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Contributions to Experimental Mechanics of Graphene

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PART I: **CONTEXT**

Chapter 1: General introduction & motivation

In 2004, Novoselov and coworkers first isolated 2D graphene sheets from graphite (Novoselov et al., 2004). Fast forward 10 years later, and it rapidly becomes one of the hottest research topics in the field of nanotechnology and has been called a “Wonder Material”. Graphene is a one-atom thick sheet of sp^2 -bonded carbon atoms packed in a honeycomb lattice with exceptional electrical, mechanical, thermal, and optical properties.

Much of the focus on graphene was on its astonishing electrical properties. The potential for its use in electronics applications was justified by its high charge carriers’ mobility reaching values up to $15,000 \text{ cm}^2/\text{V.s}$ (Novoselov et al., 2004) and its independence on temperatures and stability under high electrical fields and chemical doping drives the belief that carrier mobility can be significantly improved to reach values up to $100,000 \text{ cm}^2/\text{V.s}$ (Geim and Novoselov, 2007). Furthermore, heterostructures based on stacking graphene on hexagonal boron nitride were found to have mobilities up to $10^6 \text{ cm}^2/\text{V.s}$ (Wang et al., 2013). Mechanical properties of 2D graphene sheets were also picking interest since earlier works on carbon nanotubes which are basically graphene sheets rolled into cylindrical shapes. Theoretically, 2D carbon sheets were predicted to have mechanical properties superior to those of any other existing material (Zhao et al., 2002). In 2008, Lee et al. reported first AFM based membrane deflection experiments performed to calculate mechanical properties of graphene, where the theoretical predictions of Young’s Modulus were confirmed to be $E = 1 \text{ TPa}$, and the intrinsic strength to be $\sigma_{\text{int}} = 130 \text{ GPa}$ (Lee et al., 2008).

The superior properties of graphene have directed a lot of research into potential graphene mechanical applications. In 2007, graphene NEMS were reported to be the thinnest and one of the highest modulus resonators to date (Bunch et al., 2007). The possibility of graphene membranes with ultra-strong adhesion has also confirmed the potential of graphene being used in such applications (Koenig et al., 2011). In addition to graphene’s high strength, its impermeability (Bunch et al., 2008), transparency (Nair et

al., 2008), low friction coefficient (Shin et al., 2011) and thermal/chemical stability (De Heer et al., 2007), have also prompted the idea to use graphene as a protective and anti-wear coating material (Chen et al., 2011). Moreover, the use of graphene in composites has also yielded very promising results to strengthen different material systems. Indeed, Stankovich et al. reported first graphene/polymer based composites (Stankovich et al., 2006a), afterwards, many other graphene reinforced polymer composites were reported based on different type of matrices (Fang et al., 2009; Rafiee et al., 2009; Ramanathan et al., 2008; X. Wang et al., 2011). Metal/graphene composites have also been reported, although first results were not as promising as for polymers (Bartolucci et al., 2011) due to issues with mixing processes based on powder metallurgy. Later, new mixing techniques resulted in much better graphene homogeneity in metal matrices as well as higher strength enhanced composites (L.-Y. Chen et al., 2012; Hwang et al., 2013; Kim et al., 2013).

Mechanical manipulation of graphene has even further implications and advantages to other applications. Efforts have been made to achieve high uniaxial strains in graphene in order to achieve some novel properties predicted by theory, including bandgap opening (Ni et al., 2008), increasing storage properties (Zhou et al., 2010), and pseudo magnetic fields (Guinea et al., 2010). Therefore, it would be ideal to achieve a technique capable of reaching ultra-high strains on suspended graphene sheets to enable researchers and engineers to fully utilize its unique properties under strain.

These mentioned properties and potential applications of graphene makes it necessary to understand more about graphene's processing capabilities, mechanical properties, and its role and interactions when combined with other materials. All techniques available to mechanically probe freestanding graphene can be divided in 2 categories: Deflecting suspended graphene membranes transferred on a pre-patterned substrate (Lee et al., 2008;

Rasool et al., 2013) or applying uniaxial load on transferred graphene on flexible substrates (Mohiuddin et al., 2009; Ni et al., 2008).

The issue with deflecting suspended graphene membranes is that it requires transferring graphene onto pre-patterned substrates which increases complexities and defects in graphene. Moreover, the area around the AFM tip is under a huge stress concentration compared to the other areas of the membrane. Furthermore, Han et al. showed through their work by MD simulations that AFM deflection experiments tend to slightly underestimate the strength of pristine graphene and overestimate the strength of polycrystalline graphene depending on the tip position with respect to defects in the graphene sheet (Han et al., 2015).

Secondly, transferring graphene on flexible substrates has major drawbacks; first, it is not possible to achieve high strain values and the maximum values reported were around 1.3%, secondly, graphene is not suspended in those cases, and has to be in contact with the substrate which limits the potential applications of the strained graphene. Therefore, even though transferring graphene is unavoidable in a lot of cases, it is beneficial to work towards techniques that could eliminate this transfer step when possible.

On the other hand, mechanical testing of graphene/substrate systems has not been extensively studied and understood. A lot of theoretical and experimental work has been performed on for studying graphene's tribological properties by nanoscratching of graphene/substrate systems (Deng et al., 2012; Filleter et al., 2009; C. Lee et al., 2009; H. Lee et al., 2009). Nanoindentation studies have also been performed for different purposes and systems (Gao et al., 2015)(Chang et al., 2013; Suk et al., 2016). However, there has not been an extensive study of the effect graphene has on the response of the indented material, and on the atomistic processes involved in modifying the mechanical contact response.

The objective of this thesis is to investigate experimental techniques to strain graphene and to probe different mechanical properties of graphene. Different graphene/substrate systems have been fabricated and several mechanical probing techniques were used depending on the system being studied. First, graphene supported on substrate was probed by nanoindentation; CVD grown graphene on a Cu substrate and transferred graphene on different substrates (for comparison) were indented and the effect of graphene on the whole system is studied and analyzed. Secondly, graphene was transferred on etched circular holes in a SiO₂/Si substrate creating suspended graphene membranes; AFM was then used to perform AFM deflection tests in order to validate the mechanical quality of our CVD grown graphene compared to values reported in literature, and to obtain reference mechanical properties. Finally, a technique based on the work in Refs (Fabrègue et al., 2007; Gravier et al., 2009) for on chip tensile testing devices is developed to apply uniaxial loading on graphene and characterize its mechanical properties. The goal of this technique is to obtain fully processed and suspended graphene beams and to measure the mechanical properties of such beams on wafer.

In summary, this thesis aims to answer the following scientific questions:

1. Is it possible to deconvolute graphene's mechanical properties from testing graphene/substrate systems?
2. What effects does graphene have on the elastic and plastic contact behavior of the underlying substrate?
3. How strong is the graphene grown at UCL?
4. Is it possible to apply uniaxial loads on free-standing single layer graphene?
5. Is it possible to use the "micromachines" concept developed at UCL to mechanically test 2D materials?

This thesis is divided into 4 parts; part I provides the context of the work; the state of the art of graphene growth, structure, properties and characterization is discussed in chapter 2. Chapter 3 focuses on graphene's

mechanical properties, including graphene's behavior under different types of load and discusses the previous work in the area of graphene mechanical testing, and finally discusses into some details the techniques that will be used in this work. Chapter 4 presents an overview of the experimental techniques and characterization tools used.

Part II deals with the mechanical characterization of graphene/substrate system by nanoindentation. The methodology of samples preparation and characterization is discussed in chapter 5, and the results of the effects of graphene on the whole system are discussed in chapter 6 where the experimental observations are validated by numerical simulations.

Part III discusses the techniques for characterization of suspended graphene films. Chapter 7 discusses the experimental procedure to prepare suspended graphene membranes and the AFM membrane deflection tests are described and the results are discussed. While, in chapter 8, the fabrication techniques and details of the on-chip tensile testing devices are described, the process is analyzed and the proof of concept for these devices is illustrated.

Finally, part IV includes the conclusions of the thesis and the perspectives for future work in this field which are presented in chapter 9.

Chapter 2: State of the art on graphene processing and structure

2.1 Graphene Production

2.1.1 Graphene Synthesis

The first issue when working with graphene is how to produce it. Since the properties of graphene were first demonstrated (Novoselov et al., 2004), the interest to produce single, double or few layers graphene picked up quickly. There are several techniques that have been developed for graphene synthesis. Generally, those techniques could be divided into top-down approaches and bottom-up approaches. Top-down approaches rely on the concept of separating a graphene sheet(s) from graphite. Methods reported include mechanical exfoliation (Novoselov et al., 2004), reduction of exfoliated graphite oxide (Stankovich et al., 2007, 2006b), electrochemical exfoliation (G. Wang et al., 2009), arc discharge of graphite (Y. Chen et al., 2012; Subrahmanyam et al., 2009), and unzipping carbon nanotubes through plasma etching, oxidation, or lithium intercalation (Cano-Márquez et al., 2009; Jiao et al., 2009; Kosynkin et al., 2009). The main advantage of top-down approaches is the ability to produce graphene in any environment or on any substrate. However, those techniques in general are somewhat tedious and time consuming while the produced graphene is generally in the form of small flakes and single layers are not easily achievable.

Bottom-up approaches represent a more efficient alternative to achieve large areas of graphene in a more controlled manner. The most popular bottom-up approaches are graphene epitaxial growth on silicon carbide, and chemical vapor deposition (CVD). In the former technique, graphene is produced by high temperature heat treatment of a silicon carbide substrate to cause the sublimation of silicon, while the remaining carbon atoms form graphene (Emtsev et al., 2009).

CVD is a well-known, simple and efficient technique. In CVD process, carbon containing precursors molecules are broken on the surface of a catalytic metal at high temperatures and the carbon atoms then form graphene. There are several variations other than thermal CVD that have been reported for graphene synthesis like hot filament CVD (Hawaldar et al., 2012) and plasma enhanced CVD (Terasawa and Saiki, 2012). The CVD of graphene has been reported to use many different precursors including methane and ethylene. Moreover, a wide variety of transition metals have been shown to catalyze the synthesis of graphene. In this work however, all graphene was synthesized on copper foils and evaporated copper thin films using methane as the precursor (Huet and Raskin, 2017).

2.1.2 Graphene Transfer

For most applications, after graphene is grown by CVD, it has to be transferred on top of arbitrary substrates for further processing or characterization. There exists several techniques for graphene transfer that have been reported in literature; wet transfer (Li et al., 2009), dry transfer (Chen et al., 2013), and electrochemical transfer (Y. Wang et al., 2011).

Wet transfer methods are the most commonly used, and all graphene transfer throughout this work is based on this technique, which has been reported to lead to clean and good quality transferred graphene (Li et al., 2009). Graphene on top of Cu foils is coated by PMMA and the PMMA is cured. Afterwards, the Cu is etched in an etching solution (FeCl_3 or APS). The PMMA/graphene stack is then left floating in the solution, and after rinsing, it is deposited on the desired substrates. Fresh PMMA is then dropped on the PMMA/graphene/substrate stack to relieve the stresses, and finally the PMMA is removed by acetone leaving a graphene film on the desired substrate.

Graphene transfer is a critical step for many applications of graphene. The complication of the process increases the amount of defects in the delicate graphene sheet; moreover, it is technically difficult to align the graphene

2.2 Graphene structure

sheet on the desired surface, and the use of polymers result in residues and contamination of the final graphene surface. However, in many applications, there is no alternative to the transfer step in order to acquire graphene on top of the desired substrate, since graphene can only be grown on limited number of surfaces. Figure 1 shows a schematic illustrating the basic steps of the transfer process.

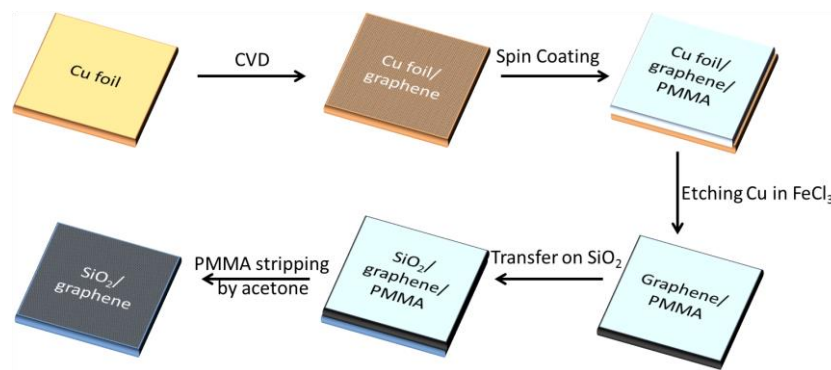


Figure 1: Schematic of the basic steps of graphene transfer process taken from (Li et al., 2009).

2.2 Graphene structure

Graphene is a 2D material, consisting of sp^2 - carbon atoms covalently bonded and packed in a honeycomb lattice with an interatomic distance of 0.142 nm. A graphene sheet could be viewed as benzene rings where the H atoms are replaced by C atoms to form another ring. Figure 2 illustrates the atomic structure of graphene and graphite.

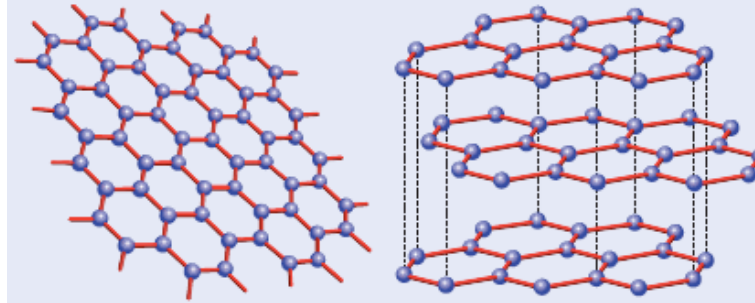


Figure 2: Graphene (left) is a honeycomb lattice of carbon atoms. Graphite (right) can be viewed as a stack of graphene layers. Figure adapted from (Neto et al., 2006).

Most of graphene's unique properties come from its 2D lattice and for long, it was believed that 2D materials cannot physically exist due to being thermodynamically unstable (Landau and Lifshitz, 1980; Mermin, 1968). Therefore, it was argued that graphene could exist only as a part of a 3D structure like graphite which is viewed as many layers of graphene stacked above each other. However, it was later shown that although perfect crystals are not allowed to exist in 2D space, it is possible for nearly perfect 2D crystals to exist in 3D space. A detailed analysis of the 2D crystal problem has led to the conclusion that the anharmonic interactions between bending and stretching long-wavelength phonons could suppress thermal fluctuations and stabilize 2D atomic membranes by deformation in the third dimension (Le Doussal and Radzihovsky, 1992; Nelson and Peliti, 1987; Nelson et al., 2004).

When graphene was first isolated in 2004 followed by reports on other 2D crystals (KS Novoselov et al., 2005; Novoselov et al., 2004) it appeared to be a perfect 2D lattice based on its high crystal quality where charge carriers mimic massless relativistic particles and can travel up to thousands of interatomic distances without scattering (KSA Novoselov et al., 2005; Novoselov et al., 2004; Zhang et al., 2005). However, Meyer et al. (Meyer et al., 2007) used TEM along with nano beam electron diffraction patterns to show that suspended graphene sheets exhibit roughening ripples with out of plane deformations of around 1 nm and a characteristic wavelength of

10-25 nm. This crumpling was debated whether it is an intrinsic property of graphene or just taking place due to experimental handling. Later, Fasolino et al. (Fasolino et al., 2007) carried out atomistic Monte Carlo simulations and found that certain ripples indeed occur spontaneously in a graphene sheet due to the thermal fluctuations, which provided strong theoretical support to earlier experimental findings. The theoretically calculated amplitudes of the ripples however are found to be as small as 0.1 nm with characteristic wavelengths of 8 nm. These theoretical predictions were explained by the fact that graphene's atomic structure responds to thermal fluctuations by varying its bond lengths. The calculated bond lengths vary from 0.13 nm to 0.154 nm. To accommodate this variation, some individual carbon atoms are displaced out of plane resulting as well in overall lattice contraction which limits the out of plane amplitudes in order to not destroy the graphene membrane.

However, the difference between theoretical calculations and experimental observations indicate that there are reasons for crumpling other than flexural phonons. Locatelli et al. (Locatelli et al., 2010) used low energy electron microscopy and microprobe diffraction to study suspended graphene sheets, and found weak temperature dependence of the crumpling which indicates that these ripples are only partially phonon induced and that extrinsic contributions to corrugations are much more significant than intrinsic ones. Extrinsic crumpling may be explained by thermal and mechanical stress from the experimental procedures including graphene growth, transfer, processing, or substrates boundary conditions (Wong and Pellegrino, 2006). In fact, it was shown that by manipulating the strains -thermally or via substrate's boundary conditions- and the shapes of the graphene membranes on the substrate, it is possible to control the ripple structures of suspended graphene (Bao et al., 2009). These ripples are characteristic of graphene as explained above. However, when graphene is supported on a substrate e.g. SiO_2 (Ishigami et al., 2007) it was shown that it tends to largely conform to the substrate's morphology. Consequently, it was reported that atomically flat graphene can be

obtained by depositing it on atomically flat substrates like mica and boron nitride substrates (Dean et al., 2010; Lui et al., 2009).

Generally, the larger the area of the suspended graphene is, the more significant the ripple structure is. The ripple structure could play a massive role in determining graphene's properties.

2.3 Defects in graphene

Graphene, like any other crystalline material is expected to have some defects in its structure as predicted by thermodynamics. Ab initio calculations have shown that some defects are intrinsic in graphene like dislocations and grain boundaries with specific energetically favorable orientations (Yazyev and Louie, 2010). Moreover, synthesis, transfer and processing of graphene also introduce more defects to its lattice. Defects in graphene are very important to consider because they play a major role in its electronic, magnetic and mechanical properties. Similar to 3D bulk materials, defects in graphene can be classified according to dimensionality (Banhart et al., 2011). However, due to the reduced dimensionality of graphene being a 2D material, defect types which could possibly appear are less than in a 3D bulk. Moreover, graphene can host defects by reconstructing its atoms arrangements in a way different to any other material. Carbon atoms have different hybridizations which could allow different number of nearest neighbors. Moreover, even sp^2 -hybridized atoms can rearrange in different polygon shapes (e.g: pentagons or octagons).

