Abstract

Graphene, a single atomic layer of carbon atoms, has continued to draw much attention due to its extraordinary properties and application potential. The electronic and mechanical properties of pristine graphene sheets are outstanding but structural defects deteriorate its mechanical properties. Defects in a graphene structure are unavoidable; they can appear during fabrication processes or environmental and operating conditions in which the graphene based device is used. However, structural defects can be useful in that, they can be used to engineer certain properties of graphene material to achieve new functionalities. Therefore, it is important to understand the relationship between structural defects and graphene’s properties. In this study, the effects of structural defects on the nanomechanical properties of graphene have been investigated using Multimode 8 AFM. Graphene sheets on SiO$_2$ substrate have been irradiated with Gallium ions to introduce controlled amounts of structural defect. Using the PeakForce QNM mode, the relationship between the nanomechanical properties and structural defect density has been found.
# Contents

Abstract i

Contents ii

Abbreviations iv

1. Introduction 1

2. Theory 1

   2.1. Graphene theory 1

   2.2. Atomic Force Microscope (AFM) 4

      2.2.1. PeakForce QNM 5

   2.3. Other related studies 7

3. Nanomechanical properties study. 9

   3.1. Structural and Raman spectroscopy studies 9

   3.2. Young’s modulus mapping 12

      3.2.1. Experimental details 12

         3.2.1.1. Young’s Modulus 13

         3.2.1.2. Evaluation 13

      3.2.2. Results and Discussion 15

         3.2.2.1. Young’s modulus of graphene samples before ion irradiation 15

         3.2.2.2. A study of defected and un-defected areas 17

         3.2.2.3. Relationship between defect density and surface roughness of samples 19

         3.2.2.4. Relationship between defect density and Young’s modulus of samples 20
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Full name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>DMT</td>
<td>Derjaguin, Muller, Toporov</td>
</tr>
<tr>
<td>DV</td>
<td>Double Vacancy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FP</td>
<td>Frenkel Pair</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly ordered pyrolytic graphite</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-electromechanical Systems</td>
</tr>
<tr>
<td>NEMS</td>
<td>Nanoelectromechanical systems</td>
</tr>
<tr>
<td>QNM</td>
<td>Quantitative NanoMechanics</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Transmission Microscope</td>
</tr>
<tr>
<td>SV</td>
<td>Single Vacancies</td>
</tr>
<tr>
<td>SW</td>
<td>Stone-Wales</td>
</tr>
</tbody>
</table>
1. Introduction

Due to the flexibility of carbon bonding, carbon-based systems show many different structures with an equally large variety of properties which are mainly as a result of the dimensionality of these structures. Fullerenes (0D), Graphite (3D), Carbon nanotubes (1D), and Graphene (2D) are all allotropes of carbon. Graphene plays an important role among the allotropes of carbon since it is the basis for the understanding of the electronic properties of other carbon allotropes. It can be said that all the other allotropes of carbon are made up of graphene sheets. Konstantin Novoselov and Andrew Geim obtained the Nobel Prize in the year 2010 for pioneering experiments on graphene a 2D material. Due to its two dimensional structure, its properties are highly influenced by structural defects. However, the effect of structural defects on its nanomechanical properties is not well understood. Therefore, in this study, the relationship between structural defect density and the nanomechanical properties of graphene sheets has been investigated.

2. Theory

2.1. Graphene theory

Andre Geim described “free-standing” or “isolated graphene” to be “a single atomic plane of graphite which is sufficiently isolated from its environment” [1]. Graphene is made out of carbon atoms arranged in a honeycomb structure composed of hexagons. The unique properties of graphene have attracted the interest of many researchers. Studies have shown pristine graphene to be the strongest material known to man, with an elastic modulus (Young’s modulus) of about 1.0TPa [2-5] and an intrinsic Tensile strength of 130GPa. [3] This strength is as a result of the strong $\sigma$-bonds between graphene's carbon atoms. However, its mechanical properties are
deteriorated by structural defects. Structural defects influence graphene properties and hence the performance of graphene based devices.

Due to its extraordinary electronic and structural flexibility, graphene properties can be modified structurally and/or chemically in various ways. For example, by particle irradiation [6, 7] depositing metal atoms or molecules on the surface, intercalation, and incorporation of nitrogen and/or boron in the structure, and using substrates with different properties that modifies its electronic structure. [8] The understanding of its properties and possible ways of modifying the properties can result to very new frontier in science.

