged 10 measurements of the displacements for each set of the fixed bias voltage for both graphene layers are shown in Fig.3. and Fig.4. It is clear that the displacements of both sheet thickness attachedonto the substrates increase with increasing tip voltage, which indicates that electrostatic forces between the tip and both attached few- and multi-layer graphene sheets is strong and dominant. However, the displacements of rippled suspended few-layer sheets appear higher with reduced tip voltage. However, this result is not clear with suspended multi-layer graphene and indicates that at lower voltage, the vdW forces between the tip and suspended sheets are attractive and dominant pull up forces, implying that electrostatic forces only generated small effects, as suggested in previous research findings [26].

Moreover, the displacements of both suspended sheets are higher than that of the sheets attached to the substrate, which is as a result of reducing the attractive vdW forces between the graphene and substrates due to suspending the sheets. Previous studies have indicated that the work function of suspended graphene is 100 times smaller than that of the graphene laying on the substrates, as the suspended sheets are free to move toward the tip when it is retracted [27].

In addition, the displacement of multi-layer sheets is higher than the displacement of few-layer sheet. This can be explained in terms of restoring elastic forces of graphene itself. The effects of restoring forces are stronger in thinner sheets as they are more elastic and can rebound more than thicker sheets, thus the size of deformations are smaller.

It can be concluded that when the biased tip is brought into tunnelling directly above the graphene sheet, the sheet will be attracted to the tip through the electrostatic force of the tip or vdW force between the tip and the graphene, and will move toward it. Then, as the tip retracts, the graphene sheet will follow it until compensated via the restoring elastic force of the graphene and the vdW force between graphene and the substrate.

IV. CONCLUSION

This study shows that the multi-probe technique can be used to manipulate graphene sheets locally and induce permanent ripples by both repulsive and attractive tip–graphene sample interactions. This provides a method for controlling the local height and curvature of the graphene. In addition, it can be a useful tool to study the elastic and electronic properties of the graphene sheets under deformation, which plays a crucial role in the progress of graphene electromechanical nano-devices.

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REFERENCES

[1] Novoselov, K.S., et al., Electric field effect in atomically thin carbon films. science, 2004. 306(5696): p. 666-669.
[2] Breitwieser, R., et al., Flipping nanoscale ripples of free-standing graphene using a scanning tunneling microscope tip. Carbon, 2014. 77: p. 236-243.
[3] Fasolino, A., J. Los, and M.I. Katsnelson, Intrinsic ripples in graphene. Nature materials, 2007. 6(11): p. 858-861.
[4] Meyer, J.C., et al., The structure of suspended graphene sheets. Nature, 2007. 446(7131): p. 60-63.
[5] Ishigami, M., et al., Atomic structure of graphene on SiO2. Nano letters, 2007. 7(6): p. 1643-1648.

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[6] Katsnelson, M. and A. Geim, Electron scattering on microscopic corrugations in graphene. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2008. 366(1863): p. 195-204.
[7] Ni, G.-X., et al., Quasi-periodic nanoripples in graphene grown by chemical vapor deposition and its impact on charge transport. ACS nano, 2012. 6(2): p. 1158-1164.
[8] Dean, C.R., et al., Boron nitride substrates for high-quality graphene electronics. Nature nanotechnology, 2010. 5(10): p. 722-726.
[9] Lui, C.H., et al., Ultraflat graphene. Nature, 2009. 462(7271): p. 339-341.
[10] Bolotin, K., et al., Temperature-dependent transport in suspended graphene. Physical review letters, 2008. 101(9): p. 096802.
[11] Lee, C., et al., Measurement of the elastic properties and intrinsic strength of monolayer graphene. science, 2008. 321(5887): p. 385-388.
[12] Boukhvalov, D., Tuneable molecular doping of corrugated graphene. Surface Science, 2010. 604(23): p. 2190-2193.
[13] Boukhvalov, D.W. and M.I. Katsnelson, Enhancement of chemical activity in corrugated graphene. The Journal of Physical Chemistry C, 2009. 113(32): p. 14176-14178.
[14] Gao, X., et al., Regioselectivity control of graphene functionalization by ripples. Physical Chemistry Chemical Physics, 2011. 13(43): p. 19449-19453.
[15] Yamamoto, M., et al., "The Princess and the Pea" at the nanoscale: wrinkling and delamination of graphene on nanoparticles. Physical Review X, 2012. 2(4): p. 041018.
[16] Scharfenberg, S., et al., Probing the mechanical properties of graphene using a corrugated elastic substrate. Applied Physics Letters, 2011. 98(9): p. 091908.
[17] Mashoff, T., et al., Bistability and oscillatory motion of natural nanomembranes appearing within monolayer graphene on silicon dioxide. Nano letters, 2010. 10(2): p. 461-465.
[18] Neek-Amal, M., et al., Thermal mirror buckling in freestanding graphene locally controlled by scanning tunnelling microscopy. Nature communications, 2014. 5.
[19] Novoselov, K., et al., Two-dimensional atomic crystals. Proceedings of the National Academy of Sciences of the United States of America, 2005. 102(30): p. 10451-10453.
[20] Hiura, H., H. Miyazaki, and K. Tsukagoshi, Determination of the number of graphene layers: Discrete distribution of the secondary electron intensity stemming from individual graphene layers. Applied Physics Express, 2010. 3(9): p. 095101.
[21] Li, X., et al., Chemically derived, ultrasmooth graphene nanoribbon semiconductors. Science, 2008. 319(5867): p. 1229-1232.
[22] Cobley, R.J., et al., Quantitative analysis of annealed scanning probe tips using energy dispersive x-ray spectroscopy. Applied Physics Letters, 2013. 102(2).
[23] Yakes, M.K., et al., Conductance anisotropy in epitaxial graphene sheets generated by substrate interactions. Nano letters, 2010. 10(5): p. 1559-1562.
[24] Klarskov, M.B., et al., Fast and direct measurements of the electrical properties of graphene using micro four-point probes. Nanotechnology, 2011. 22(44): p. 445702.
[25] Kochat, V., et al., High contrast imaging and thickness determination of graphene with in-column secondary electron microscopy. Journal of Applied Physics, 2011. 110(1): p. 014315.
[26] Klimov, N.N., et al., Electromechanical properties of graphene drumheads. Science, 2012. 336(6088): p. 1557-1561.
[27] Xu, P., et al., Atomic control of strain in freestanding graphene. Physical Review B, 2012. 85(12): p. 121406.

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