Examples of point defects present in graphene are Stone-Wales defects (Stone and Wales, 1986), single and multiple vacancies (Lee et al., 2005), adatoms (Tsetseris and Pantelides, 2009) and substitutional impurities including Boron (Ci et al., 2010), Nitrogen (Nevidomskyy et al., 2003), and transition metals (Krasheninnikov et al., 2009). Figure 3 illustrates few examples of point defects in graphene. On the other hand, line defects are also present in graphene in the form of dislocation-like defects (Hashimoto

et al., 2004) or defects at the edges of graphene (Koskinen et al., 2009, 2008).

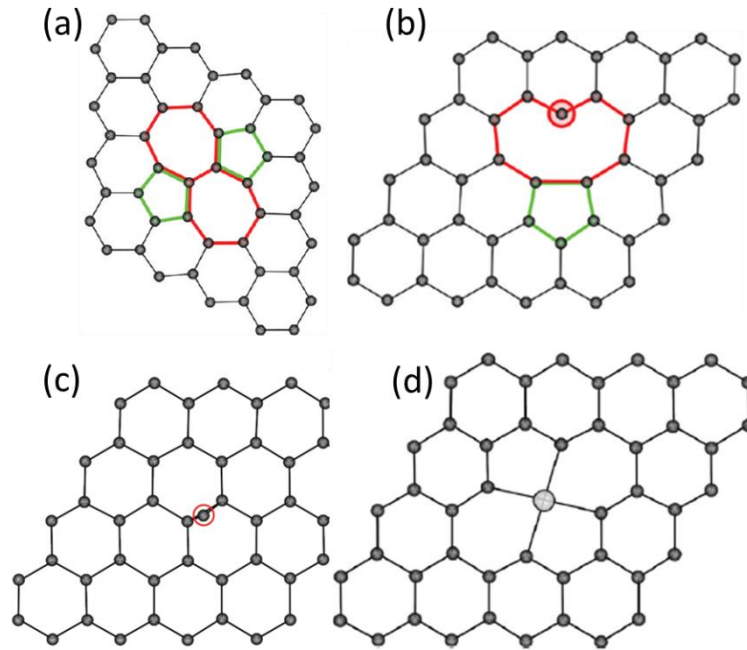


Figure 3: Atomic structure of graphene with (a) Stone-Wales defect, (b) single vacancy, (c) adatom, and (d) substitutional atom. Figure taken from (Banhart et al., 2011).

Defects can also be used to tailor properties of graphene or to get a specific response. Defects such as vacancies, substitutional atoms, adatoms or edge defects will change the chemical properties of graphene by making it more reactive (Denis and Iribarne, 2013). Electronic properties are also significantly affected by defects. For example, density functional calculations have shown that Stone-Wales defects can open a bandgap in graphene through breaking its lattice symmetry (Peng and Ahuja, 2008). Moreover, defects in graphene can also act as electron scattering centers which will lead to a decrease in conductivity (Wehling et al., 2010). Magnetism of graphene can also be engineered by defects which have local magnetic moments and therefore could lead to a magnetic order (Wang et

al., 2008). Defects can also have an influence on the mechanical properties of graphene. Polycrystalline graphene has been shown to exhibit comparable strength and elastic modulus to single crystalline graphene (Rasool et al., 2013), indicating that line defects or grain boundaries do not play a significant role in changing graphene's mechanical properties. However, it has been demonstrated that point defects; specifically vacancy type defects have the biggest impact on graphene's mechanical properties with a significant drop in both the elastic modulus as well as the fracture strength (Zandiatashbar et al., 2014). But, Lopez-Polin et al. (López-Polin et al., 2015b) showed that with increasing the vacancy defects in graphene up to a concentration of about 0.2%, graphene's Young's modulus actually increases before it starts to drop by further increasing the defects concentration, while fracture strength starts to deteriorate as soon as defects are introduced in graphene.

2.4 Graphene characterization

The characterization of graphene is not a straightforward process. Since graphene is only one sheet of single atoms, characterizing and observing it is more challenging than its 3D counterparts. Graphene characterization techniques most commonly used are:

1. Optical characterization
2. Scanning probe microscopy
3. Electron microscopy
4. Raman spectroscopy

Optical characterization of graphene is the easiest, cheapest and quickest way to characterize graphene. However, certain conditions have to be met in order to enable optical detection of graphene. CVD grown graphene on Cu foils or thin films is optically invisible. However, transferred graphene on SiO₂ films is visible under optical light due to higher contrast. The thickness of the underlying SiO₂ film affects the contrast of graphene imaging and it was calculated that the optimum thickness to visualize graphene by white light is either 90 nm or 280 nm due to constructive interference between

graphene and SiO₂ films (Blake et al., 2007). It was also shown that by selecting the right material and layer thickness, the number of graphene layers could be determined optically through color variations (Gao et al., 2008). Moreover, rotational angles between graphene layers could be determined optically. Campos-Delgado et al. (Campos-Delgado et al., 2013) has demonstrated that depending on the angle between 2 layers of graphene, different colorations appear under white light. To optically detect CVD grown graphene directly on Cu, a simple and effective technique has been reported which is to oxidize the Cu foil or film and since graphene is impermeable, the areas covered with graphene will not be oxidized and therefore appear brighter than bare Cu surface (Jia et al., 2012). Examples of optical images of graphene are illustrated in Figure 4.

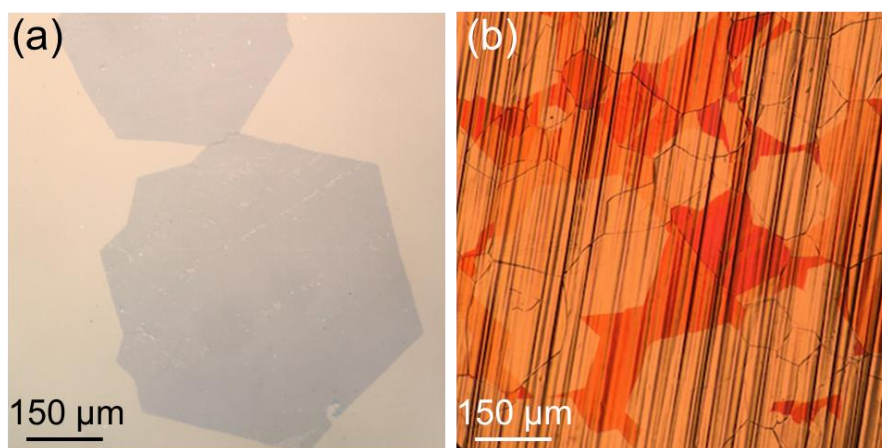


Figure 4: Optical images of (a) graphene flakes transferred on 90 nm SiO₂ film, (b) graphene grown on Cu foil (bright areas indicate presence of graphene, and red areas indicate oxidized bare Cu)

Second technique to characterize graphene is scanning probe microscopy. Atomic force microscopy (AFM) was the first technique along with optical microscopy to be used to detect and characterize graphene (Novoselov et al., 2004). AFM measurements have shown a step height of around 4 Å, which was expected to be the thickness of a single atomic layer of graphene. Measuring graphene thickness by AFM has been performed in

many works with thickness results varying between 0.35 and 1 nm. Gupta et al. measured an offset in AFM measurements equal to 0.33 nm (Gupta et al., 2006). This offset is believed to be a result of the differences in interaction force between the surface measured and the tip. It was later demonstrated that using tapping contact mode AFM in a repulsive regime instead of an attractive regime, will yield better accuracy and minimize the errors in thickness measurement (Figure 5) (Nemes-Incze et al., 2008).

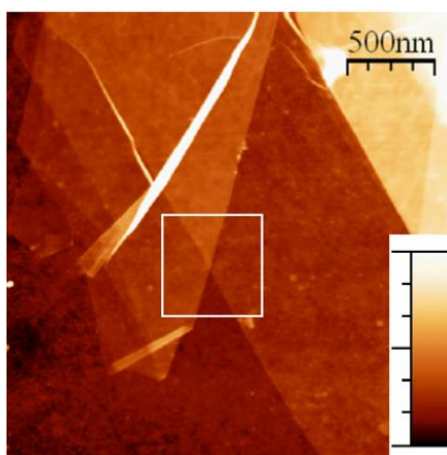


Figure 5: AFM image of two overlapping graphene films on SiO₂. Adapted from (Nemes-Incze et al., 2008).

Furthermore, measurements give different results depending on the environment in which the test is performed, measurements under vacuum result in thicknesses smaller than those measured under ambient conditions (Ishigami et al., 2007). This is due to the fact that under ambient conditions other species of gases or liquids can be trapped between the graphene layer and the substrate. So far, the most accurate way to measure the thickness of a graphene flake is to measure the thickness of folds or wrinkles on the layer. AFM along with Scanning tunneling microscope (STM) have also been used to obtain atomic resolution of graphene lattice and it was shown that hexagonal and triangular lattice patterns do exist in close proximity (Figure 6) (Ishigami et al., 2007). Moreover, AFM is also used to

characterize further properties of graphene, including its nanoscale morphology, mechanical properties (Lee et al., 2008; López-Polin et al., 2015b; Rasool et al., 2013), and tribological properties (Filleter et al., 2009; H. Lee et al., 2009; Liu et al., 2014).

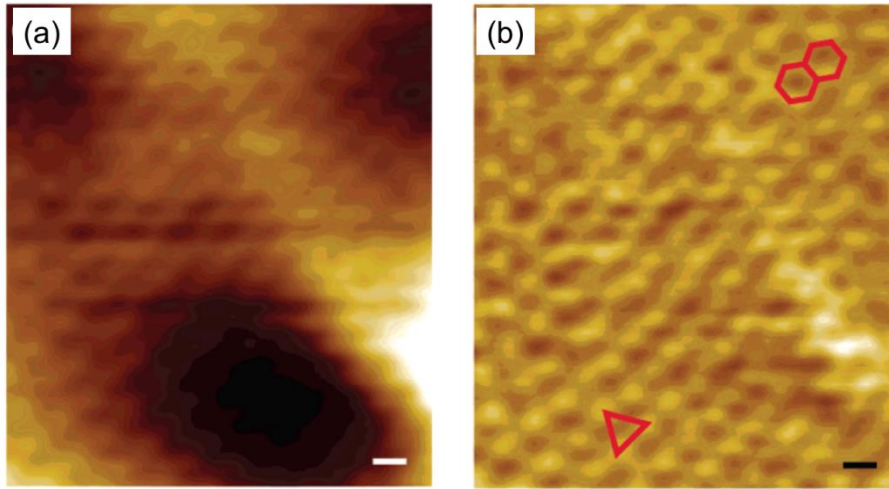


Figure 6: (a) STM image of a large area graphene. The scale bar is 2.5 Å. $V_{\text{sample}} = 1.2$ V and $I_{\text{tunnel}} = 0.33$ nA. (b) A high-pass filtered image of the large area scan shown in (a). Both triangular and hexagonal patterns are observed. The orientations of the red triangle and hexagons are same. The scale bar is 2.5 Å. Adapted from (Ishigami et al., 2007).

Electron microscopy has also been one of the most valuable techniques to characterize and detect graphene. Although graphene is virtually transparent to electrons especially at high energies (Longchamp et al., 2012; Meyer et al., 2008; Mutus et al., 2011; Yan et al., 2011), any type of defect, wrinkle, or lattice perturbation would give a clear signal. Meyer et al. (Meyer et al., 2007) used transmission electron microscopy (TEM) to obtain information about the structure of graphene and its defects. Other types of electron microscopy have been reported to be capable of providing accurate estimates for the number of graphene layers, namely, Low-Energy Electron Microscopy (LEEM) (Hibino et al., 2008) and Auger electron spectroscopy (AES) (Xu et al., 2010). Conventional scanning electron microscopy (SEM) being a robust, simple and non-invasive technique which

does not require a complicated sample preparation procedure is also commonly used for high contrast imaging of graphene. Early works on carbon nanotubes showed the capability of SEM to provide high contrast images for the nanotubes on insulating substrates by using low energy electrons as well as secondary electrons detectors (Brintlinger et al., 2002; Homma et al., 2004). The same technique has been applied to graphene, and depending on the surrounding environment, the incident electrons energy and the number of graphene layers, the source of contrast is different. The contrast mechanisms of graphene include roughness, edge, and thickness contrasts, differential surface potential, electron beam induced current, changes in work function and secondary electron attenuation (Hiura et al., 2010; Kochat et al., 2011; Wang et al., 2015; Xie and Spallas, 2012). Figure 7 shows an example SEM image of CVD grown graphene on Cu thin film.

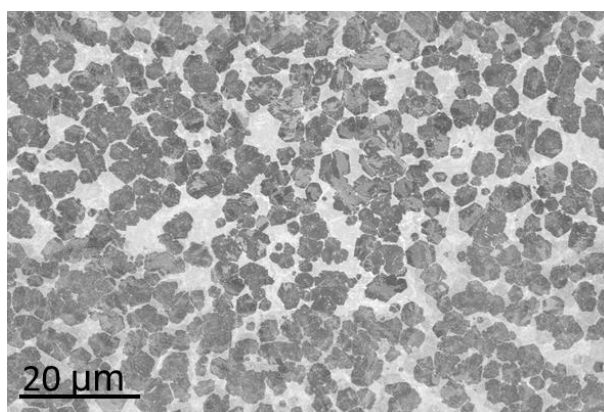


Figure 7: SEM image of CVD grown graphene on Cu thin film. The dark areas show the incomplete graphene domains, the bright areas show the bare Cu surface.

Finally, Raman spectroscopy is the most common technique to characterize and detect graphene layers since it is a rapid, unambiguous, efficient, and non-destructive technique. The signature of graphene was first shown to be captured by Raman spectroscopy by Ferrari et al. (Ferrari et al., 2006); it was also shown that the signature is sensitive to the number of graphene layers and defects in the layer. Raman spectroscopy relies on Raman

inelastic scattering of photons upon interaction with the probed material. Historically, Raman spectroscopy has been used to characterize graphitic materials (Tuinstra and Koenig, 1970). For graphene, the most commonly used laser to probe it is green laser with a wavelength of around 514 nm (Ferrari et al., 2006). Figure 8 shows a comparison between typical Raman spectra for a single layer graphene and graphite. Three Raman bands identify graphitic materials in general, namely the D band appearing at around 1350 cm^{-1} which is activated by the presence of defects in the material, the G band (1580 cm^{-1}) which is indicative of a doubly degenerate phonon mode caused by the vibration of sp^2 -carbon atoms, and the 2D band (2700 cm^{-1}) which is indicative of the stacking order of graphene layers (Pimenta et al., 2007; Tuinstra and Koenig, 1970). Accordingly, the 2D band is usually used to estimate the thickness and number of graphene layers, indeed it was shown that for monolayer graphene the 2D band is very sharp (around 30 cm^{-1}), and has an intensity almost double that of the G band, while for multilayer graphene, the 2D band gets broader and even splits into 2 peaks as the number of layers increases (Graf et al., 2007). The Raman signature of graphene is very sensitive and can be used to obtain a vast amount of information about dopants (Das et al., 2008), charged impurities (Ni et al., 2009), strain (Mohiuddin et al., 2009; Ni et al., 2008), thermal conductivity (Lee et al., 2011) and electron-phonon coupling (Yan et al., 2007), as well as the effects of the substrate on which graphene is deposited (Berciaud et al., 2008; Calizo et al., 2007).

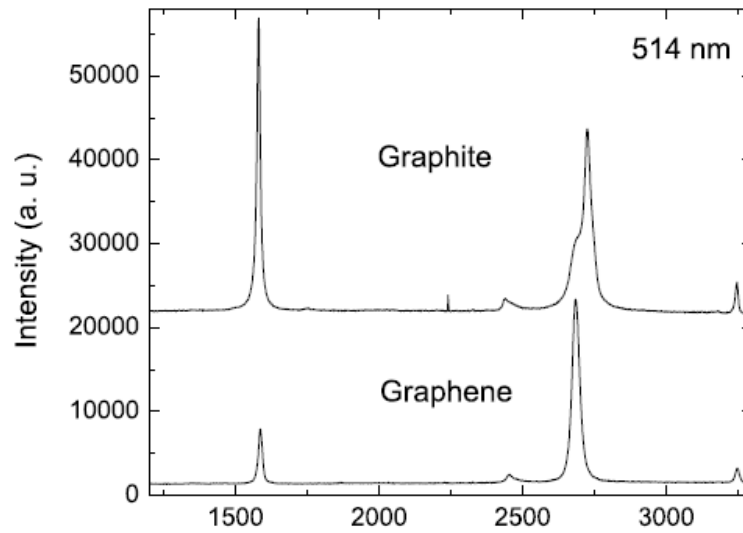


Figure 8: Raman spectra illustrating the difference between graphene and graphite. Taken from (Ferrari et al., 2006).

Chapter 3: State of the art on mechanical properties of graphene

3.1 Applying deformation to graphene

Applying extreme uniaxial strains to graphene has been one of the most important topics in graphene's research. The interest in applying high deformation to graphene is two-fold; first it has been predicted that graphene under extreme strains would exhibit novel properties that include altering the band structure (Pereira et al., 2009) and opening a bandgap (Ni et al., 2008), enhanced hydrogen storage (Zhou et al., 2010), and uniform magnetic fields (Guinea et al., 2010). However, these novel properties all require graphene to be under large strains with values more than 10%. Secondly, by performing uniaxial tension tests on graphene, it would be possible to measure its mechanical properties more easily and more accurately. Up to this point, most mechanical testing of graphene is done by AFM membrane deflection tests, and even though this technique is powerful and provided a lot of results and insights to the mechanical properties of graphene, the values measured show a large scatter and dependence on the interactions between the membrane and the substrate. Furthermore, Han et al. showed through their work by MD simulations that AFM deflection experiments tend to underestimate the strength of pristine graphene and overestimate the strength of polycrystalline graphene (Han et al., 2015).