It should be noted that, an infinite number of various lattice defects could exist in graphene structure as noted by Banhart et al. [9]. In three-dimensional materials, defects are said to be intrinsic if the crystalline order of the material is disturbed without foreign atoms or force. The latter create extrinsic defects. For macroscopic crystal-like materials, the intrinsic imperfections have various dimensionalities [9]. Zero dimensional defects in 2D graphene structure are similar to that in 3D materials, but line defects have different effects in graphene. 3D defects do not occur in a graphene sheet. Stone-Wales (SW) defects, Single Vacancies (SV), Multiple Vacancies, carbon adatoms, foreign adatoms, Substitution impurities, Dislocation-like defects, grain boundaries, cracks, and edge defects are some of the common defect types and structural disorders observed in graphene structure.

Previous studies have shown that, vacancy defects have greater effect on the nanomechanical properties of graphene than other types of defects. [10-14] According to Jing et al. [2] the Stone Wales defects do not break the sp²-bonding hence they have minor influence on the young
modulus of graphene. Jing et al. [2] predicted that, vacancy defects with more dangling bonds deteriorate the Young’s modulus of graphene sheets more than defects with few dangling bonds. For Vacancy defects, the missing carbon atoms result to dangling bonds near the carbon atoms and weaken the structure of graphene. This leads to a decrease in the Young’s modulus of graphene. Graphene sheet with Single Vacancy (SV) defects has more dangling bonds than the one with Double Vacancy (DV) defects and hence its Young’s modulus drops more than sheets with DV defects. [2] The sp$^3$-type defects do not affect the Young’s modulus of graphene while vacancy defects leads to a significant drop in the mechanical properties of graphene. [14] Therefore, the elastic properties of graphene are affected by these defects differently and the effect increases with increase in defect density as seen in this study.

In practice, all these different types of defect occur in a graphene sheet at the same time. Therefore, it is important to understand the effect of all these defects on the properties of graphene. In this study, graphene sheets have been irradiated with Gallium ions to create structural defects on the sheets. [6, 7] Practically, the different types of defects mentioned above are introduced in the graphene sheets. The aim of this study is to investigate the collective effect of these defects on the nanomechanical properties of graphene sheets. A quantitative relationship between the structural defect density and the nanomechanical properties of graphene sheets has been found in this study. To be able to use graphene in designing efficient and durable graphene-based devices, it is important to understand the defects-properties relationship of a graphene sheet.
2.2. Atomic Force Microscope (AFM)

Atomic Force Microscope (AFM) utilizes the tip-sample surface interatomic interaction forces. A sharp probe is scanned along the sample surface. While the tip is being scanned on the sample surface, the interatomic forces between the surface of the sample and the tip causes a vertical displacement of the tip and corresponding bending of the cantilever. The cantilever can be displaced by direct contact force, van der Waals forces, electric force, magnetic force, etc. One major method used to detect this movement of the cantilever is the use of a laser beam. A laser beam is transmitted to and reflected by the cantilever to form a spot on a position-sensitive photo-detector (PSPD) as shown in figure 1.

![Schematic diagram of the basic principle of AFM (Image extracted from Keysight Technologies)](image)

If the cantilever vibrates, the spot also vibrate correspondingly. The detector then converts the laser spot movement to electric signals, which is then provided to a computer for processing. This movement of the spot is interpreted by the AFM software to give information about the movement of the probe and hence the topography of the sample. The system can sense sub-
Ångstrom vertical movement at the free end of the cantilever, where the tip is located. The signal from the photodetector passes through a feedback circuit into the z-movement part of the scanner. This is used to control the distance or force between the probe and the sample surface.

There are numerous AFM Modes. In this study, the PeakForce QNM mode has been used to measure the quantitative mechanical properties of samples.

### 2.2.1. PeakForce QNM

PeakForce QNM is an imaging AFM mode the gives height images and Quantitative Nano-Mechanical sample property images at the same time. In this mode, the peak force (the maximum force applied on the sample surface by the AFM tip) is used as the feedback signal. PeakForce QNM enables quantitative measurement of nano-scale properties of materials. These properties include elastic modulus, dissipation, adhesion, and deformation. This mode contains two parts. The PeakForce Tapping part, which acts as the feedback mode used to track and image the sample surface, and the QNM part in which the PeakForce Tapping mode performs force curves, which are used to extract quantitative mechanical properties of the material.

