The Dynamics and Control of Bubbles Residing under Graphene Films

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Introduction:

Graphene, a single atomic sheet of carbon atoms, is known for its superior electrical, thermal and mechanical properties. Because of these advantageous qualities, graphene is currently being used in a variety of applications and must undergo various fabrication processes. In one such process, mechanically exfoliated graphene is transferred from poly(methyl methacrylate) (PMMA) to an hexagonal boron nitride (hBN) substrate. After the transfer, the formation of bubbles between the graphene and substrate are observed. Previous studies have also observed the formation of these bubbles and have detected mass transport beneath the graphene films when annealed, observing the bubbles coalescing into larger units [1]. It is not known with certainty what is trapped beneath these bubbles or why they occur, however understanding this could lead to improved fabrication methods or even new, innovative applications of the material. In this project the properties of the observed bubbles are further investigated by manipulation via an applied back gate voltage and obtaining force-distance curves. Additionally, the interaction between graphene and substrate is of interest and can be probed with these methods.

Methods:

Graphene was acquired by mechanical exfoliation and transferred onto a silicon (Si)-wafer with a top layer of Aquasave and PMMA. Monolayer graphene flakes were found by optical contrast and confirmed via Raman spectroscopy. The hBN flakes were transferred to the Si substrate by exfoliation and measured to be 20-30 nm in height using atomic force microscopy (AFM). Graphene was then transferred from PMMA to the hBN substrate in ambient conditions via the 'dry transfer method' [2]. At this point, small bubbles were observed with the optical microscope. To enlarge the bubbles, the sample was annealed in hydrogen (H_2) and silver (Ag) at 400°C for three hours. Gold contacts were patterned via electron beam lithography and the sample was glued onto a printed circuit board (PCB) where wires were bonded for electrical measurements.

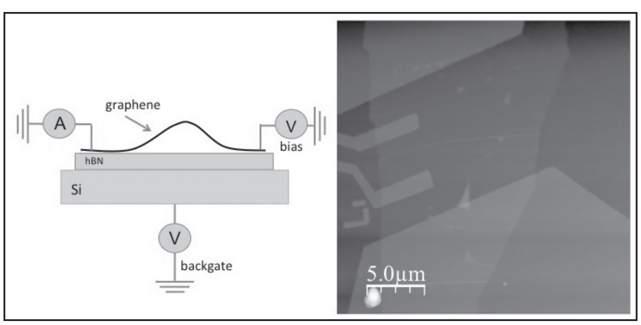

Figure 1: Schematic (left) and AFM image (right) of the device.

Figure 1 depicts a schematic of the final device. Two devices were fabricated, each with several bubbles on which measurements could be conducted. Bubble size ranged from 0.4-1.0 μm in diameter and between 30-150 nm in height.

Measurements were carried out using a Nanoscope Multi-mode atomic force microscope (AFM) in conjunction with an electrical set up. The contacts of the sample were connected to IVVI rack via a matrix box, allowing a bubble to be imaged by AFM while a back gate voltage was applied.

Using WxSM image software, AFM images were used to obtain quantitative data on the volume of the bubble at each applied back gate voltage. AFM images were taken using both contact mode and tapping mode. The following measurements were carried out using this set up: volume changes in response to applied backgate voltage swept from -30 to 30V in 3V intervals, volume changes in response to a constant voltage sustained over a period of 48 hours, and IV curves.

Additionally, force distance curves were obtained using AFM for regions both on the graphene bubble and on graphene flush with the substrate. The probes used were MicroCantilever contact mode tips, model OMCL-AC160TS-R3 with a spring constant of ~ 26.1 N/m.

Results:

The graphene bubbles presented a diverse array of responses when subject to the AFM measurements. Irreversible changes in volume were observed over the sweep from

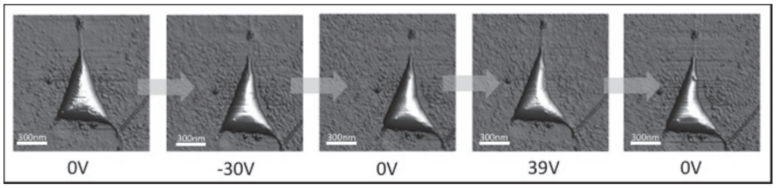

Figure 2: Changes in volume in response to applied backgate voltage.