The efforts to apply uniaxial traction to graphene sheets started with depositing graphene flakes on flexible substrates. Polyethyleneterephthalate (PET) (Mohiuddin et al., 2009; Ni et al., 2008), acrylic (Mohiuddin et al., 2009), and plastic (Tsoukleri et al., 2009) substrates were used. The maximum strain attained has been reported to be around 1.3% with Raman peaks shifts and splitting validating the technique. This is far below the value required to achieve the predicted novel properties of graphene, and also is not enough to characterize the mechanical properties of graphene which ideally is predicted to fracture at

strains up to 25% (Lee et al., 2008; Liu et al., 2007). It is worth mentioning that Kim et al. (Kim et al., 2009) reported transferring large scale graphene to pre-strained PDMS substrates and then further stretching the substrate/graphene system up to 30% for flexible electronics applications. The resistance of graphene sheets showed very good mechanical stability when measured at different levels of strain.

Applying deformation on suspended graphene proves to be even more complicated. Several reports discussed different techniques to apply multi-axial strain on graphene. These techniques include: deflecting graphene membranes on substrate trenches (Lee et al., 2008), applying a pressure difference between both sides of a suspended graphene sheet (bulge test) (Bunch et al., 2008), and suspending graphene between dielectric nanopillars on a substrate (Tomori et al., 2011). However, only one technique has been reported to apply high uniaxial strain on suspended graphene sheets by transferring graphene on a separate stage which can be manipulated to strain the graphene. Zhang et al. (Zhang et al., 2014) used this technique by transferring graphene on an SEM stage and measured graphene's fracture toughness by performing in-situ tensile test on pre-cracked graphene. Perez Garza et al. (Pérez Garza et al., 2014) reported another technique which utilized an in-plane tensile testing device actuated by a thermal actuator while graphene was fixed at the stage using epoxy, with this technique, deformations of more than 10% have been achieved. However, the issue remains with such techniques that graphene has to be transferred on an external stage and the complexity of needing external sources of actuation to apply strains remain. A simple technique fully compatible with fabrication process technologies capable of straining suspended graphene on wafer is yet to be reported.

3.2 Graphene response under load

3.2.1 Elastic stiffness and strength

Graphene has often been labelled the strongest material in the world. Even before planar sheets of graphene physically existed (Novoselov et al., 2004),

carbon nanotubes (rolled up graphene sheets) have been theoretically and experimentally investigated and have shown remarkable strength and elastic behavior (Falvo et al., 1997; Iijima et al., 1996; Treacy et al., 1996; Yakobson et al., 1996). It has been observed that carbon nanotubes can withstand very large deformations without failure far beyond Hooke's law through deforming into the nonlinear elastic regime. It is understood that the flexibility of the hexagonal network of carbon atoms -in the graphene sheets which the carbon nanotubes are made from- resists bond breaking and therefore can withstand very high strains (Iijima et al., 1996). TEM images have shown that under high strains carbon nanotubes have some kinks in their shapes and further simulations have confirmed that under high strains carbon nanotubes reversibly transform into different morphological patterns (Yakobson et al., 1996).

Based on the above, it was expected that graphene would have similarly remarkable mechanical properties, and early theoretical studies have confirmed the same (Kudin et al., 2001; Van Lier et al., 2000; Zhou and Huang, 2008). Measuring graphene's Young's modulus proved to be more complicated than for bulk materials, due to the difficulties in determining graphene's thickness. The first and most prominent experimental work on pristine 2D planar graphene's mechanical properties was reported by Lee et al. (Lee et al., 2008) where graphene was exfoliated and transferred on a pre-patterned oxidized wafer with trenches and AFM was used to deflect the suspended membranes over the trenches. Since, graphene exhibits nonlinear elastic behavior, the stress-strain relationship was expressed as follows:

$$\sigma = E\varepsilon + D\varepsilon^2 \quad (1)$$

where σ is the applied stress, ε is the observed strain, E is the Young's modulus, and D is the effective nonlinear elastic modulus. It is worth noting that the nonlinear elastic modulus of graphene typically has a negative value and therefore leads to a softening at higher tensile strains and stiffening at high compressive strains. Moreover, finite elements analysis

simulations have shown that the nonlinear elastic modulus D can be ignored, since even close to the breaking point of graphene, only 1% of the membrane is strained to the point where the nonlinear term becomes significant. Recent work on graphene has also revealed that graphene with no significant ripples or crumpling (i.e: hidden area $\sim 0\%$) fully obey linear elasticity and deformation does not go into the non-linear regime (Nicholl et al., 2017). Therefore, it is safe to only account for the linear deformation part and neglect the non-linear part in this case. The intrinsic strength of graphene is then defined as $\sigma_{int} = \frac{-E^2}{4D}$, and the failure strain is defined as $\varepsilon_{int} = \frac{-E}{2D}$. By recording the load-displacement curve of the AFM tip on the suspended membrane and applying its values to a finite element model, it was possible to determine the 2D Young's modulus of the graphene sheet. The value calculated was $342 \text{ N.m}^{-1} \pm 30 \text{ N.m}^{-1}$. For purposes of comparing with bulk materials, these values were divided by the interlayer spacing of graphite (0.335 nm), leading to a bulk Young's of 1 TPa. Moreover, the nonlinear elastic modulus was calculated to be $-690 \pm 120 \text{ N.m}^{-1}$, giving an intrinsic strength of $42 \pm 4 \text{ N.m}^{-1}$, and a fracture strain of around 24.7%. Theoretical simulations were performed specifically to further understand and describe the nonlinear elastic stiffness of graphene (Cadelano et al., 2009; Lu and Huang, 2009; Wei et al., 2009).

AFM membrane deflection technique was applied in other works as well; Rasool et al. used the same technique to study the mechanical properties of CVD-grown polycrystalline graphene (Rasool et al., 2013), and obtained comparable strengths and stiffness to the single crystal graphene measured in Ref. (Lee et al., 2008). Gomez-Navarro et al. (Gómez-Navarro et al., 2008) also used AFM to measure the mechanical properties of reduced graphene oxide and obtained a Young's modulus of around 0.25 TPa, the difference from the values of pristine graphene are expected to stem from the fact that reduced graphene oxide contains more point defects in its lattice than pristine graphene (Gómez-Navarro et al., 2007). Lopez-Polin et al. performed AFM deflection tests to demonstrate the effect of the pre-

tension and controlled defects on stiffening graphene to values of 2D Young's modulus up to 700 N.m^{-1} and 550 N.m^{-1} , respectively (López-Polin et al., 2015b, 2015c).

Other techniques have also been employed to measure the elastic properties of graphene. Lee et al. (Lee et al., 2012) prepared graphene balloons by transferring graphene over circular holes patterned onto a substrate and then placing the sample in a vacuum chamber. Due to the impermeability of graphene, the atmospheric pressure is trapped in the circular hole and a pressure difference is created on both sides of the suspended membrane. Afterwards, they obtained Raman spectra of the strained graphene "balloon", and by comparing the spectra with numerical simulations, they estimated a single layer graphene's Young's modulus to be around $2.4 \pm 0.4 \text{ TPa}$. Another technique recently reported is using high resolution electron energy loss spectroscopy (HREELS) on graphene grown on different transition metal substrates to investigate the phonons dispersion in graphene from which the elastic properties can be estimated (Politano and Chiarello, 2015). This technique resulted in values for graphene's 2D modulus around 310 N.m^{-1} , and it was shown that the substrate on which graphene is grown also plays a role in determining the properties of graphene.

3.2.2 Bending response

Classical theories for plates and shells predict that a single atomic layer material like graphene would not have a measurable bending stiffness; however, theoretical studies have shown that graphene has a measurable bending stiffness (Kudin et al., 2001). Understanding the bending behavior of graphene is quite essential for many applications. Early studies have repeatedly shown ripples and wrinkles of graphene sheets whether suspended or supported on a substrate (Fasolino et al., 2007; Locatelli et al., 2010; Meyer et al., 2007) (section 2.2), these structural abnormalities are strongly related to graphene's bending behavior (C. Wang et al., 2009; Zhang et al., 2011). Moreover, the properties of carbon nanotubes which

are essentially graphene sheets subjected to bending also rely on the bending radius and stiffness of the graphene sheets.

The plate theory states that the bending stiffness of an elastic thin plate should scale with the thickness as follows, $D \sim Eh^3$, where D is the bending stiffness, E is the Young's modulus, and h is the plate thickness. This formula follows the classic Kirchhoff theory which assumes that stress and strain linearly vary along plate's thickness. However, Kirchhoff hypothesis cannot be applied to graphene because for an atomically thin graphene sheet, the physical thickness cannot be unambiguously defined in a continuum sense and therefore there has to be a different origin of graphene's bending stiffness. Huang et al. (Huang et al., 2006) derived an analytical method to determine graphene's bending stiffness directly from its interatomic potentials. They have shown that multibody atomistic interactions play a significant role in defining graphene's bending rigidity, and without these interactions, graphene would have no bending stiffness. Lu et al. (Lu et al., 2009) have also shown that the bending stiffness of graphene stems from the carbon atomistic interactions to the second and third nearest neighbors and calculated the bending modulus from an analytical model to be equal to 0.255 nN.nm. Additionally, it has also been shown that the bending stiffness becomes nonlinear as the radius of curvature increases. Wei et al. (Wei et al., 2012) used density functional theory calculations to predict a value for graphene's bending stiffness equal to 0.231 nN.nm. Further theoretical models have been reported to account for the dependence of the bending stiffness on temperature (Liu and Zhang, 2009), pre-strain (Shi et al., 2012), and chirality (Ma et al., 2011).

3.2.3 Shear response

Shear properties of graphene play a very significant role in its mechanical and electromechanical applications, especially in nanoelectromechanical resonators (Bunch et al., 2007) as graphene shear modulus determines the resonance frequency of vibration modes involving torsion which are advantageous since they do not suffer thermoelastic losses (Houston et al.,

2002). A lot of theoretical models and simulations have been performed to predict graphene's shear modulus. Reported values are ranging between 0.2 TPa and 0.4 TPa, moreover, high dependence on temperature and chirality is also reported (Georgantzinis et al., 2010; Min and Aluru, 2011; Sakhaee-Pour, 2009; Scarpa et al., 2009; Zakharchenko et al., 2009).

Liu et al. (Liu et al., 2010) reported first experimental measurements of graphene's shear modulus by transferring multilayered reduced graphene oxide and CVD grown graphene on Ni thin films on a the neck area of a double paddle oscillator (DPO) fabricated from p-doped <100> silicon wafers. DPO is a device designed to have a very high quality factor in some of its resonance modes. The resonance frequency of the oscillator was measured before and after depositing the graphene film and the difference is linked to the shear modulus. The calculated shear modulus value was reported to be around 53 GPa, which is much smaller than theoretically predicted values. The reason argued was that due to the graphene being multilayered, a lot of structure disorder is present which weakens the overall mechanical performance. Later, another experiment was reported to measure the shear modulus of a CVD-grown monolayer graphene by the same DPO technique (Liu et al., 2012). The measured shear modulus is 0.28 TPa; 5 times larger than that of multilayered graphene. This striking difference between shear moduli of single and multilayered graphene is in contrast with Young's modulus values which are only weakly affected by the number of layers of graphene.

In order to compare, graphene Young's modulus is similar to that of bulk graphite. Oppositely, the shear modulus of a monolayer graphene (280 GPa) is 5 times larger than multilayered graphene (53 GPa), which is in turn 5 times larger than the shear modulus of bulk graphite (~ 10 GPa). This thickness dependence of the shear modulus was explained by the fact that the shear restoring force in multilayer graphene is a result of the van der Waals interlayer interactions, while as the number of layers decreases and approaches a single layer graphene, the shear restoring force becomes

more governed by covalent intralayer interactions leading to a higher shear rigidity (Liu et al., 2012).

3.2.4 Fracture of graphene

In addition to graphene's elastic properties and strength as well as studying its linear and nonlinear response, a significant amount of work has also been dedicated to understanding the mechanisms by which graphene fails under load. Theoretical simulations have shown that graphene inherently fails by brittle fracture (Liu et al., 2007). Ab-initio studies have shown that tensile strain leads to phonon elastic instabilities in graphene in the form of longitudinal elastic waves, which is indicative of brittle fracture (Li et al., 2003). Brittle fracture takes place by the formation of crack defects and through the propagation of cracks, the atomic bonds in the material break successively, leading to mechanical failure. This behavior has also been observed experimentally where non-defective exfoliated graphene undergoes failure without any plastic deformation when deformed by an AFM tip (Lee et al., 2008). Density functional theory studies have reported that in addition to phonon elastic instabilities being the mechanism of failure of graphene, another mechanism takes place especially under biaxial strains, which is soft-mode phonon instability (Marianetti and Yevick, 2010). The fracture dynamics of graphene was studied by Terdalkar et al. (Terdalkar et al., 2010), and it was found that fracture occurs by an alternating sequence of atomic bonds fracture and atomic bonds rotation.

The fracture properties of graphene have also been experimentally investigated; Kim et al. (K. Kim et al., 2011) studied the preferred directions of crack propagation in graphene and found that cracks tend to align with the zigzag or armchair directions. More importantly, they reported that even the presence of a grain boundary does not stop cracks from propagating; instead the cracks cross the grain boundary. Moreover, MD simulations show that fracture of graphene nanoribbons (GNRs) can be insensitive to existing defects (Zhang et al., 2012). However, earlier molecular dynamics simulations have shown a tendency of graphene to

3.3 Tribological properties of graphene

undergo a transition from brittle to ductile behavior in the presence of vacancies and Stone-Wales defects (Xu et al., 2013). Zhang et al. (Zhang et al., 2014) later performed tensile tests on a pre-cracked graphene sheet and showed that the classic Griffith theory can be applied to calculate its fracture toughness and reported a value of $K_{IC} = 4 \text{ MPa}\cdot\sqrt{\text{m}}$. In the aforementioned work, it has also been demonstrated that the presence of grain boundaries does not significantly affect the crack propagation in graphene; however, other types of defects may significantly increase the fracture toughness to more than 25% of its value in pristine graphene. Lopez-Polin et al. (López-Polin et al., 2015a) then reported a systematic study of confining crack propagation in graphene by introducing vacancy defects in graphene by Ar ions irradiation. Accordingly, experiments were performed on reduced graphene oxide (known to have higher defects density), and it was indeed evident that crack propagation becomes very limited.

In summary, graphene has exceptional mechanical properties. It has a very high intrinsic strength, elastic modulus and shear modulus. Despite its structure as a single atomic layer, it also has a finite bending stiffness. Grain boundaries in polycrystalline graphene do not affect its mechanical properties significantly. Moreover, they do not stop crack propagation in the inherently brittle graphene which would lead to catastrophic failure. On the other hand, other types of defects (e.g: vacancies) significantly reduce the intrinsic strength and stiffness of graphene (although still higher than most materials), but they have a large effect on stopping crack propagation and transforming graphene into a ductile material. Graphene's properties and behavior under load can thus be tailored, depending on the application and the loading conditions.

3.3 Tribological properties of graphene

As discussed in the previous section, graphene has exceptional mechanical properties. Moreover, its atomically thin nature (Geim and Novoselov, 2007), impermeability (Bunch et al., 2008), and transparency (Nair et al.,

2008) have prompted its use in surface coating applications (Chen et al., 2011; Goli et al., 2013; K.-S. Kim et al., 2011; Won et al., 2013) and composites (Fang et al., 2009; Hwang et al., 2013; Kim et al., 2013; Rafiee et al., 2009; Ramanathan et al., 2008; Stankovich et al., 2006a). This in turn has made the study of graphene tribological properties very important from an engineering point of view in addition to the fundamental interest.

Tribology is essentially the science of solids in contact and graphene has very interesting surface properties. Wang et al. (S. Wang et al., 2009) reported first experimental measurements of surface properties, by preparing exfoliated graphene sheets and measuring its liquid contact angle, and reported graphene to be highly hydrophobic with very low surface energy. Kim et al. (K.-S. Kim et al., 2011) then showed that graphene modifies the adhesion and friction properties of a substrate when coating it. Their pull off forces measurements have shown that when graphene coated SiO₂ is in contact with a hard tip, the adhesion is small even at high contact loads. They attributed this less adhesive contact to a very small contact area between the rough tip and the surface. However, even with softer tips where the contact area is large enough, the presence of graphene lowers the surface adhesion by 13-26% (K.-S. Kim et al., 2011). Later, Pourzand et al. (Pourzand and Tabib-Azar, 2014) also performed measurements of adhesion between graphene covered substrate and an AFM tip and demonstrated that the tip's surface roughness plays a significant role in determining the adhesion with graphene. Ageing and oxidation of graphene also affects its adhesion properties. It was shown that with longer exposure to air or N₂ atmospheres, where graphene becomes slightly oxidized, the adhesion increases accordingly due to the increase in surface polarity (Lee et al., 2010). The interaction between graphene and the substrate underneath it also has a high impact on graphene's adhesion behavior. It was shown that graphene on SiO₂ substrates tends to have higher adhesion with an AFM tip than graphene on a Mica substrate after pre-strain (Liu et al., 2014). This effect is explained due to the fact that when graphene is weakly bound to a substrate (as in

3.3 Tribological properties of graphene

the case of SiO_2), graphene tends to locally delaminate under tensile loading from the tip; however with a strong interaction between graphene and the substrate this delamination is prevented which leads to less adhesion between the tip and the graphene. This indicates that graphene's adhesion properties are dependent on many factors including synthesis, number of layers, substrate morphology, transfer process, aging, and loading history.