In PeakForce Tapping, the AFM probe usually in intermittent contact with the sample surface as it is scanned across the surface of the sample. The cantilever vibrates at a frequency just below its resonance frequency. The z-piezo vibrates at a frequency of about 2 kHz. The AFM makes extremely hurried force curves at every data point in the image. Analysis of the force curve data occurs on a fly, which give a map of the mechanical properties of the sample with high resolutions.
The curve is measured at each data point of the image by examining the cantilever deflection as it advances, contacts and retracts from the sample surface. When the tip is far from the sample surface, (point A in figure 2) the tip experiences little or no force. When the tip is moved towards the sample surface, it experiences an attractive force (this is due to Van der Waals, electrostatic, or capillary forces).

![Figure 2](image)

**Figure 2.** (i) Shows a plot of force and piezo Z position as a function of time, point B is the jump-to-contact point, C the peak force, and D the adhesion between the tip and the sample. Figure (ii) shows a plot Force versus Z piezo position, and (iii) is a plot of force versus separation in which separation has been determined out of the cantilever deflection and the Z piezo position. The plot in (iii) is useful in the analysis of the mechanical properties of the sample. Image retrieved from (Pittenger *et al.*, 2010)

At point B, the attractive force becomes greater compared with the cantilever stiffness and the tip is attracted to touch the sample surface. The tip then remains on the surface and the interaction force between the tip and the sample surface increases to a maximum (the peak force, the force at point C) when the z-position of the scanner reaches its lowest position C. When the direction of motion of the probe is reversed, tip-sample interaction force drops to a minimum at point D in Fig 2. This force gives the adhesion force between the sample and the tip. The tip then leaves the surface and then experiences long-range forces. [15]
2.3. Other related studies

Several studies have focused on the Young’s modulus of pristine graphene and measured a value of about 1.0TPa. [2-5] although, this is the agreed value for the Young’s modulus of pristine graphene, some studies has given different values. For instance, a Young’s modulus of 0.5GPa has been reported. [16] Lee et al. [17] estimated the Young’s modulus value of about 2.4TPa and 2.0GPa for single and bilayer graphene respectively. These different values could be as a result of the sample condition and/or the experimental setup factors.

Previous theoretical studies have predicted a drop in Young’s modulus of graphene films with increasing structural defect density. [2, 10, 11, 12, 13, 17,18] Increase in grain size of the graphene structure leads to an increase in the tensile strength and elastic modulus of polycrystalline graphene. [5] Increase in Structural defect coverage/density lead to a decrease in the strength and fracture strain of graphene sheets, [20] and increased bending/displacement of a simply supported or clamped graphene sheets. [21] However, the effect is small for small amounts of defects.

Very few experimental results, on the relationship of structural defect density and the mechanical properties of graphene, have been reported and there is need for more studies. Zandiatashbar et al. [14] using AFM nanoindentation technique of suspended graphene sheets found that, vacancy defects leads to reduction in elastic modulus of graphene sheets. No reported studies on the effect of structural defects on the elastic properties of graphene on a substrate. Therefore, in this study the Young’s modulus of defected graphene sheets on SiO₂ substrate has been investigated.
The adhesion energy between graphene and SiO$_x$ for 1-5 layers of graphene has been determined by employing pressurized blister test [22]; they obtained adhesion energy of 310mJ/m$^2$ for 2-5 layers graphene and 450mJ/m$^2$ for a monolayer graphene. Other studies have reported the adhesion energy of 720mJ/m$^2$ [23] and 12,800 J/m$^2$ [24] between graphene and copper. Li et al. [25] measured adhesion energy of about 255mJ/m$^2$, 270 mJ/m$^2$, and 307 mJ/m$^2$, for graphene/gold, graphene/SiO2, and graphene/graphene respectively. However, studies on the effect of structural defects on the adhesion energy are lacking. In this study, the relationship between adhesion energy and structural defect density has been studied.
3. Nanomechanical properties study.