-30V to 39V both qualitatively in the AFM images as well as quantitatively in the flooded volume measurements. As the applied voltage increased, the bubble pulled into contact with the substrate along its edges, as shown in Figure 2. Modeling the bubble as a parallel plate capacitor, the electrostatic force initially required to pull graphene into contact with the substrate was approximately 19.6 pN, corresponding to 3V.

In response to the constant backgate voltage applied over an extended time (48 hrs), there was evidence of the graphene bubble deflating. Before and after images reveal the occurrence of mass transport beneath the graphene film (Figure 3). The proximity of the deflated graphene bubble to the edge of the graphene film is an indication that the contents of the bubble may have escaped out the edge. Additionally, several graphene bubbles ruptured under the force of the AFM tip due to shear forces present during contact mode imaging.

Force-distance measurements taken on the bubble show that the bubble is deformed by the AFM tip ~ 12 nm before tip deflection occurs (Figure 4). Upon deflection, the slope of the curve is consistent with the slope of an AFM tip interacting with graphene on the substrate, indicating that after initial deformation the tip is deflected as if it were on a hard substrate. The applied force necessary to deform the bubble was calculated to be 300 nN.

Conclusions:

The measurements and observations gathered do much in helping us to characterize these graphene bubbles. The deformation of the bubbles reveals that the contents are a compressible substance. While further study is necessary to fully to understand these bubbles, the ability to rupture, move, deflate and control the shape of the bubbles by applying shear, normal and electrostatic forces make graphene bubbles an exciting prospect for future applications of the material.

Future Work:

Measurements should be repeated to confirm the above observations. Additionally, puncturing a graphene bubble via focused ion beam will give insight as to the contents of bubble.

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References:

[1] E. Stolyarova, et al. Observation of Graphene Bubbles and Effective Mass Transport under Graphene Films. Nano Lett., 2009, 9(1) 332-337.

[2] Baart, T.A. February 2011. Quantum Dots on Bilayer Graphene made on a Substrate of Boron Nitride using Split Gates. Master Thesis, Delft University of Technology.

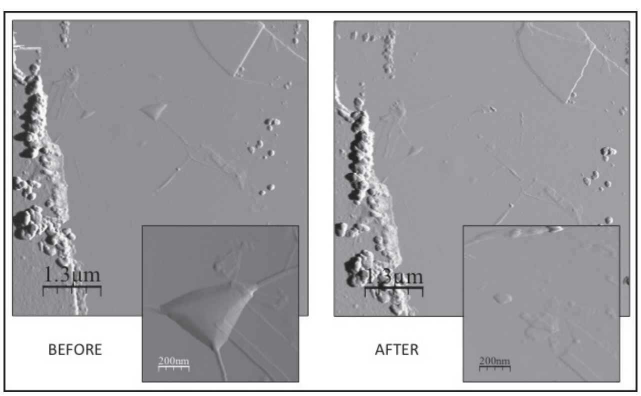

Figure 3: Deflated bubble after constant voltage applied for 48 hours.

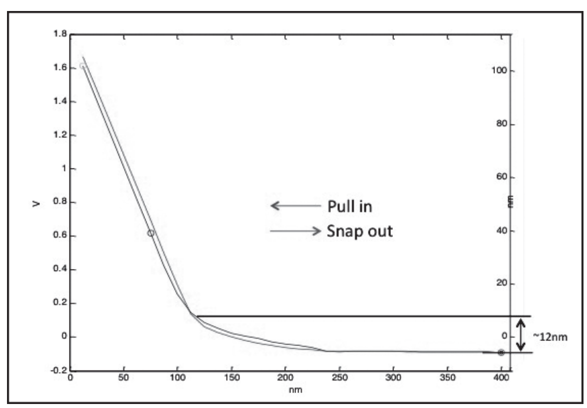

Figure 4: Force-distance curve produced on graphene bubble.