Frictional characteristics of graphene have also been extensively studied, both theoretically and experimentally. Lee et al. (Lee et al., 2010) have shown that increasing the number of graphene layers leads to a decrease of the frictional force. Finite element models explained this phenomenon by the "puckering effect" where, when a tip makes contact with the graphene surface, due to its low bending stiffness it puckers locally around the tip and so increases the friction force as the tip slides across the surface. As the number of graphene layers increases, the bending stiffness increases, and therefore this effect has less significance. Lee et al. (Lee et al., 2010) have also shown that graphene on mica substrates does not show this trend, and, as discussed previously, this is because of the strong interaction between the graphene and the mica substrate (Lee et al., 2010; Lui et al., 2009). Filleter et al. studied the friction of epitaxially grown graphene on SiC (Filleter et al., 2009), and correlated the difference in friction coefficient between single and bilayer graphene to much lower electron-phonon coupling in the bilayer system.

There has been some evidence as well suggesting that friction in graphene is closely related to its adhesion properties (van der Waals interactions) (H. Lee et al., 2009). Deng et al. (Deng et al., 2012) studied the effect of adhesion on graphite's friction, the adhesion properties were varied by exposing the graphite to air and oxidizing it to varying degrees. It was found that with the increase of the surface energy, the friction increases accordingly. Furthermore, a surprising phenomenon was reported in the same work, which is that of an effective negative friction coefficient of graphite. It was demonstrated that as the tip-surface adhesion increases,

the friction tends to increase with decreasing normal loads. This phenomenon was explained as follows; when the tip is strongly adhering to the surface (due to oxidation), the adhesion force gets close to the exfoliation energy of graphene. Therefore, by decreasing the load, a graphene layer is delaminated from the bulk graphite and is in contact with the tip. As previously discussed, the friction of graphene (graphite) increases as the number of layers decrease, therefore, an essentially negative friction coefficient is observed for graphite with high surface energy (Deng et al., 2012).

In conclusion, in addition to graphene's exceptional strength and stiffness, graphene's tribological properties are unique and highly advantageous in different applications. Graphene coatings can be used to enhance wear resistance due to lower friction coefficient and it can also be used to lower surface adhesion. The tribological properties can also be tailored depending on the substrate supporting the graphene, the synthesis and transfer processes, and the environmental conditions.

3.4 Mechanical characterization tools used in this work

As discussed earlier, the objective of this thesis is to develop and test techniques to characterize mechanical properties of graphene, and to unravel the underlying physical mechanisms leading to those properties. Two different systems are characterized; graphene/substrate system and freestanding (suspended) graphene films. Three techniques are used throughout this work:

1. Nanoindentation of graphene/substrate system;
2. AFM graphene membrane deflection tests for suspended membranes;
3. On-chip tensile testing micro devices for suspended beams.

In this section, we provide the necessary background for each of these techniques.

3.4.1 Nanoindentation

Nanoindentation is one of the most widespread used techniques to characterize mechanical properties of materials at the micro and nano scale. It gives valuable insight into the material's elastic as well as plastic response and surface properties. Nanoindentation experiments are performed in the following way (illustrated in Figure 9); a sharp tip approaches the surface of the test material, and as it makes contact, the load increases and the tip goes deeper into the material until a certain point and then it starts unloading. The tip used for indentation is usually made from diamond to ensure it is hard enough and does not undergo deformation during the test. There are two modes to perform this experiment:

1. Load-controlled nanoindentation: the indentation depth is set and the corresponding load to reach this depth is measured.
2. Displacement-controlled nanoindentation: the load is set and the indentation depth corresponding to this load is measured.

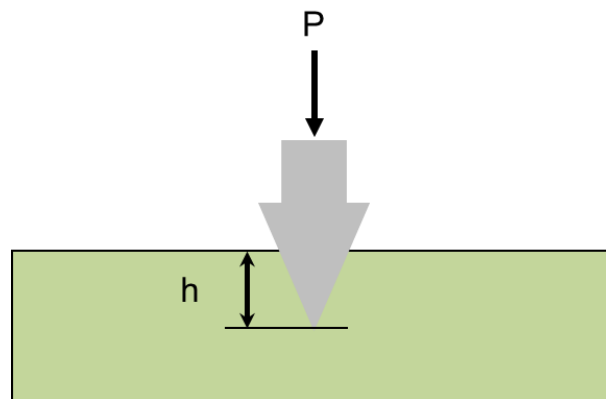


Figure 9: Schematic illustrating the concept of nanoindentation

Usually, nanoindentation is used to extract mechanical properties such as hardness and the Young's modulus. To extract these values, the load-displacement data from the nanoindentation test are analyzed. At the

loading part, the material undergoes elastic as well as plastic deformations. In the unloading part, only the elastic deformation is reversed. Imaging of the surface after indenting usually reveals a mark with a shape similar to the tip indicating irreversible plastic deformation. The material's hardness is defined as the load applied divided by the contact area. The load is directly measured during the test, while the area needs to be calculated. The contact area between the tip and the surface depends on the contact depth and on the tip geometry. Doerner and Nix (Doerner and Nix, 1986) developed a method to determine the contact depth (h_c), by assuming an initial linear unloading curve and extrapolating to a value of zero-load with the intercept being the contact depth. However Doerner and Nix's method was found to only apply to flat punch geometry tips. Oliver and Pharr (Oliver and Pharr, 1992) then proposed an improved method to determine the contact depth by finding the difference between the maximum depth during loading and the displacement of the surface at the perimeter of the contact. After determining the contact depth, the area can be calculated via a function usually taking the form of:

$$A(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{\frac{1}{2}} + \dots \quad (2)$$

where $C_0, C_1, C_2, \dots$ are fitting coefficients, and h_c is the contact depth. For a perfect Berkovich tip which is the most common shape in use, the lead coefficient is 24.5 while the rest of the coefficients describe deviations from the Berkovich geometry due to blunting, the area function can then be simplified to $A(h_c) = 24.5 h_c^2$. The hardness is then obtained as follows;

$$H = \frac{P_{max}}{A(h_c)} \quad (3)$$

where P_{max} is the peak load under the tip.

The Young's modulus is extracted through its relationship with the contact area and the unloading stiffness as follows

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \quad (4)$$

3.4 Mechanical characterization tools used in this work

where S is the unloading stiffness given by $\frac{dP}{dh}$, β is a geometrical dimensionless parameter and is in most cases equal to unity, and E_r is the reduced effective modulus given by

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_0^2}{E_0} \quad (5)$$

where E and E_0 are the Young's moduli of the test material and of the indenter, respectively, while ν and ν_0 are the Poisson's ratio of the test material and the indenter, respectively.

In addition to these models for extracting mechanical properties from the unloading curves of nanoindentation, the loading curves can also be used to obtain a lot of information about the material's elastic and plastic deformation. Figure 10 shows a typical loading curve for a ductile material. Usually, the initial part of a load-displacement loading curve is governed by the elastic properties of the material. According to Hertz model of contact between 2 isotropic elastic bodies, the load and the indentation depth are related by the formula (Johnson and Johnson, 1987):

$$P = \frac{4}{3}E_r\sqrt{Rh^3} \quad (6)$$

where P is the load, R is the sphere radius, h is the depth, and E_r is the reduced modulus as given by equation 5. It is clear from equation 6 that $P \propto h^{1.5}$ in the case of an ideal Hertz contact.

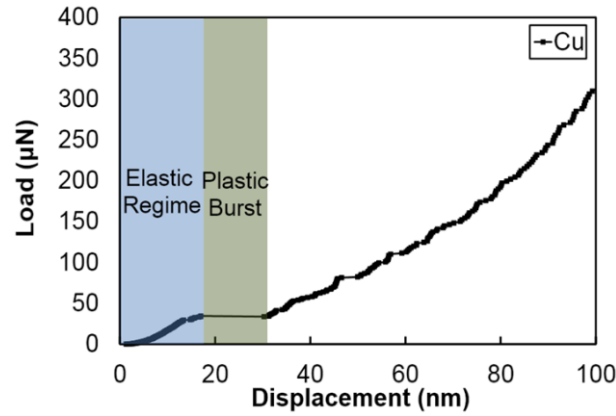


Figure 10: A typical load-displacement curve of a ductile material with a low defect density

Hertz theory has a few assumptions in order to be valid:

1. Two isotropic elastic bodies are in contact.
2. The surfaces in contact are frictionless.
3. Surfaces are continuous and non-conforming.
4. Strains involved are small, as well as displacements when compared to the radius of curvature R .

For most practical cases, these conditions are not present during contact. However, at very shallow indentation depths ($h \ll R$), the loading curve can be modelled by the Hertz law. Gouldstone et al. (Gouldstone et al., 2000) predicted that for a Berkovich tip, the Hertz model can accurately describe the load-displacement curve until a depth equal to $0.09R$. Moreover, it has been shown by experiments and simulations on tungsten that even if the system does not exactly fit the Hertz criteria, the elastic load-displacement data could still reasonably be described by a fit using the Hertzian relationship (Ma et al., 2012).

In metals, the load-displacement curve (Figure 10) -after the initial elastic part- shows a burst or pop-in in the form of a sudden increase in displacement with no increase in load (load-controlled experiments) or a sudden drop in load with no increase in displacement (displacement-controlled experiments). Different theories have been reported to explain

3.4 Mechanical characterization tools used in this work

this phenomenon. Numerical and experimental studies on Cu, Al, W, and steel have shown that these pop-in events are mainly due to dislocations emission under the tip when the load applied corresponds to a shear stress close to the theoretical shear strength of the material tested (Bahr et al., 1998; Gouldstone et al., 2000; Liang et al., 2003; Suresh et al., 1999). The length of the pop-in is corresponding to the number of the dislocations emitted during the event, which can be expressed as $N_{disloc.} = \frac{\Delta h_{max}}{b}$, where, N is the number of dislocations, Δh_{max} is the length of the pop-in in the load-displacement curve, and b is the Burger vector of the material.

Applying this technique to thin films, although very advantageous, is also complicated. The thickness of the film is important parameter in extracting accurate information about its mechanical properties. If the film is too thin, the substrate on which the film is deposited will play a significant role in the measured data. As a rule of thumb, the indentation depth should not be deeper than 10% of the film thickness in order to avoid any substrate effect. Furthermore, several models have been developed to extract thin film's properties from nanoindentation after accounting for the substrate effects (Bec et al., 2006; Chudoba et al., 2004; Saha and Nix, 2002; Schwarzer et al., 2006).

3.4.2 AFM graphene membranes deflection test

AFM membrane deflection is -as discussed previously- the most commonly used tools to characterize graphene's mechanical properties. A lot of work on graphene's mechanical properties has been performed using this technique (Lee et al., 2008; López-Polin et al., 2015b, 2015c; Rasool et al., 2013). The concept is to use an AFM tip to stretch a suspended circular membrane of graphene (over trenches or holes), and to record the load applied and the deflection the membrane undergoes. From membrane mechanics models, the stiffness and other mechanical properties could be calculated.

Lee et al. (Lee et al., 2008) showed that although graphene is a non-linear elastic material, the non-linear component is insignificant in calculating its response to load. Also, it was shown that experimental error in setting the point where graphene membrane is loaded does not have a significant effect on the load-displacement response. Moreover, their work showed that as long as the tip radius is very small compared to the membrane diameter, the radius does not have a prominent effect on the load-displacement response. Based on these observations, it was concluded that this system can be modelled as a 2D clamped circular membrane of a linear isotropic elastic material subject to central loading. Therefore, the load-displacement response should be governed by the following model (Komaragiri et al., 2005; Wan et al., 2003):

$$F = \varepsilon_{2D}\pi d + E^{2D}q^3 \frac{d^3}{a^2} \quad (7)$$

where F is the load, ε_{2D} is the pre-strain in the membrane, d is the membrane deflection, E^{2D} is the 2D elastic constant of graphene, a is the membrane radius, and q is a dimensionless parameter equal to $1/(1.05 - 0.15\nu - 0.16\nu^2)$ which can be approximated to 1.

After obtaining the load and deflection from AFM measurements, equation 7 can be used to fit for ε_{2D} (pre-tension) and E^{2D} (elastic constant) of graphene. Therefore, the load and displacement values must be very accurately determined with the AFM equipment. Figure 11 shows a schematic for the AFM membrane deflection technique. A cantilever with the tip at its end is brought close to the suspended membrane, and the displacement of the cantilever is given as z . When the cantilever gets in contact with the membrane, it starts deflecting the membrane depending on the load applied. The membrane deflection is given as d . However, because the tip/cantilever system is not infinitely stiff, some bending of the cantilever also takes place which has to be accounted for in the form of the displacement d_0 . In order to accurately obtain the load and displacement values, the z and d are measured, and then, the displacement is calculated

3.4 Mechanical characterization tools used in this work

as $\delta = z - d_0$, while the load is calculated as $F = k * d$, where k is the spring constant of the cantilever.

Last parameter that has to be carefully considered for this test is setting the zero-point of the curve, which is defined as the point where the tip first makes contact with the surface of the membrane. This process will be further explained in chapter 7.

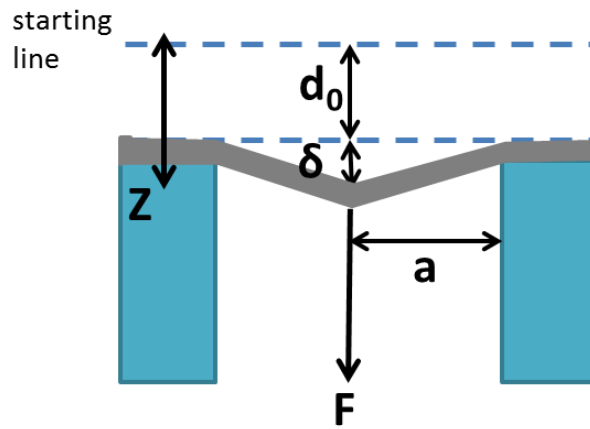


Figure 11: A schematic illustrating the AFM deflection test on graphene membranes

3.4.3 On-chip tensile testing devices

Tensile tests on thin films offer a direct and accurate way of measuring loads and strains on test samples. However, performing a tensile test on samples in the micro or nano scale is extremely challenging. Challenges stem from fabrication techniques, handling of micro or nano scale samples, load generation, and measurements resolution.

Several techniques and devices have been proposed to perform such tests on thin films. Sharpe et al. (Sharpe et al., 1997) reported a technique to fabricate a silicon frame containing the desired specimen. The specimen is then released by etching the layer underneath and freed from the frame by cutting the supports and then mounted on a testing stage actuated by a

piezoelectric actuator, the load is then measured by a load cell and the displacement by an interferometric strain displacement gauge. Tsuchiya et al. (Tsuchiya et al., 1998) also reported a technique where a specimen is fabricated on a substrate so that it is fixed on one end and freestanding on the other, and by using an electrostatic gripper and a piezoelectric actuator, the specimen is uniaxially loaded and the strain is measured by a strain gauge. Later, Cheng et al. (Cheng et al., 2005) reported a technique where a specimen is created by microfabrication techniques with a holed pad, the specimen is then released and freed from the substrate except for one end, and a hooked arm is connected to the specimen through the hole, and by an external micromanipulator the load is applied to the hooked arm and to the specimen, and finally the displacement and strain are calculated using digital image correlation. Espinosa et al. (Espinosa et al., 2003) reported a technique where a dog boned specimen is fixed at both sides, and a nanoindenter loads the wider middle part of the specimen causing stretching at the dogbones, and by using an interferometer below the specimen, the strain is measured.

In all those techniques, the main problem is the connection between the specimen and the external source of actuation. In order to avoid this problem, a MEMS-based technique would be needed where the actuator and the specimen are integrated on the wafer. Saif et al. (Haque and Saif, 2002) thus fabricated a stage made of single crystal silicon, with one end attached to a piezoelectric actuator, and the other is fixed. The specimen is then deposited on the stage with one end connected to the fixed beam acting as a load sensor and the other to the supporting beam assembly, the whole chip is then pulled, and the displacement is directly measured by cursors next to the specimen. Espinosa et al. (Espinosa et al., 2007) then reported a technique where electrostatic or electrothermal actuators are used to load the test specimens on a stage with capacitive sensors to measure the loads.

The technique used in this work to apply uniaxial strain on graphene and to characterize its mechanical properties has been developed to avoid the

3.4 Mechanical characterization tools used in this work

issues with the previously mentioned techniques and to provide a simple yet versatile tool to perform tensile testing on materials at the micro scale (André et al., 2007; Boe et al., 2009a; Fabrègue et al., 2007; Gravier et al., 2009). It has 2 main advantages over the techniques mentioned before in this section:

1. It utilizes the internal stress in the films deposited on the wafer to actuate the testing devices
2. It makes use of the capability of microfabrication technologies to fabricate hundreds or thousands of devices on a single wafer

The devices are created in the following way; first a sacrificial layer is deposited on a Si wafer, followed by another thin film which is then patterned into beam shapes and these beams act as actuators. Finally the test material layer is deposited and also patterned into beam shapes. Figure 12 shows a schematic of the process flow to create the testing devices. The actuator layer should have a high mismatch strain when deposited, so that after the sacrificial layer is etched away, the actuator beams contract due to relaxation of the internal stress. Since the specimen beams are attached to the actuator beams through adhesion, the contraction of the actuator beams applies a displacement on the specimens. If the test specimens are long enough ($\text{length} \gg \text{width}$), the stress state is almost perfectly uniaxial with negligible misdisplacements. By creating many of these devices on wafer with different lengths and widths for both the samples and the actuators, a wide range of loads could be applied to the test specimens. The deformation of the specimen material can be determined by measuring the displacement between fixed and moving cursors. These cursors are patterned into the actuator beams.