3.1. Structural and Raman spectroscopy studies

Three types of samples were studied; graphene samples prepared in Cryo-temperatures on SiO$_2$ substrate, graphene samples prepared in room temperature (RT) on SiO$_2$ substrate and the SiO$_2$ substrate samples. The AFM image and Raman spectrum of graphene before ion irradiation is shown in figure 3. In that spectrum, the intensity ratio of 2D peak (2700 cm$^{-1}$) and G peak (1550 cm$^{-1}$) is three, indicating the single layer property of graphene. Normally, the D peak at 1350 cm$^{-1}$ is the representative feature of defects, and in our case it is low, which means the quality of our graphene is good.

![Raman spectrum and AFM image](image)

Fig 3. (a) Raman spectrum for pristine graphene (before ion irradiation) (b) Height image of graphene sheets on SiO$_2$ substrate before irradiation.

The AFM image (Figure 3 (b)) revealed the presence of foreign nanoparticles, and grain boundaries in the samples. To study the influence of structural defects on the mechanical properties of graphene sheets, thirteen (13) areas of the sample (shown in figure 4 (a)) were...
Defected areas irradiated with different ion doses using the Focused Ion Beam (FIB). A beam of gallium primary ions is scanned across the surface of the sample in order to create structural defects. The ion beam knocks the sample surface, which leads to defect formation on the graphene sheets by atom displacement and bond rotation. The amount of defects formed depends on the primary current applied or the energy and amount of ion particles. Therefore, by controlling this current, different levels of defects were introduced in different areas (This was done by another member of the group).

![Defected areas illustration](image)

**Fig. 4.** (a) An illustration of the defected areas in the samples (b) AFM image of ion irradiated graphene.

Ion irradiation causes defects in the sample structure. Lehtinen *et al.* [26] studies show that, single and double vacancy defects are the dominant defects in an ion irradiated graphene. The study also shows few triple vacancies, spatially close Frenkel pairs (FP) i.e., adatom-vacancy pairs and Stone-Wales defects. The effect of ion irradiation is more pronounced for a single layer graphene than in bilayer and multi-layer graphene. [27] Compagninia *et al.* [27] observed that, for the same amount of ion dose, higher amount of disorder appear in a single layer graphene on
a SiO$_2$ substrate than in bilayer and multilayer graphene. They however, noted that, the interaction of the graphene sheets and the substrate plays a big role on the observation.

AFM images of the irradiated graphene surfaces did not have observable defects caused by the ion bombardment as shown in figure 4 (b).

![Graph showing I$_D$/I$_G$ ratio vs ion dosage](image)

**Fig 5.** Plot of I$_D$/I$_G$ as a function of ion dosage in RT-graphene (black) and Cryo-graphene (red)

STM images (not shown in this report) of irradiated graphene revealed presence of vacancy defects and even nano-holes on the sheets after high ion dose exposure. For low ion dose, graphene sheets did not show major structural defects, Stone-Wales and some few vacancy defects are however expected to be present.

In Raman, the intensity ratio of D peak and G peak indicates the defect level. Normally this can be well explained by the structure change in graphene lattice. Figure 5 shows the relation of the
intensity ratio of D peak and G peak in Raman spectroscopy as a function of the applied ion dosage. When the defects increase, the ratio of $I_D/I_G$ will also increase until a peak, this is the typical transfer of graphene from single crystal to polycrystalline. Then the ratio will drop, indicating the transfer from polycrystalline to amorphous carbon. In figure 5, both samples show this typical curve above, but Cryo-graphene indicates a significant left-shift compared with RT-graphene, which means that at a certain ion dosage, Cryo-graphene has higher defects density than RT-graphene and this could imply the property change in the following mechanical test.

3.2. Young’s modulus mapping

3.2.1. Experimental details

In this study, MultiMode 8 Atomic Force Microscope (AFM) was used to study the nanomechanical properties of the defected samples using the PeakForce QNM mode. These experiments were performed in ambient conditions. In order to experimentally study, the effect of atomic scale structural defects and disorders on the elastic modulus of graphene, each of the three sample types mentioned above was studied separately. Each sample’s nanomechanical properties were mapped using TAP525A probe with a spring constant of 200N/m and resonance frequency $f_0 = 525 kHz$. The scan areas were set at $2 \times 2 \mu m^2$ and a theoretical Poisson’s ratio of 0.17 was used. HOPG calibration sample was used in the calibration process. The tip radius and cantilevers spring constant were calibrated using the procedure given by Bruker Corporation, [28]. The samples were scanned at a scan rate of 2kHz. To analyze the images, the NanoScope Analysis software was used; quantitative measurement of the Young’s modulus of the samples
was extracted from the PeakForce QNM images. Nanomechanical properties of defected samples were compared with that of defect-free samples.

### 3.2.1.1. Young’s Modulus

Young’s modulus (elastic modulus) is a measure of the stiffness of an elastic material. The study of Young’s modulus using AFM in this experiment has utilized the Derjaguin, Muller, Toporov (DMT) model. Young’s Modulus was obtained from the retract curve fit using the model, which is defined by the following equation,

\[
F_{\text{tip}} - F_{\text{adh}} = \frac{4}{3} \frac{E_s}{1-v_s^2} \sqrt{R(d - d_o)^3} \quad \text{for} \quad E_s \ll E_{\text{tip}}
\]  

where \(F_{\text{tip}} - F_{\text{adh}}\) is the force on the tip relative to the adhesive force, \(R\) is the tip end radius, \(d - d_o\) is the sample deformation, \(E_{\text{tip}}\) is the Young’s modulus of the tip, and \(E_s\) and \(v_s\) are the Young’s modulus and Poisson’s ratio of the sample respectively.

If the AFM is supplied with the Poisson’s ratio of the sample, the DMT Modulus channel will give the Young’s modulus of the samples according to the model described above.

### 3.2.1.2. Evaluation

In this study, the use of AFM PeakForce QNM has been found to be an effective method of studying the elastic properties of materials. Compared with nano-indentation experiment used previously, the mapping technique is more reliable since multiple indentations (262, 144 indentations) are performed per each scan area of the sample in this study. This can effectively give very reliable information on the properties of the material.
While scanning at a rate of 2kHz, the AFM performs force curves at each pixel. Although, this is done at a very high speed, the force curves were found to be in good shape as shown in figure 6. This shows that, errors were minimal. The dissipation, as seen from the force curves (hysteresis between the load and unload curves), [28] is small. This confirms that, the deformation in this study was purely elastic unlike the nanoindentation where plastic deformation occurs.

![Graphs showing force curves](image)

**Fig 6.** Force curves (a) a pair of force curves (b) multiple force curves showing small variations. blue is the approach while red the retract curve.

However, in addition to the structural defect induced by ion bombardment, other defects were present in the samples that could influence the mechanical properties of graphene. These include grain boundaries, cracks, foreign particles on the surface, and disorders due to the interaction of the graphene sheets and the substrate. These kinds of defects are expected to influence the mechanical properties of the graphene sheets in addition to the introduced defects by ion irradiation.

Nevertheless, the observed relationship between structural defects and the mechanical properties in this study agree with previous studies. [14] It has been found that, ion irradiation does not
significantly change the elastic modulus of the SiO$_2$ substrate. Therefore, the measured change in Young’s modulus is as a result of the properties of the graphene sheets; the substrate’s contribution to the change is insignificant. This makes the results in this study more reliable.

3.2.2. Results and Discussion

3.2.2.1. Young’s modulus of graphene samples before ion irradiation

The Young’s modulus of graphene/SiO$_2$ was determined using the AFM as described above. Particles of foreign materials with lower elastic modulus were observed on the graphene surface as shown in figure 7. Thus, these particles could generally lower the measured elastic modulus of the samples.

![Fig 7. DMT modulus of defect-free Graphene. (a) DMT modulus image (b) Cross-section graph](image)

The measured values of Young’s modulus for graphene/SiO$_2$ before ion irradiation were ~97.4GPa for RT graphene and ~96.8GPa for Cryo graphene. Compared to the previous measured value for pristine graphene (1TPa) the values obtained in this experiment were found to be low. To understand the difference we consider the technique used to measure Young’s modulus of graphene sheets. Previous studies have employed nanoindentation technique [2, 3,
14] to determine the Young’s modulus of suspended pristine graphene sheets while in this study, nanomechanical-mapping technique has been used. Nanoindentation experiments (using AFM) of graphene suspended above a trench or a Hole) probe the σ-bond; the indentation involve stretching graphene sheets along the σ-bond. This can lead to breaking of the σ-bonds (i.e., plastic deformation is involved). However, the mapping technique (using AFM) of graphene on a substrate probe the properties of both the σ-bonds and π-bonds. The deformation mechanism for graphene on a substrate is a complicated combination of stretching of the σ-bonds and compressing along the π-bonds but depends largely on the properties of the π-bond. The properties of the substrate also have an effect on the measured value of the Young’s modulus. In our case, the substrate SiO$_2$ is very soft (with a Young’s modulus of about 60GPa [29] compared to graphene (with a Young’s modulus of about 1TPa). The spring constant of the cantilever is also another factor that can affect the measured Young’s modulus.
3.2.2.2. A study of defected and un-defected areas