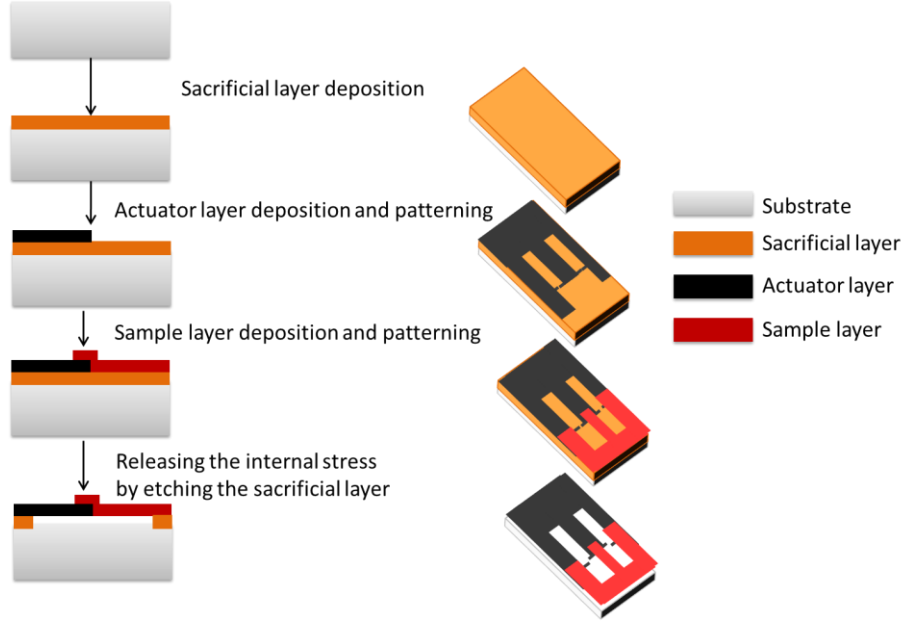


Figure 12: Illustration for the process flow of fabricating an on-chip tensile testing devices

The strain is defined as the amount of deformation (measured displacement) divided by the initial length of the specimen;

$$\varepsilon_{tot} = \frac{u}{L_i^t} \quad (8)$$

where ε_{tot} , u and L_i^t are the total strain, displacement, and initial length of the specimen, respectively. The stress is then calculated by applying force equilibrium to the actuator-specimen system at their final position. In order to successfully apply this technique; the actuator beam must only undergo elastic deformation. The force in the actuator needs first to be considered and the strain in the actuator beam is defined as the sum of the mechanical and the mismatch strain:

$$\varepsilon_{tot} = \varepsilon_{mech.} + \varepsilon_{mis} \quad (9)$$

The total strain in the actuator beam can also be defined as the displacement divided by the initial length as in equation 8. In this case, we have:

3.4 Mechanical characterization tools used in this work

$$\varepsilon_{tot} = \frac{-u}{L_i^a} \quad (10)$$

where L_i^a is the initial length of the actuator beam, note the negative sign is because the direction of strain in the actuator beam is opposite to the direction of strain in the specimen beam.

The mismatch strain is then defined as:

$$\varepsilon_{mis} = \frac{-u_{free}}{L_i^a} \quad (11)$$

By substituting equation (10) & (11), into equation (9), the mechanical strain in the actuator beam can be written as:

$$\varepsilon_{mech.} = \frac{-u}{L_i^a} - \frac{-u_{free}}{L_i^a} \quad (12)$$

The mechanical stress in the actuator beam according to Hooke's law is written as:

$$\sigma = E_a \varepsilon_{mech.} \quad (13)$$

where E_a is the actuator material's Young's modulus. The force is then defined as the stress multiplied by the cross section area of the beam, so by substituting in equation 12, it can be written as follows:

$$F = \frac{S_a E_a}{L_i^a} (u_{free} - u) \quad (14)$$

where S_a is the actuator beam's cross section area. By considering the force in the actuator beam to be equal to the force in the specimen beam, the stress in the specimen can be calculated as follows:

$$\sigma = \frac{F}{S} = \frac{S_a E_a}{S L_i^a} (u_{free} - u) \quad (15)$$

where S is the cross section area of the specimen beam. From equations (8) & (15), it is clear that the stress and strain of the specimen material can be calculated by simply measuring the displacements of the actuator-specimen system, the displacement of the free actuator, and by knowing the

mechanical properties of the actuator material used. It is worth noting that by using this technique; each individual device will deliver one point on the stress strain curve, and by varying the geometries of the actuator and the specimen beams, different points can be calculated, resulting in the end in a full stress strain behavior curve of the tested material.

This technique has several advantages compared to the methods previously described:

1. Extraction of mechanical properties is simple and just needs measuring the displacements after release.
2. It avoids the use of external sources of actuation, and external means to join the actuator and the specimen together since they adhere to one another during fabrication.
3. It is a very versatile method, and by few design adjustments can also be used to test shear, bending, and compression deformations. It can also provide information about creep and strain hardening by in-situ TEM loading (Colla et al., 2015). Moreover, by depositing metallic contacts, piezoelectric properties can also be measured (Pardoen et al., 2016).

This method has been used successfully to characterize the mechanical properties of several materials including thin films made of Al (Coulombier et al., 2010), Al_2O_3 (van der Rest et al., 2017), polysilicon (Mulay et al., 2015), single crystal Si (Bhaskar et al., 2012), Cu (Lapouge et al., 2017), Si_3N_4 (Boe et al., 2009b), Pd (Idrissi et al., 2011), and metallic glass (Ghidelli et al., 2017). Accommodating a single layer graphene into this process involves a series of processing challenges that are addressed in chapter 8.

Chapter 4: Experimental techniques

In this research, several experimental techniques are used for samples fabrication, preparation, and characterization. In this chapter, the most important and significant techniques used during this thesis are discussed.

4.1 Clean room fabrication techniques

All the fabrication work in this work has been performed at the WINFAB¹ facilities. As a priori for all processes, a silicon wafer is the substrate onto which all subsequent steps are performed. At WINFAB, the wafers used are 3 inch diameter wafers, with a thickness of 380 μm . The wafers are polished on one side, and are made of monocrystalline silicon. Afterwards, in order to grow graphene by CVD, a thermal oxide layer is grown onto the wafer, followed by a copper thin film deposited by electron beam evaporation as described in section 5.1.

The most significant fabrication tools that have been used in this work are:

1. Plasma enhanced chemical vapor deposition (PECVD)
2. Etching (dry and wet etching)
3. Lithography (photolithography & electron beam lithography)
4. Critical point drying (CPD)

4.1.1 Plasma enhanced chemical vapor deposition (PECVD)

In this work, PECVD is used to deposit thin films of silicon nitride. PECVD works by creating plasma of the desired gas species by an RF source, which then undergo chemical reactions, and deposit on the substrate in a solid state, while the byproducts of the reaction are pumped away. In the case of depositing nitride films, the gases used are SiH_4 which acts as a precursor of Si, NH_3 which acts as precursor of nitrogen. Other gases also take part in the process as carrier gases, namely N_2 and He.

¹ WINFAB stands for Wallonia Infrastructure Nano FABrication, and is a clean room facility used for microelectronics and MEMS fabrication

The most important parameters to control during PECVD are the power at which the plasma is created, the chamber pressure, and the temperature at which the substrate is heated. Typically, a PECVD process takes place at a temperature range from 200 °C - 400 °C, and is considered a low temperature alternative to low pressure chemical vapor deposition (LPCVD) which typically takes place at temperatures between 600 °C and 800 °C. However, the thin films produced by PECVD typically are less dense and less stiff than those produced by LPCVD. As a rule, a higher temperature and a higher power will lead to a stiffer and a more dense film. Another issue with PECVD nitride is that it tends to be non-stoichiometric taking the form of SiN_x instead of Si_3N_4 . Furthermore, in some cases there might exist some hydrogen atoms in the deposited film due to the use of SiH_4 , which indicates that a more accurate description of the film is SiN_xH_y . However, for the sake of the simplicity, the nitride film will be denoted as Si_3N_4 in the rest of this work.

The deposition rate is critically dependent on the flow of the reactive gases, and on the power at which the plasma is created. Normally, a higher gas flow and a higher power will lead to a higher deposition rate. A PECVD nitride film is amorphous and therefore its thickness can be characterized by optical ellipsometry.

4.1.2 Etching

In this work, etching is a main and a critical step during the fabrication process. There exists two principal methods of etching; dry and wet etching. Dry etching is usually a mixture of physical and chemical processes, and the most commonly used technique is reactive ion etching (RIE), while wet etching is a purely chemical process using a chemical solution depending on the material to be etched.

RIE is essentially similar to the PECVD process explained in the previous section. A mixture of etching gases flows into the chamber, and an RF powered magnetic field creates plasma of those gas species, which then bombards the target substrate sputtering some material by transferring

kinetic energy while undergoing a chemical reaction with the target material on the surface. The gases typically used with RIE in this work are O_2 , CHF_3 , SF_6 , and Cl . Due to the vertical nature of the plasma ions bombardment RIE produces a highly anisotropic etch profile. This means that the etching is directional, and shapes with high aspect ratios can easily be achieved. However, one drawback of RIE is the poor etching selectivity. Etching selectivity is the ratio between the etch rate of the target material, and the etch rate of other materials present in the system. As an example, if the target is to etch a nitride layer on top of an oxide layer, the etching will not stop when the nitride layer is removed, instead, it will continue and etch some of the oxide layer as well. Normally, recipes with very high etching selectivity can be achieved, and therefore minimizing the unwanted etching.

On the other hand, wet etching uses a chemically active solution to react with the target material. Usually, high selectivity can be achieved by wet etching by selecting the right solution. However, wet etching reacts with the target material in all directions leaving an isotropic profile, which means that structures with a high aspect ratio cannot be patterned by wet etching. Figure 13 illustrates the difference between anisotropic and isotropic etch profiles.

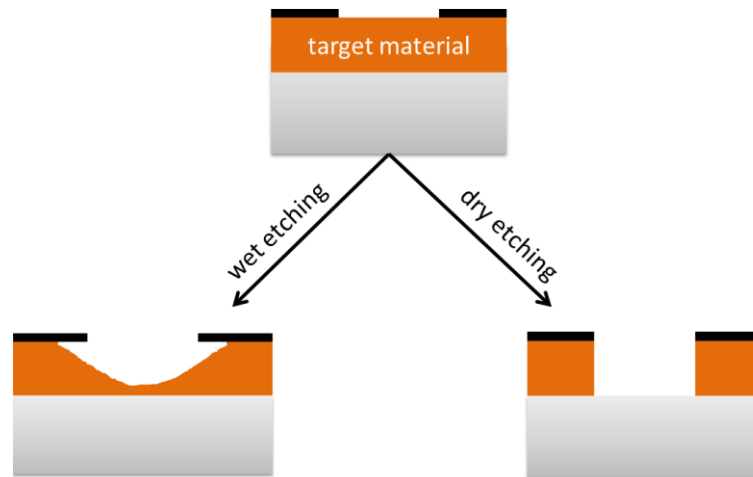


Figure 13: A schematic comparing anisotropic dry etching vs. isotropic wet etching profiles

4.1.3 Lithography

During this work, a lot of different designs and structures have been fabricated in order to achieve the desired devices and samples. Lithography is one of the most important techniques to be used in any microfabrication process. There are two main types of lithography used throughout this work; first, photolithography, and second electron beam (e-beam) lithography. Lithography uses an electromagnetic source exposing a resist to print a predefined structure on it, which, combined with etching methods, transfers this structure to the thin film underneath. Figure 14 shows a schematic illustrating the concept of lithography.

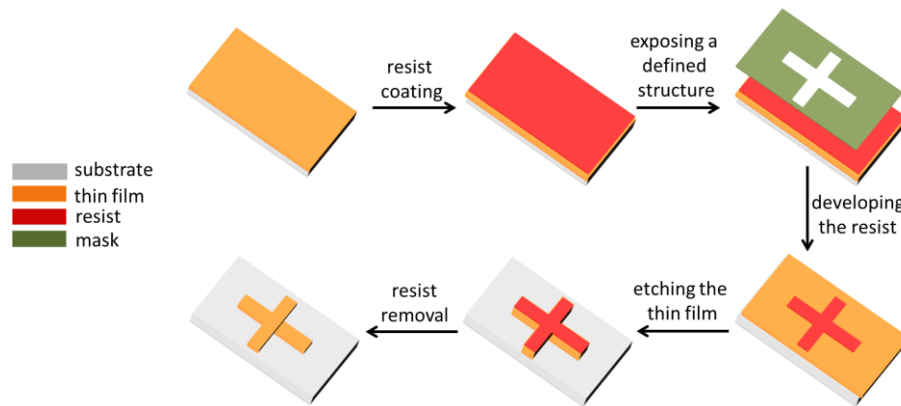


Figure 14: schematic illustrating the concept of thin films lithography

In photolithography, a UV light source is used as the source of exposure. The resist used at WINFAB is AZ6612 photoresist. The process starts by coating the substrate first with a HMDS thin layer to act as an adhesion promoter, followed by spin coating the photoresist. The photoresist is then exposed using the desired photomask (usually made of Cr). Afterwards, the photoresist is developed by an AZ726MIF developer, and the exposed areas of the resist are removed. In most cases, this is followed by etching exposed material and stripping the photoresist in order to achieve the final structure.

E-beam lithography works similar to photolithography; however, in this case the source of exposure is a high energy electron beam. In e-beam lithography no mask is used, instead, a predefined structure is fed to the electron beam controller, and so the beam scans the surface according to this structure. In e-beam lithography, the resist used is PMMA, which can then be developed using a solution of isopropanol (IPA) and methyl isobutyl ketone (MIBK).

In most cases, photolithography is the preferred technique, since one photomask can have thousands of structures and the exposure is done at once, and therefore, it is easy to process a whole wafer in a short time. In e-

beam lithography, the electron beam scans each structure one by one, which makes it much less efficient if many structures are to be patterned. However, e-beam lithography is superior to photolithography in terms of resolution of the structures that could be achieved. Photolithography at UCL typically has a resolution of around 1 μm , while e-beam lithography can go down to few tens of nanometers.

4.1.4 Critical point drying (CPD)

CPD is the technique mostly used for drying the samples of the micro tensile testing devices. The advantage of CPD is that it allows removing the liquid in a controlled way, which minimizes the capillary and surface tension forces resulting from the transition of the liquid from a liquid to a gas state, which may lead to damaging the devices. Instead, CPD uses high temperature and high pressure conditions to reach a supercritical state where distinction between liquid and gas phases is not applicable anymore. Figure 15 shows a schematic of a fluid phase diagram illustrating the supercritical state.

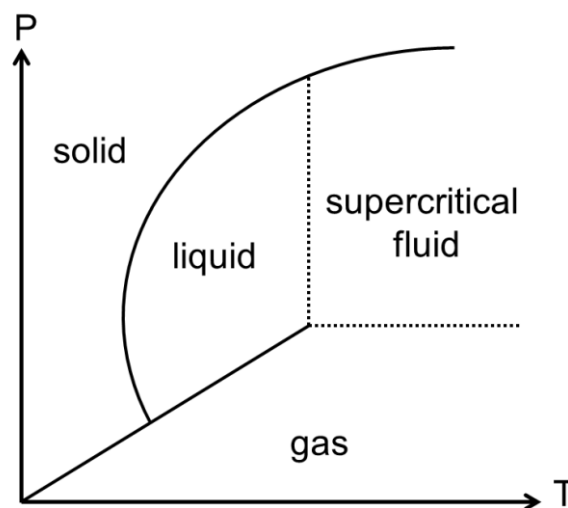


Figure 15: Schematic of a fluid phase diagram as used in CPD

At WINFAB, the CPD is performed after the samples are well rinsed in DI water and then in either IPA or methanol. The CPD chamber is then cooled down, and is filled with fluid CO₂ to wash away the IPA (or methanol), the pressure of the CO₂ is then increased along with increasing the temperature of the chamber, which leads to the CO₂ to reach the supercritical state. Afterwards, the gas CO₂ is pumped from the chamber, and the sample is dry.

4.2 Characterization tools

In this work, several tools of microscopy and spectroscopy are used for characterizing the samples. The tools used include SEM, TEM, AFM, and Raman spectroscopy. The two most important tools that affected the results are AFM and Raman. Therefore, in this section, a short background on the methodology of each technique is introduced. The different modes and calibration procedures are discussed.

4.2.1 Raman spectroscopy

Raman spectroscopy is arguably the most important tool used for characterizing graphene and interpreting the Raman spectra provides a huge amount of information. In this work, Raman spectroscopy is used in many cases to assess the graphene's quality after each processing step. The Raman system at UCL is a Horiba HR 800. The Raman setup is shown in the schematic in Figure 16.

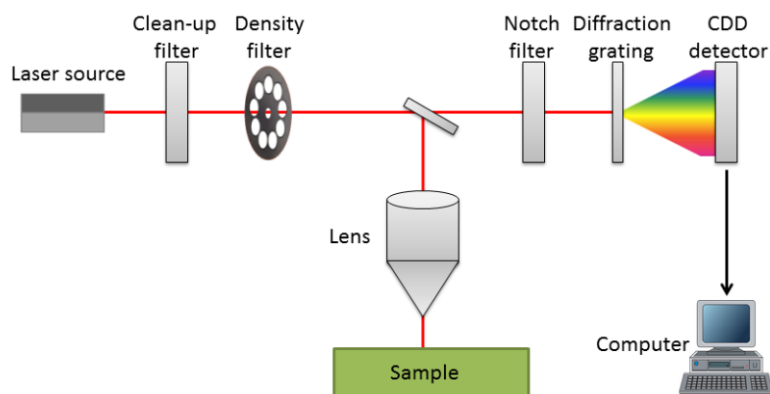


Figure 16: Schematic of the Raman measurement setup

The laser with the desired wavelength is directed on the sample, and a clean-up filter ensures the desired wavelength only goes through, afterwards a density filter controls the power of the laser directed on the sample. In our case, 100%, 50%, 25%, 10%, 1%, or 0.1% of the power are possible. The power is usually chosen as low as possible to avoid any heating effect in the spectra, however, large enough so that a high signal to noise ratio can be acquired. Afterwards, the reflected light from the sample is passed through a notch filter to eliminate the elastically scattered light (i.e.: light with same wavelength as the incident laser), and the inelastically scattered light is passed to a spectrometer where a diffraction grating is used to disperse the light into different wavelengths on a CDD detector.