The RT graphene sample was mapped on the boundary between the non-defective and defective areas. The height of the irradiated area was observed to have increased by about 0.94nm compared to the non-defective area for Room Temperature graphene samples as shown by the cross section graph in Fig 8 (a).

Fig 8. (a) Height Image of non-defective (left) and defective (Area 12) (right) areas of RT graphene and its cross section graph. Ion irradiated RT graphene engorge. (b) DMT Modulus Image of defect-free (left) and defective (right) (area 12) RT graphene. Defective graphene has a lower elastic modulus than pristine graphene.
It was observed that the DMT modulus of defective sample is lower than that of non-defective one as seen in Fig 8. (b). A similar study was carried out for the SiO$_2$ substrate. The SiO$_2$ sample was mapped on the boundary between non-defective and defective areas. It was found that, there was swelling effect observed for the irradiated region of SiO$_2$ as shown in Fig 9 (a). The height of the irradiated sample increased by about 0.5-0.8nm. Etching effect was also observed at the boundary.

Fig. 9. (a) Height image of defect-free (left) and defective (right) (Area 13) SiO$_2$. The irradiated area expanded. (b) DMT modulus of defect-free (left) and defective (right) (Area 13) SiO$_2$. Ion irradiation slightly change the elastic modulus of SiO$_2$.
A slight decrease in the DMT Modulus of SiO$_2$ was observed for high ion dose as shown in Fig 9 (b). For ion dose of $5.219 \times 10^{14}$ ions/cm$^2$, the elastic modulus of SiO$_2$ reduces by only 2.8% of the pure SiO$_2$. This is a very small change compared with the change in DMT modulus for graphene/SiO$_2$. The swelling effect observed in the height image could have been induced by the formation of voids and the intercalation of Gallium atoms in the atomic structure. This can also be attributed to the defect-mediated changes like the formation of interstitials which may lead to formation of new lattice planes.

### 3.2.2.3. Relationship between defect density and surface roughness of samples

A study of the effect of ion irradiation on the surface roughness of the samples was also carried out; using the NanoScope Analysis software, the PeakForce QNM height images of the samples were analysed and information about surface roughness extracted.

![Graph of Roughness vs log(ion dose) for (a) SiO$_2$ samples, (b) Cryo-graphene samples, and (c) room temperature graphene samples.](image)

**Fig. 10.** Graph of Roughness vs log(ion dose) for (a) SiO$_2$ samples, (b) Cryo-graphene samples, and (c) room temperature graphene samples.

It was observed that, there was no significant effect of ion irradiation on the surface roughness of the SiO$_2$ as seen in the graph in Fig 10.(a) The measurement on graphene sample roughness did not give good results to explain how the surface roughness change with ion dose exposure. It is expected that, the roughness of the samples would increase as a result of ion irradiation.
However, there were large variations as shown in figure 10 (b) and (c). This shows that the AFM may not be able to image atomic scale defects.

3.2.2.4. Relationship between defect density and Young’s modulus of samples

Graphene sample show lower elastic modulus after ion irradiation. It was observed that, the Young’s modulus of graphene samples remained unchanged for small ion doses. Additional ion irradiation result to a decrease in Young’s modulus for both Cryo- and RT-graphene sheets as shown in Fig 11. For higher ion doses, the Young’s moduli of graphene samples become even lower than that of the SiO$_2$ substrate.

![Graph of elastic modulus of graphene samples vs. log (ion dose). Red line is the normalized Young’s modulus of SiO$_2$ samples.](image)

A comparison of the Young’s modulus of Cryo-graphene and RT graphene samples revealed that, ion irradiation influence the Young’s modulus of Cryo-graphene more than that of RT graphene as seen in the Graphs above. For an ion dose of $5.219 \times 10^{14}$ ions/cm$^2$, the elastic modulus of Cryo-Graphene reduce by about 54.2% while that of RT graphene reduce by 45.6% of the un-irradiated graphene. The decrease set-in at a lower ion doses for Cryo-graphene than for room
temperature graphene. The Young’s modulus start decreasing at an ion dose of about $2.088 \times 10^{12}$ and $4.175 \times 10^{12}$ ion/cm$^2$ for Cryo-graphene and RT graphene respectively.