With Raman spectroscopy, two important parameters have to be set; the laser to be used which would also control the blazing angle for the grating, and the groove density in the grating. In this work, a green laser with a wavelength of 514 nm is used. The groove density is chosen based on the resolution required for the measurement, and the wavelength range that should be covered. As a rule, as the groove density increases, the resolution also improves, but the covered wavelength range is reduced. At our lab, the options of the groove density are 150, 1200, and 2400 grooves/mm, and all measurements are done by using the 2400 grating. To account for reduced

wavelength range covering, several scans are done at different ranges. Normally, for graphene, the spectra are recorded between 1000 and 3000 cm^{-1} . The laser spot size is $\sim 1 \mu\text{m}$.

Raman does not require any special sample preparation; however, a calibration of the instrument has to be made before the measurements are performed. The idea is to calibrate the position of the grooves to the peak correct peak positions. For this, a standard Si sample is used with a well-known Raman peak at 520 nm. Moreover, the zero-band beak is also calibrated to ensure that not only the absolute position of the grating is correct, but also the relative wavelength shift.

4.2.2 Atomic force microscopy (AFM)

AFM was used in this work for deflecting suspended graphene membranes. Before the tests were performed, scanning the surface is also necessary in order to verify which membranes are suspended and would give correct mechanical response when the load is applied. The working principle of AFM is shown in Figure 17.

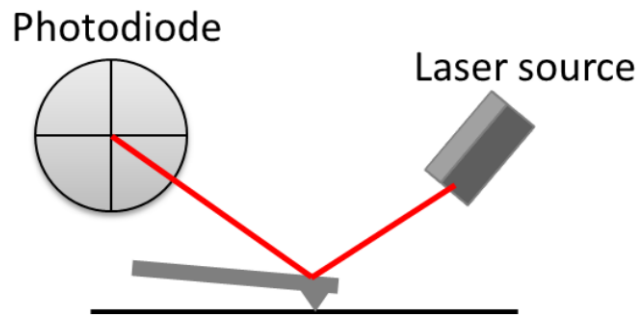


Figure 17: Schematic representing the working principle of AFM

A sharp tip mounted on a cantilever raster scans the surface either in contact or in close proximity, and depending on the surface profile; attractive or repulsive forces arise between the sample surface and the tip which causes the tip to deflect. The tip deflection is measured by a laser which is reflected from the tip to a position sensitive photodiode which

detects the position of the tip at each point on the surface, thus giving a total scan of the surface topography with a resolution down to few Angstroms.

There are several modes of AFM operation; contact mode, non-contact mode, and tapping mode. In contact mode, the tip is in soft contact with the sample and the interatomic forces between the atoms in the tip and the atoms on the sample surface cause the deflection of the tip. While, in non-contact mode, the sample is in proximity of the surface, and the long range van der Waals forces are used to detect the topography of the sample, however, in non-contact mode, it is extremely difficult to measure the tip deflection accurately. Therefore, the tip is usually vibrated at its natural resonant frequency or just above, and when the tip is close to the surface, the van der Waals forces cause the vibration to shift its amplitude or its frequency leading to an image of the surface. However, non-contact mode is a slow technique compared to other modes, and in some cases, vacuum might be needed for accurate imaging. Finally, tapping mode works also by oscillating the tip close to its resonant frequency, with the amplitude kept constant, and as the sample comes closer to the surface, the amplitude changes leading to a full topography profile depending on the recorded amplitude shifts.

In this work, we use the Dimension Icon model AFM by Bruker. For scanning the sample surface, peak force tapping mode is used. It is a form of tapping mode; however, the tip is vibrated at frequencies well below the resonant frequency which allows control of the force during the intermittent contact between the tip and the sample surface, thus enabling the use of very low contact forces in the order of pN to avoid any damage to the surface, while, keeping the scan much faster than by using non-contact mode and eliminates the need for vacuum.

The membrane deflection is performed at the center of the membrane by applying an increasing load up to a set maximum value, while recording the displacement of the cantilever.

PART II:
MECHANICAL TESTING OF
GRAPHENE-ON-
SUBSTRATE SYSTEMS

Chapter 5: Nanoindentation samples preparation and test methodology

Copper/graphene is the system selected to be studied in this part of the work, mainly because, graphene is easily deposited on copper surfaces (thin films or foils) by CVD. Therefore, studying this system to understand its mechanics is very beneficial for applications of graphene in coatings and composites. Nanoindentation is a very powerful and versatile tool to probe the mechanical properties at the nanoscale. The information from the nanoindentation load-displacement curve can be used to extract characteristics of the elastic, plastic, and fracture response of the probed material in very small volumes. The objective of using this technique with copper/graphene is to first study the possibility of deconvoluting its response in order to obtain graphene's mechanical properties; specifically graphene's stiffness. The second objective is to understand the effect graphene has on the elastic and on the plastic response of Cu during nanoindentation; therefore, all nanoindentation tests were performed on bare Cu surfaces to compare with Cu/graphene.

5.1 Samples preparation

The first step in fabrication is the thermal oxidation of the Si wafer; this is performed in a vertical Koyo furnace at a temperature range between 800 and 1200 °C. In this step, an oxidizing agent diffuses into the wafer at high temperature for the oxidation reaction to take place. The reaction time is set so that the final oxide layer has a thickness of 300 nm. Optical ellipsometry is used to confirm the thickness of the oxide layer.

Graphene was grown for these experiments on both Cu thin films to characterize Cu/graphene systems and Cu foils by CVD to transfer graphene from the foils to other substrates. Cu thin films with thickness of 1 μm are deposited by electron-beam evaporation of Cu pellets (Kurt J. Lesker, 99.9999% pure) onto the thermally oxidized silicon wafer. Electron beam evaporation is a form of physical vapor deposition (PVD). In this process, a

charged tungsten filament under vacuum emits an electron beam which bombards the anode made of the target material (Cu in this case), causing the target material atoms to transform into the gaseous phase, which then precipitates in a solid phase on the wafer in the chamber. The Cu foils are purchased from Advent Research Materials Ltd, Oxford and has a purity level of 99.9% (ref: Cu130318).

Afterwards, the substrates are placed in the CVD reactor. The CVD reactor consists of a horizontal hot-wall CVD reactor from MTI corporation (1,2 meter-long quartz tube with a 4-inch outer diameter, lot type: EQ-OFT-1200x). The gas inlet is monitored using 3 mass flow controllers connected to a pure Ar, a CH₄/Ar (2500 ppm) and a H₂/Ar (10 %) gas bottle. The gas exhaust is carried out by a dry compressing SCROLLVAC SC-15D from Oerlikon Leybold Vacuum. To regulate the global pressure, two valves were arranged in parallel and placed between the pump and the furnace. The first valve (Pfeiffer Vacuum, Diaphragm manual valve) can achieve a larger aperture and therefore is mainly used during the gas line purge and the pumping to base vacuum. The second valve (fine metering valve, Pfeiffer Vacuum EVN 116) is used to precisely control the pressure during the graphene formation stage. In order to measure the pressure as accurately as possible, two gauges located between the CVD reactor outlet and the set of valves are used. The first pressure gauge (Pirani, Pfeiffer Vacuum TPR 270) measures the base pressure and make sure that the CVD reactor is hermetically sealed. The second pressure gauge (gas-independent capacitance transmitter, Pfeiffer vacuum CMR361) monitors the actual gas pressure during the CVD process. Using a gas-independent capacitance gauge in addition to the Pirani Gauge is critical given the high concentration of Ar in the gas phase.

To start graphene growth, the tube is evacuated down to a pressure of about 0.02 mbar and the feedstock gas lines are purged to prevent the presence of undesired species and ensure negligible furnace contamination. Then a one hour long heating ramp is performed under a constant flow rate

of pure Ar (Praxair, 6.0 grade, 200 sccm) which increases the global pressure up to 400 mbar. Once the growth temperature (1035 °C) is reached, the Ar flow is stopped and replaced by H₂/Ar (10%, 350 sccm) and CH₄/Ar (2500 ppm, 23.5 sccm) flows which raise the global pressure up to 750 mbar. The Ar/H₂ and Ar/CH₄ flows are injected during the 60 minutes high temperature graphene growth step and during the cooling down. For the samples of bare Cu surface, the exact same procedure is performed with the exception of injecting Ar/CH₄ in order to avoid the growth of graphene while having the same surface conditions for both samples. Figure 18 shows the temperature profile and the pressure during the CVD process.

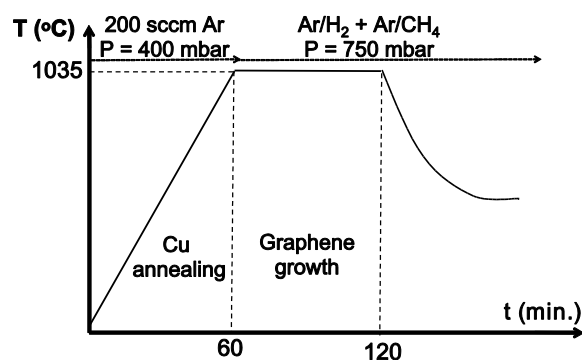


Figure 18: Temperature and pressure profile during CVD growth of graphene

SEM images (Figure 19a) show that the domains grown are of high quality single layer graphene with domain sizes in the order of millimeters which is very sufficient to perform nanoindentation tests. Moreover, Raman spectra (Figure 19b) confirm that graphene is a single layer and that there are nearly no defect sources in the deposited graphene.

In this work, graphene grown on Cu foils has been transferred on different types of substrates; namely SiO₂/Si and 1 μm Cu thin films deposited on SiO₂/Si wafers. Graphene transfer on both types of substrate is done the same way as explained in section 2.1.2. However, more care has to be

taken when transferring graphene on Cu thin films, especially with the rinsing and drying steps. The reason for this is that any residues left on the graphene/PMMA film from the Cu etchant used to remove the Cu foil will attach to the Cu thin film after transfer. To avoid this, the graphene is rinsed for longer and in more fresh water baths, and during drying, the substrate has to be left in vertical position so that any residues can leave the surface of the wafer as soon as possible.

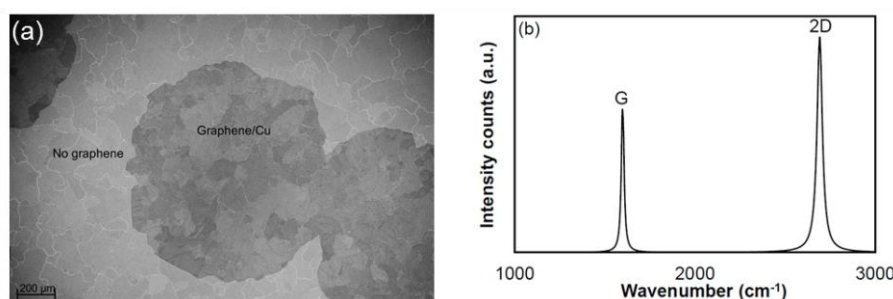


Figure 19: a) SEM image of the CVD grown graphene on Cu thin film, b) Raman spectrum of the CVD grown graphene on Cu thin film fitted to Lorentzian peaks. Note the absence of a sizable D peak.

5.2 Nanoindentation measurements

Nanoindentation experiments were performed on an Agilent nanoindenter utilizing the continuous stiffness measurement (CSM) method with a dynamic contact module (DCM) head of a diamond Berkovich tip with a diameter of the rounded extremity of around 40 nm. CSM is used as it is more accurate while measuring the mechanical properties, due to its capability of separating the in-phase and out of phase components of the load-displacement measurements. Moreover, the DCM head is used owing to its superior resolution (displacement resolution = 0.0002 nm, while load resolution = 3 nN) which facilitates studying the samples at the surface contact level. The tip was calibrated before measurements on a reference silica sample with a known Young's modulus. 16 indents are performed on silica, and the resulting load-displacement curves are used to calibrate the

tip's area function. Figure 20 shows the load displacement curve of silica, and the area function of the tip is found to be in the form of $A(h_c) = 23.53h_c^2 + 509.9h_c - 2343.24h_c^{\frac{1}{2}} - 768h_c^{\frac{1}{4}} + 4146.15h_c^{\frac{1}{8}} \dots$.

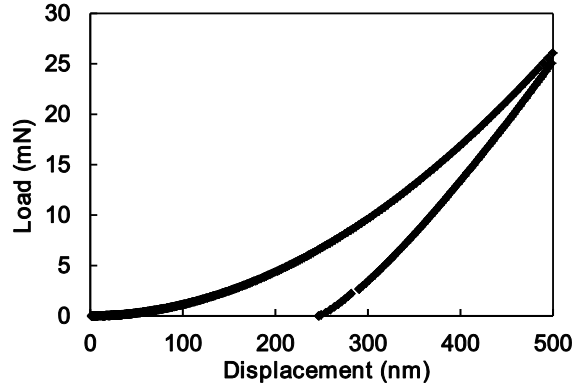


Figure 20: Load-displacement curve of nanoindenting (loading & unloading) the reference silica sample.

Afterwards, 120 indents are performed under displacement controlled mode on each Cu and Cu/graphene in order to generate statistically robust results. First treatment of the data showed that the point of surface contact has to be defined on the curve. This is done by investigating the contact stiffness curve of each indent, and manually setting the zero point when the contact stiffness first shows a sudden increase.

As discussed in section 3.4.1, and as shown in Figure 10, typical load-displacement curves for a metal show a purely elastic behavior as long as the indentation depth is low enough. The end of the elastic regime appears with a first “pop-in”, typically at an indentation depth between 8 and 12 nm for Cu. This pop-in normally occurs at loads corresponding to the theoretical shear strength of the indented material. The pop-in indicates the onset of dislocations nucleation and propagation in the material. The length of the pop-in is proportional to the number of dislocations involved in this plasticity event.

Figure 21a shows a single indentation load-displacement curves for both Cu and Cu/graphene surfaces. It is observed that the overall behavior is similar for both. However, careful investigations revealed differences in both the elastic and plastic parts of the curve. Also, averaging the load-displacement curves of the 120 indents performed (Figure 21b) revealed significant differences for both the elastic and the plastic response in the presence of graphene. The effects of graphene on the elastic and plastic responses will be discussed separately in the next chapter.

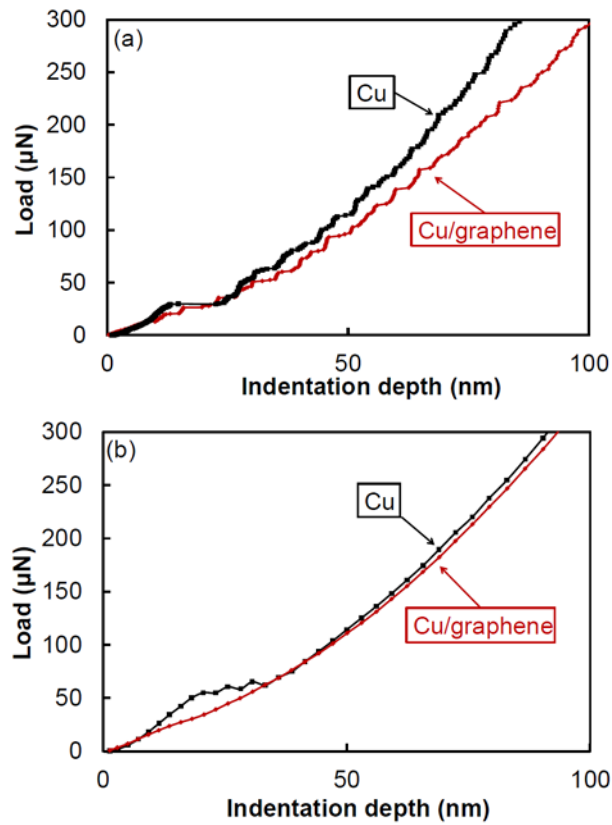


Figure 21: a) Load-displacement curves of single indents performed on Cu and Cu/graphene,
b) Average load-displacement curves of 120 indents performed on Cu and Cu/graphene

Chapter 6: Nanoindentation response of Cu/graphene system

6.1 Elastic contact response

To investigate the elastic response to nanoindentation of Cu and Cu/graphene, one needs to zoom in the initial part of the load-displacement curves in Figure 21. Figure 22 displays the initial elastic part of the load-displacement curve for both Cu and Cu/graphene surfaces. The curves represent an average of the 120 single indents. The Cu/graphene surface exhibits an initial stiffer response, and withstands higher loads than bare Cu at the same indentation depth; similar to what has been suggested by simulations on Pt/graphene and bare Pt surfaces (Klemenzt et al., 2014).

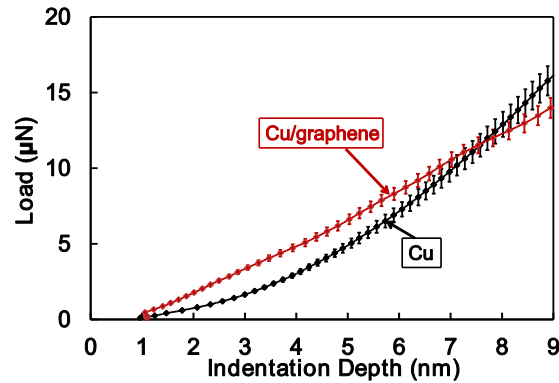


Figure 22: Initial elastic part of the load-displacement curves of Cu and Cu/graphene

As discussed in section 3.4.1, as long as the indentation depth is low enough, the contact between the indenter and the surface is purely elastic. The end of the elastic regime appears with a first “pop-in” indicating the first major plastic burst, typically at an indentation depth between 8 and 12 nm for Cu. At the initial shallow indentation depth, the mechanics of the contact is dictated by the rounded shape of the tip, assimilated here as a sphere with 20 nm radius. Ideally, it should follow the Hertz law of contact which is an ideal scenario between two isotropic elastic bodies (Johnson and Johnson, 1987). The latter explicitly defines that the relationship

between load and displacement is of the form $P = k \cdot h^n$, with $n = 1.5$, where P is the load, k is a constant, and h is the displacement. Most frequently, experimental results do not match with the Hertz model due to several factors: tip sharpness which leads to plastic events even at shallow depths, surface anisotropy, friction, and adhesion between the surface and the tip. As discussed in section 3.4.1, the Hertz model in this case is expected to accurately predict the load-displacement behavior within an indentation depth of ~ 2 nm (Gouldstone et al., 2000). Moreover, based on previous experiments and simulations on tungsten, it is expected that up to the onset of plasticity, the load-displacement data could reasonably be described by Hertz law (Ma et al., 2012). Note that another model was proposed by Larsson et al. (Larsson et al., 1996) in order to take into account the sharpness of the Berkovich tip during shallow contact which states that the value of the coefficient of the power law should be more appropriately estimated to $n = 2$.