The strong $\sigma$-bond in graphene structure is responsible for the high strength of graphene sheets. Small ion doses may not have sufficient energy to break these bonds but may be sufficient to cause bond rotation. This result to SW defects. As the ion dose increase, we expect vacancy defects will start appearing in the samples’ structure. The defect density increase with increase in ion irradiation (or with increase in ion dose exposure). Finally, for higher ion doses, holes and more complex defects and structural disorder will be created in the graphene structures. These varying defect density and type affect the elastic properties of graphene differently as observed in this experiment. Vacancy defects, which are expected to dominate, involve bond breaking.

Fig. 12. Graphs of Elastic Modulus Vs log (Ion dose) for SiO$_2$ substrate. The Young’s modulus of SiO$_2$ remains fairly unchanged.
These defects influence the nanomechanical properties of graphene more than SW defects. [10-14] Bond breaking weakens the graphene structure and hence lowers its Young’s modulus.

It was observed that, the effect of ion irradiation on the Young’s modulus of SiO$_2$ samples is very small. Figure 12 show that, the DMT modulus is fairly constant after ion irradiation. For ion dose of $5.219 \times 10^{14}$ ions/cm$^2$, the elastic modulus of SiO$_2$ reduce by only about 2.8% of the pure SiO$_2$ as confirmed from the image in Fig 9 (b). This change in Young’s modulus of SiO$_2$ due to ion irradiation was insignificant, therefore we are justified to conclude that, the substrate did not contribute to the changes in Young’s modulus observed in this experiment. One could expect that these defects will considerably reduce Young’s modulus of the material. However, as seen in this study, the effect is very small. This could be attributed to the fact that SiO$_2$ is amorphous and the sample are relatively very thick, about 280nm.

3.2.3. **Summary**

Using PeakForce QNM, the influence of structural defect density on the Young’s modulus of graphene has been studied. It has been observed that, small ion dose exposure do not change the Young’s modulus of graphene. However, for high ion dose the Young’s modulus of graphene reduce with increase in ion dose exposure. Thus, increase in structural defect density causes a decrease in Young’s modulus of both Cryo-graphene and RT graphene. Although, the Young’s modulus of Cryo-graphene is highly affected by ion irradiation than that of RT graphene.
3.3. Adhesion Mapping

3.3.1. Experimental details

The AFM is a powerful tool in the measurement of adhesive force of samples. Using the PeakForce QNM, the adhesion property mapping was done simultaneously with the DMT modulus mapping described in section 3.2.1 above. As the tip approaches and retracts from the sample surface, the AFM is able to detect small forces on the tip. AFM records the force on the tip as it approaches and pulls away from the sample surface. The force curves extracted from this movement give information on the tip-sample interaction. The force at point D in figure 2 (i) give the adhesive force between the sample surface and the tip. The AFM software extracts this force for each point of the scan area to give a map of the adhesive force of the sample. According to Johnson [30] this adhesive force is related to the adhesive energy by the relation

\[ F_{adh} = 2\pi R\gamma \]  

[2]

where \( R \) is the tip radius, \( F_{adh} \) is the adhesive force, and \( \gamma \) is the work of adhesion per unit area. Adhesive energy of a material is greatly determined by the van der Waals force, however water meniscus on the surface [31] and surface roughness [32] can influence the measured adhesive energy. The knowledge of Adhesion properties of graphene is important in various application of graphene material and in choosing appropriate substrates for graphene sheets.
3.3.1.1. Evaluation

The PeakForce QNM has been shown to be a reliable method to study the adhesion energy of materials. However, the study is limited to the tip material; it is not possible to, directly, determine the adhesion energy between graphene and other different materials unless one has tips of different materials. In this study, the AFM tip and cantilever spring constant were calibrated using the procedure given in Bruker Corporation, [28]. Therefore, the results obtained here are reliable results. In addition, the sample/line was set at 512. This ensures that, surface adhesion property is properly probed for the entire scan area.

3.3.2. Results and discussion

The Adhesive force for the irradiated graphene samples was found to be lower compared to the defect-free ones. From the image shown in Fig 13 (a), the adhesive force for the non-defective RT graphene is about 17.0nN while for the irradiated region (Area 12) it is about 13.4nN. The adhesive force due to SiO$_2$ surface increased after ion irradiation as shown in Fig 13 (b); the adhesive force in the non-defective region was found to be 13.6nN while that due to the defective region (Area 13) was about 14.7nN. Using the NanoScope Analysis software, quantitative measurements for adhesive force between graphene surfaces and the tip were extracted from the adhesion images. Applying equation 2 to the adhesive force obtained in this study, an adhesive energy of 381.8mJ/m$^2$ was found for un-irradiated graphene surface. The adhesion energy however dropped to 145.97mJ/m$^2$ after ion irradiation dose of $5.219 \times 10^{14}$ ions/cm$^2$. This range of adhesion energy agrees with values observed in previous studies [22, 25] between graphene sheets and silicon dioxide surfaces.
Fig. 13. (a) Adhesion Image of defect-free (left) and defective (Area 12) RT graphene. Ion irradiated RT graphene has a lower sample-tip adhesion force. (b) Adhesion image of Defect free/Defective (Area 13) SiO$_2$. The adhesive force of irradiated sample is higher than that of non-irradiated one.

A graph of adhesion energy against defect density (shown in figure 14) revealed that, adhesive energy between graphene and the tip decrees with increase in defect density. The tip material is Antimony (n) doped silicon, therefore these results give us information about the adhesive force between graphene and the material. This observation gives us information on the influence of structural defects on the van der Waals force of graphene sheets, which is the force responsible for the adhesion energy of a material. This force is important in many areas of graphene.
technology; graphene sheets are clamped to a substrate by this force. In addition, the van der Waals force holds the graphene sheets together in a multilayer graphene.

![Graph of Adhesive force against log(ion dose) for graphene surface and AFM tip (Antimony (n) doped silicon)](image)

**Fig 14.** Graph of Adhesive force against log(ion dose) for graphene surface and AFM tip (Antimony (n) doped silicon)

The adhesion energy of graphene sheets with other materials has a significant effect on its mechanical properties and its performance in nanoelectromechanical systems (NEMS), for instance it causes graphene to clamp to substrate hence causing failure [33] and leads to hysteresis effect in micro-electromechanical systems (MEMS). [34] Therefore, it is important to understand the behavior of this force in different conditions of graphene sheets. The results in this study are useful in designing graphene-based devices in which adhesive force has a vital role. The knowledge of adhesion energy of graphene may open opportunities for the studies of surface force on 2D materials. [22]
3.3.3. **Summary**

Using the PeakForce QNM mode of Multimode 8 AFM, the adhesion energy of graphene has been studied. This mode has been shown to be effective in investigating the adhesion energy of materials. It was found that, the adhesion energy of graphene decrease with increase in defect density. This information is important in designing graphene-based devices. Where the graphene sheets need to be attached to a substrate, then one has to be aware of the amount of structural defect in the graphene sheet that may make it leave the substrate due to low adhesion. This study gives the relationship of the adhesion energy and defect density, which is of great help.

4. **Conclusion**

In this experiment, the effect of structural defects on the mechanical properties of graphene samples was studied using the Multimode 8 AFM. The nanomechanical properties of defective graphene samples were measured using PeakForce QNM mode. A relationship between Young’s modulus and defect density for graphene on SiO$_2$ has been established. It has been shown that, ion irradiation lower the adhesive energy of graphene surface. The results obtained in this study offer important information on the behavior of defective graphene. This information is useful in the designing of graphene M/NEMS and in other studies and applications of graphene. The relationship between defect density and Young’s modulus of graphene obtained in this study could be a powerful tool in determining the amount of defects present in a graphene sheet.
ACKNOWLEDGEMENTS

First, I would like to thank my supervisor, Prof Klaus Leifer for his fatherly advice, support and guidance. Additionally, I would like to thank Hu Li and Ishtiaq H. Wani for their immense support throughout the project. I greatly appreciate the work of my examiner, Prof Håkan Rensmo and the support from the whole group. I cannot forget my sponsor Erasmus Mundu organization. This work could not be possible without your support. Thank you.
References