By fitting the curves with the Hertz relation $P = K \cdot h^n$, one finds $n = 2.1$ for Cu and $n = 1.42$ for Cu/graphene, indicating that bare Cu response is closer to what is expected for a sharp Berkovich tip indentation on a metallic surface, while Cu/graphene system leads to indent responses closer to the Hertz theoretical prediction similar to results shown for epitaxial graphene on SiC (Gao et al., 2015). These results demonstrate that graphene drastically modifies the contact between Cu and the tip. In order to understand the specific impact that the single graphene layer has on the contact response, a few possible causes have been considered and investigated:

1. The high stiffness of graphene;
2. The difference of friction between the tip and bare Cu versus Cu/graphene;
3. The difference of adhesion between the tip and bare Cu versus Cu/graphene.

In order to assess the first hypothesis, finite elements (FE) simulations have been performed to check for the effect of the high graphene stiffness. As discussed previously, it is agreed that a graphene single layer has a Young's modulus (E_f) of around 1000 GPa. On the other hand, the Young's modulus of Cu (E_s) was estimated to be around 100 GPa by fitting the load-displacement curve of bare Cu films to the sharp Berkovich model (Suresh et al., 1999); $F = 2.189 \cdot E_r \cdot h^2 \cdot (1 - 0.21\nu - 0.01\nu^2 - 0.41\nu^3)$, where F is the load, h is the displacement, ν is the Cu Poisson's ratio, and E_r is the reduced modulus given as $1/E_r = 1-\nu_f^2/E_f + 1-\nu_i^2/E_i$, where ν_f and E_f are the film's Poisson's ratio and the film's Young's modulus, while ν_i and E_i are the tip's Poisson's ratio and Young's modulus, respectively. Figure 23 shows the fitting result, yielding a reduced modulus of 100.8 GPa, and taking into account that $\nu_f=0.343$, $\nu_i=0.07$, and $E_i=1000$ GPa, E_f is then calculated to be equal to 100 GPa.

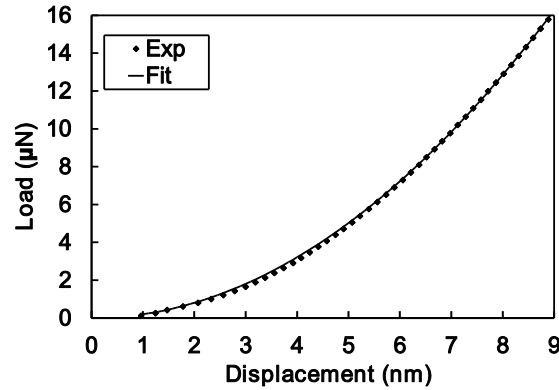


Figure 23: Experimental and sharp Berkovich tip model fitting of the load-displacement curve of nanoidnenting bare Cu

Accordingly, an axisymmetric finite elements model was created with a rigid spherical tip surface indenting a surface consisting of two materials; this finite element model of spherical indentation of a hard film on copper substrate was setup using the commercial finite element software ABAQUS/Standard. The objectives of the model are to identify the loading profile of a diamond tip in a graphene coated copper substrates with the

main finality to extract at very low loads the proper modulus of the graphene. A fully parametric 2D model is created using the ABAQUS, involving the tip radius, the layer thicknesses and the associated material properties. Due to the small scales involved, the tip has been assumed as a spherical tip considering a rounded defect on the tip. Due to the specimen and loading symmetry, a 2D model is used with symmetric boundary conditions applied along loading direction. The bottom surface of the specimen is completely fixed considering the substrate as rigid and infinite. The model is meshed using 2D elements CAX4. The simulation is divided in two steps: a first approaching step initiates the contact between the tip and the top layer, followed by the indentation step during which the load is imposed. The contact is obtained between the master tip surface and the slave sample surface with frictionless conditions. The indenter is considered as a rigid body. The graphene layer is considered as purely elastic with an elastic modulus between 1 and 1000 times the copper modulus and a Poisson ratio equal to 0.2. Figure 24 shows an illustration of the FE model described.

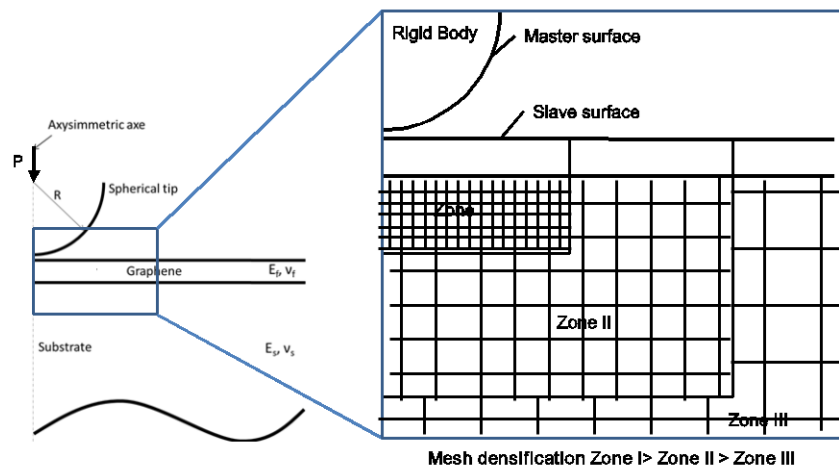


Figure 24: An illustration of the FE model used

However, due to the extremely small thickness of the graphene film, its stiffness, regardless of how high it is, appears that it does not significantly affect the load-displacement curve for indents deeper than a single graphene layer (~ 0.3 nm) as shown in Figure 25 plotting dimensionless load vs dimensionless indentation depth for various ratios of film modulus to substrate modulus. Hence, the stiffening experimentally measured by nanoindentation tests cannot be a result of the presence of a very stiff layer of graphene on top of the Cu substrate.

In order to test for the effect of friction between the tip and the indented surface, the same FE model described above is used. Graphene can act as a solid lubricant, reducing the friction between the coated surface and other surfaces (K.-S. Kim et al., 2011). Therefore, it is assumed, as a lower bound, that in the presence of graphene, the contact between the tip and the surface is frictionless with a friction coefficient $\mu=0$, and that in the absence of graphene the friction coefficient $\mu=0.5$. The predicted load-displacement curves (Figure 25) show that changing the friction between the tip and the surface does not result in any significant change in the apparent indentation stiffness. As a matter of fact, a lower friction coefficient like in the case of Cu/graphene leads to a softer response opposite to the experimental evidence.

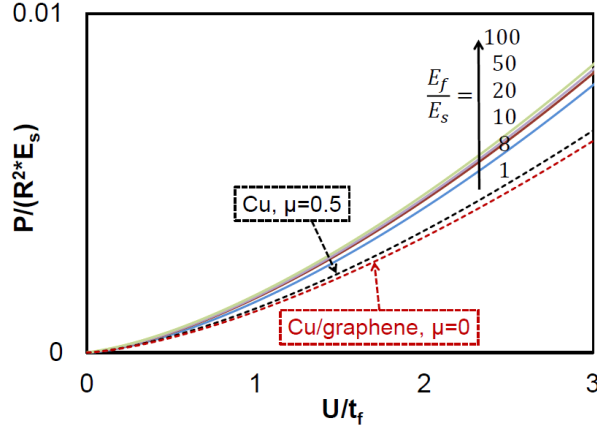


Figure 25: Load-displacement curves: theoretical modelling using a FE approach for different film/substrate moduli ratio (solid lines) and for different friction coefficients between the tip and the surface

The last option remaining to explain the results of Figure 22 (i.e: the apparent higher stiffness for Cu/graphene than Cu) is to invoke the possible impact of the adhesion forces between the tip and the indented surface. The underlying rationale is that adhesionless contact will show higher load responses for the same displacement. Indeed, in the presence of an adhesion force, the load required to achieve a certain displacement is partly provided by this adhesion force. However, when this adhesion force is absent, the tip must exert the entire load required to achieve the same displacement. In order to validate this assumption, molecular dynamics (MD) simulations have been performed (Note: MD simulations are performed by collaboration) using the code LAMMPS (Plimpton, 1995). A rigid fullerene-like tip is placed 2 Å above a single graphene layer on a Cu (111) substrate. For the simulation, the copper volume has a size of 100 nm length, 100 nm width and 7 nm depth. Periodic boundaries are used in x and y atomic directions in order to avoid any edge effect. Figure 26 shows a schematic for the MD model used.

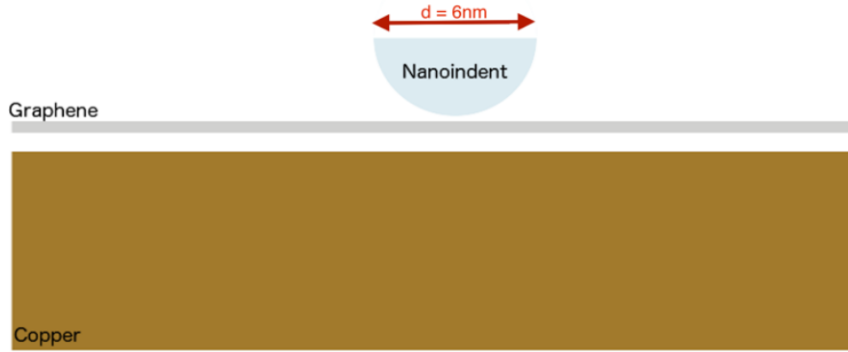


Figure 26: A schematic illustration of the MD model used

The fullerene tip diameters chosen for the simulations are 30 nm and 6 nm. 30 nm was chosen in order to match the diameter of the tip with which the experiments were performed. While 6 nm was chosen due to the fact that a diamond tip like the one used in experiments is rough and hard, and therefore, anomalies and defects are expected to be present which would result in a smaller effective diameter of the tip especially at very shallow indentation depths.

The choice of the interatomic potentials is crucial, especially to accurately model the forces between Cu and C atoms. There have been previous theoretical studies with various potentials (Fang and Weng, 2000; Fang et al., 2002; Klaver et al., 2015; Long et al., 2016; Oluwajobi and Chen, 2011; Wang et al., 2016; Xu and Buehler, 2010; Zhang and Tanaka, 1997) to model the interaction of C and Cu. These studies were carried out to simulate nanoindentation, nanoscratching and nanofriction experiments. In this study, the Tersoff potential for C atoms (Kinaci et al., 2012), the EAM potential for Cu atoms (Mishin et al., 2001) and a Morse potential for Cu-C interaction ($D=0.1$ eV, $\alpha = 1.7$ Å and $r_0 = 2.1$ Å) (Maekawa and Itoh, 1995) were used. The bottom layer of the Cu slab is fixed, and the tip is initially fixed as well. A conjugate gradient algorithm, as implemented in LAMMPS, is used for energy minimization. The forces on all C atoms from the tip are recorded and summed up to calculate the overall load. Then, the tip is

moved down by 0.125 Å and this is repeated until the tip has penetrated the surface by 1.5 nm. The load-displacement curve is then extrapolated to larger indentation depths to facilitate comparison with experimental data.

Figure 27 shows the load displacement curves from the theoretical data. A fit is applied to both sets of data using a polynomial law $f(x) = ax^b$. Table 1 gives each individual parameter a and b resulting from the fit, suggesting a good agreement (for the b term) between theory and experiment. There is a slight mismatch in the coefficient for nanoindentation on bare Cu (111) for the 6 nm tip. Theory predicts an exponent of 1.805 while experiments give 2.112. This small discrepancy could be due to the geometrical differences for the tips used, as evident by the agreement between the experimental coefficient and the 30 nm tip theoretical one. Interestingly, this discrepancy does not show up in the load-displacement curve of Cu/graphene as shown by the similarity between the coefficients extracted from experimental and both theoretical curves. This indicates that in the presence of graphene, the mechanisms governing the contact are less dependent on the tip geometry.

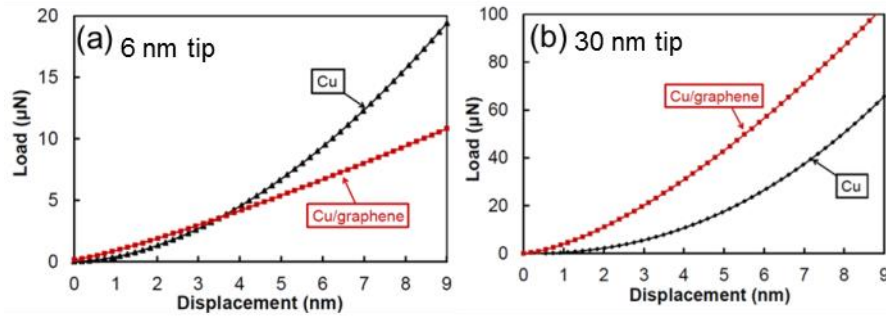


Figure 27: Load-displacement curves from MD simulations of nanoindentation on Cu and Cu/graphene with a tip radius of (a) 6 nm and (b) 30 nm

Table 1: Fitting parameters a , and b for experimental and simulated load-displacement curves of Cu and Cu/graphene

	Copper			Copper/graphene		
	Exp.	Simul. (6 nm)	Simul. (30 nm)	Exp.	Simul. (6 nm)	Simul. (30 nm)
a	0.166	0.377	0.47	0.68	0.735	3.8
b	2.1	1.8	2.24	1.42	1.39	1.49

The MD simulations were then analyzed in details in order to unravel at the atomic scale the microscopic mechanisms related to the behaviors in both curves. In the case of bare Cu, Figure 28a clearly shows that atoms are transferred to the tip during the contact which indicates adhesion between the tip and the surface. The presence of a single layer graphene completely eliminates this process as illustrated in Figure 28b. Indeed, no atom is transferred from the surface to the tip, and no adhesion is observed.

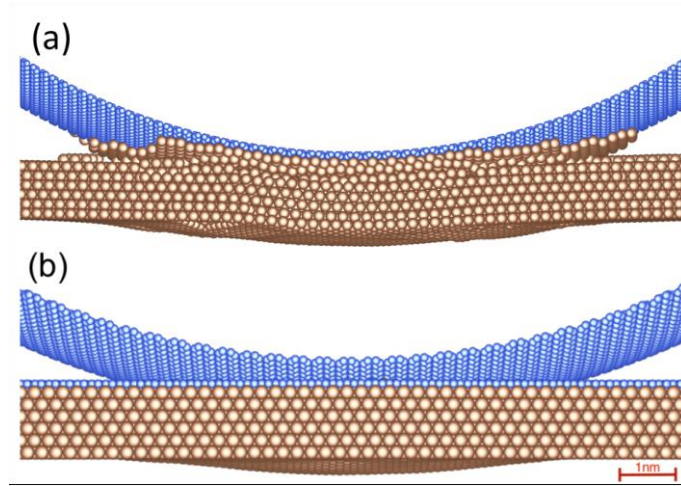


Figure 28: Atomistic MD simulations of nanoindentation in (a) bare Cu and (b) Cu/graphene thin films. For a better visualization, a bigger tip (30 nm in diameter) is used to illustrate (a) the adhesion of Cu atoms to the nanoindenter tip and (b) the absence of transfer of Cu atoms (no adhesion) in the presence of a single layer of graphene.

Graphene was known to lower surface adhesion (K.-S. Kim et al., 2011). However, our results show that graphene eliminates this atomic process completely, thus inducing an almost ideal contact behavior which follows the Hertz law of contact. MD simulations also suggest that when a larger tip (~ 30 nm) is indenting the surface, the effect is even more pronounced (see Figure 27).

This aspect leads to additional points of discussion. In Ref. (K.-S. Kim et al., 2011), graphene was transferred onto a SiO_2/Si substrate. The graphene surface contained polymer residues from the transfer process which increased the surface energy. In this work, graphene is CVD-grown on the Cu surface, and is in its pristine state. Moreover, the adhesion between graphene and the underlying Cu film in our case is larger than for transferred graphene, since during transfer, wrinkles and bends may form thus weakening the interaction between graphene and the substrate. Such a weaker interaction between graphene and the substrate allows the carbon layer to deform around the tip increasing the contact area between them which leads to higher adhesion (see also recent analysis of friction with similar findings (Li et al., 2016)). On the contrary, a stronger interaction between graphene and the substrate prevents the carbon layer from deformation and so keeps the adhesion minimal. This atomistic scenario also explains why the effect measured by a 30 nm tip is more pronounced than with a 6 nm tip, as a sharp tip will facilitate bending and deformation of graphene around it. Indeed, additional nanoindentation experiments are performed on transferred graphene onto SiO_2/Si substrates and onto Cu thin films. Graphene was grown on 25 μm thick Cu foil, and then spin coated by 4% PMMA to create a 300 nm layer on top of the graphene film. The Cu foil was then placed in a FeCl_3 solution to etch the Cu foil; the graphene/PMMA layer is then transferred on a Si wafer with a 300 nm layer of SiO_2 , and on a 1 μm Cu thin film, and left to dry in air. Finally, the PMMA is shortly heated and cured with fresh PMMA before removing it by acetone to finally obtain graphene transferred on the desired surface. The nanoindentation tests on those samples present an

opposite effect for SiO_2 /transferred graphene (see Figure 29), while graphene transferred onto Cu thin films show a similar but weaker effect (see Figure 30) to the results of CVD grown graphene (Figure 22) (Table 2 shows the fitting parameters for both samples). It has been shown that adhesion between graphene and metals like Cu is almost 1.5 times larger than that between graphene and dielectrics like SiO_2 (Jiang and Zhu, 2015; Yoon et al., 2012). Therefore, even with graphene being similarly transferred on both surfaces, graphene on Cu shows a lower adhesion response than graphene on SiO_2 . This further confirms the hypothesis that the interaction between the graphene and the substrate plays a crucial role in determining the contact behavior of graphene coated surfaces.

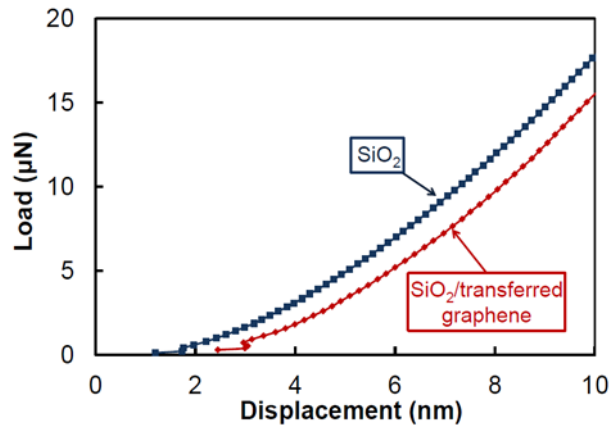


Figure 29: Experimental load-displacement curves for nanoindentation on SiO_2 and graphene/ SiO_2

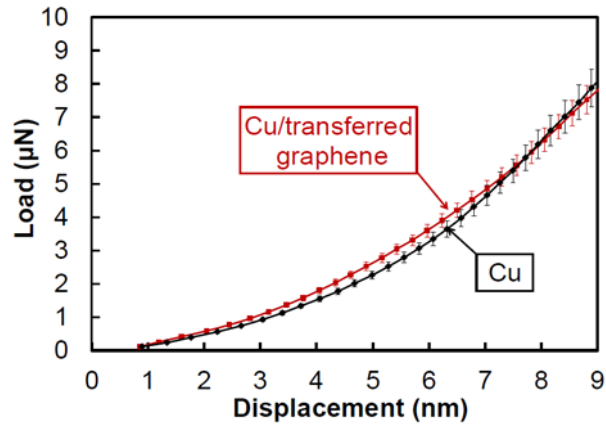


Figure 30: Experimental load-displacement curves for nanoindentation on Cu and graphene transferred on Cu

Table 2: Experimental fitting parameters of load-displacement curves of graphene transferred SiO₂ and on Cu substrates compared to the bare substrates

	Cu	Cu/transferred graphene	SiO₂	SiO₂/transferred graphene
<i>A</i>	0.12	0.157	0.17	0.047
<i>B</i>	1.85	1.75	2.2	2.6

Conclusion: nanoindentation measurements show a significant stiffer response for Cu/graphene coated thin film than for bare Cu. This effect cannot be fully explained by the high stiffness of graphene. However, it originates from the modification of the interaction forces between the tip and the indented surface. Our results show that a single layer of CVD graphene on Cu leads thus to a near ideal Hertz condition by providing adhesionless (and frictionless) contact with almost no bilayer effect (Figure 22 and Figure 27). Nanoindentation tests on graphene transferred on SiO₂ and Cu have shown opposite and weaker effects, respectively, suggesting that in order to achieve this type of adhesionless surface; the graphene-substrate interaction must be strong enough. Furthermore, this outstanding role of graphene in preventing material transfer could be very beneficial for various types of surface contact and MEMS applications.

6.2 Plastic contact response

6.2.1 Introduction about dislocations under nanoindentation in Cu

The plastic deformation regime in the nanoindentation experiments is addressed through two aspects. First, the starting load at which dislocation activity is noticed in the load-displacement curves, and secondly, the major dislocation activity characterized by the pop-in taking place at the end of the elastic loading regime. To understand the effect of graphene on both phenomena, the load-displacement curves of Cu and Cu/graphene are considered. In the previous sections, two different Cu/graphene systems are studied; CVD grown graphene on Cu thin films, and transferred graphene on as-deposited Cu thin films. Figure 31 shows the load-displacement curves of a single indent performed on both systems of Cu and Cu/graphene.

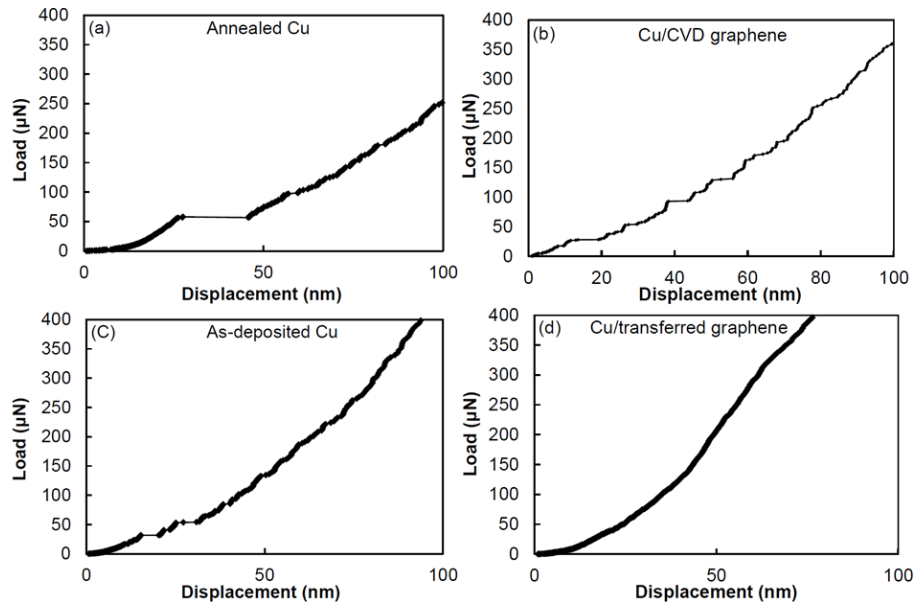


Figure 31: Load-displacement curves of (a) CVD annealed Cu, (b) CVD grown graphene on Cu, (c) as-deposited Cu, and (d) transferred graphene on as-deposited Cu

First, it is clearly seen that the response of as-deposited Cu is different than that of annealed Cu, and consequently the response is also different with graphene covering the Cu surface. For annealed Cu, the curves in Figure 31a and b show a clear “pop-in” at a certain load; this is considered the point at which the first major dislocation event occurs. Different results on nanoindenting Cu and other metals have shown the same phenomenon. The reason for this “pop-in” is considered to be the homogeneous nucleation of a number of dislocation loops under the indenter tip when the shear stress due to the applied load approaches the theoretical shear strength of the indented material. Part of the movement of these dislocation loops to accommodate the tip inside the sample in addition to the volume conservation of the material during this plastic deformation cause a material pile-up to happen around the indenter which is indeed seen in this work, and will be shown later (Figure 35). On the other hand, this phenomenon does not clearly appear in the load-displacement curves for as-deposited Cu (Figure 31c), instead successive short bursts appear on the curve. This is attributed to the fact that as-deposited Cu is expected to have a high density of pre-existing dislocations which would be more easily moved by the indenter tip as it goes deeper into the sample; therefore the plasticity events take place due to activation of existing dislocations rather than nucleating new dislocations. While, in annealed Cu, the grain is considered defect-free, and given its increasing grain size, the onset of plasticity takes place through nucleation of dislocations by the tip. Moreover, the measurements on as-deposited Cu were performed later than those on annealed Cu, which means that there is a possibility that the tip has been degraded, and the effective radius has increased which would also lead to a less clear pop-in in the load-displacement curve (this phenomenon has also been demonstrated in ref (Xia et al., 2016)).

The load and the displacement at which the first “pop-in” occurs are referred to as critical load and critical displacement, respectively. Figure 32 shows the critical load vs the critical displacement plotted for 120 indents on both samples (annealed and as-deposited Cu). It is clear that for the

annealed Cu, the critical load is larger for a given displacement, which means that the shear stress required to nucleate dislocations in the annealed samples is larger than that required to activate existing dislocations in as-deposited sample.

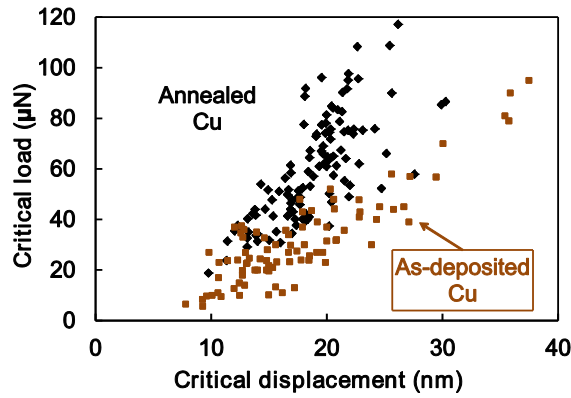


Figure 32: Critical load vs critical displacement for annealed and as-deposited Cu

6.2.2 Analyzing results of Cu vs Cu/graphene

The effect of graphene is then studied on the response of annealed Cu, i.e: bare annealed Cu surface is compared to CVD grown graphene on Cu. First, Figure 33 shows the critical load vs the critical displacement for Cu/graphene compared to Cu. As observed, for a certain critical load, the onset of the “pop-in” in Cu/Graphene trends to be at a deeper indentation depth than for that in Cu. This means that even though the Cu/graphene response is initially stiffer than that of Cu (due to the adhesionless property), the behavior reverses at a certain point before the onset of major plasticity events in Cu, and Cu/graphene becomes less stiff along the indentation direction (this has also been shown in simulations of Ni-graphene composites (Chang et al., 2013)). This could be explained by the fact that although graphene’s in-plane Young’s modulus is exceptionally high, its cross-plane direction modulus is indeed lower than that of Cu (~ 36 GPa (Michel and Verberck, 2008)).

Another clear difference observed from the load-displacement curves for indents on CVD annealed Cu and Cu/Graphene (Figure 31a and b) is in the length of the “pop-in” i.e. the displacement burst at a constant load in the curve. It is observed that for Cu/Graphene this burst is much shorter than for Cu, while in as-deposited Cu, this pop-in completely disappears (Figure 31d). To confirm this, the “pop-in” length of each indent on the annealed samples was extracted and plotted vs the critical load (Figure 34). It is clear that the length of the “pop-in” is significantly reduced in the presence of graphene on the surface.

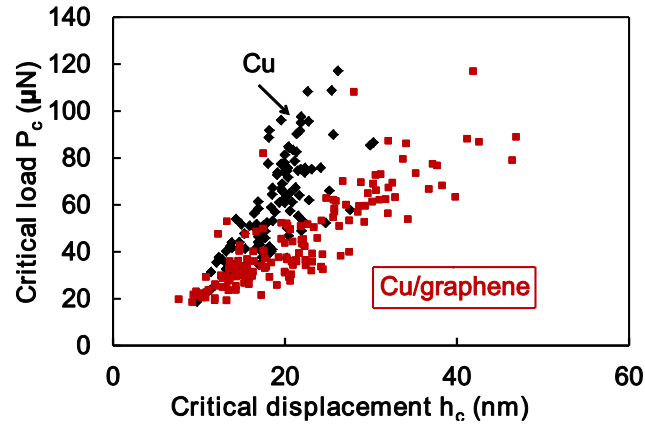


Figure 33: Critical load vs Critical displacement for onset of dislocation nucleation from indenting Cu and Cu/Graphene

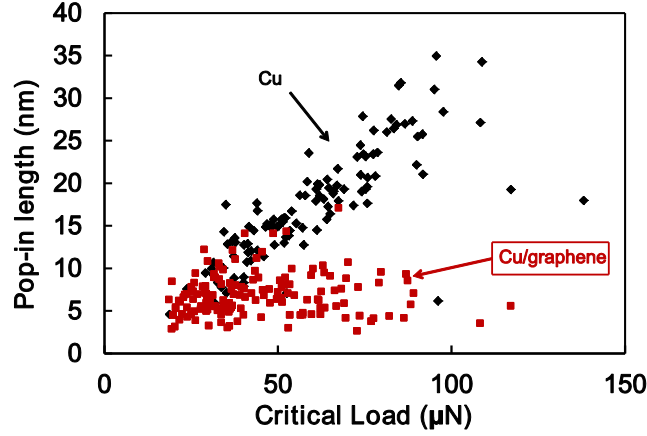


Figure 34: Pop-in length vs the critical load for Cu and Cu/graphene

As discussed before, the “pop-in” corresponds to the nucleation of dislocation loops under the indenter and the plastic deformation of the Cu leading to the material pile-up around the indenter. The length of the “pop-in” could be related to the number of dislocation loops as follows, $N = \frac{\Delta h}{b}$ where, Δh is the “pop-in” length and b is the Burgers vector magnitude. From this relation, it is concluded that in Cu/Graphene less dislocation loops nucleate and participate in the plastic deformation of Cu. Furthermore, it is also seen that for Cu, the “pop-in” length increases linearly with the load at which the “pop-in” occurs. This behavior is explained by Shibutani et al. (Shibutani et al., 2007), that for each indent, the load at which the pop-in occurs is different due to different local surface state and conditions. Ideally, the elastic load applied by the indenter is dissipated by the nucleation and motion of a certain number of dislocations. Therefore, for a higher load on a certain dislocations source results in a higher number of dislocations to be emitted to dissipate this elastic energy. However, in the case of Cu/Graphene it is clear from Figure 34 that the “pop-in” length and therefore the number of dislocations emitted remains almost constant for any load. This means that there are a certain number of dislocations that could be emitted, and then no more

dislocations can further nucleate or move to cause plastic deformation. This is due to the presence of graphene which represents a barrier to dislocation motion, causing the dislocations to pile at the interface between Cu and graphene and therefore exert a back stress on the dislocations source preventing more dislocations from nucleation. This dislocation barrier property of graphene was also found and discussed by Kim et al. (Kim et al., 2013) by fabricating ultra-strong nano-pillars made of metal (Cu and Ni)-graphene multilayered composites, and performing compression tests, they showed that these composites showed a higher strength than those of just Cu or Ni, due to the blocking of dislocations motion at the interface between graphene and the metallic layer.

Based on this observation, the pile-up of Cu around the indenter should be significantly reduced in the presence of graphene on top of it, due to the less number of dislocations involved in plastic deformation. To check this, AFM images were taken for indents on both samples. Due to the very high surface roughness of the samples due to the preparation steps including annealing, and gas flows, it was very hard to image the 100 nm depth indents, as the pile up heights of such indents were in the same size range of the roughness profile. Instead, deeper indents to a depth of 500 nm were investigated. Figure 35 (a,b) shows AFM images of 500 nm indents made on Cu and Cu/Graphene, the pile up at the edges of the indent are clearly seen. Figure 35 (c,d) shows the corresponding height profiles along the lines shown on the AFM images. There are few interesting observations to be made from the AFM images. First, the pile-up height for Cu is clearly larger than that for Cu/Graphene; this is expected due to the less number of dislocations which are involved in the plastic deformation due to the back stress exerted by the dislocations trapped at the interface between Cu and graphene. Another very important observation from the AFM images is the slip lines seen around the indent of Cu. These slip lines appear in the form of semi-circular bands around the indent area. On Cu/Graphene, these lines do not appear around the indent. Slip lines correspond to dislocations reaching the free surface of the indented material (Nibur and Bahr, 2003).

Therefore, it is expected that in the case of Cu, as dislocations reach the free surface they form such slip lines, while in Cu/Graphene, due to the presence of a strong barrier preventing dislocations from reaching the free surface, we see no slip lines in the AFM image. This is another proof of how a strong barrier a single atomic layer of graphene is. To verify that graphene is actually still present on the surface of Cu after the nanoindentation, SEM images were taken for the indents on the surface of Cu/graphene in order to check for graphene failure. Figure 36 shows SEM images of a 500 nm deep indent and a 100 nm deep indent. It is seen that for the 500 nm indent, the graphene is only broken in a small area in the center of the indent but still covers the surface of Cu and the pile up, while for the 100 nm indent, even though imaging is not perfectly clear due to the limits of the SEM, no cracks appear, and it can safely be assumed that graphene remains intact after the nanoindentation and therefore acts as the dislocation barrier as explained.

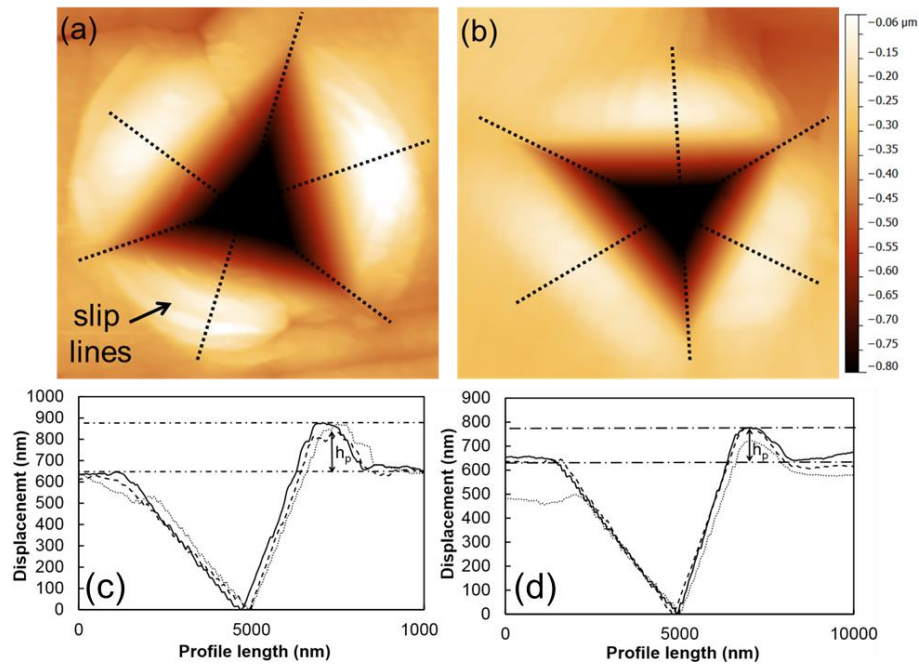


Figure 35: (a,b) AFM images of 500 nm deep indents made on Cu and Cu/graphene, respectively, and (c,d) Corresponding height profile showing pile-up height for both samples

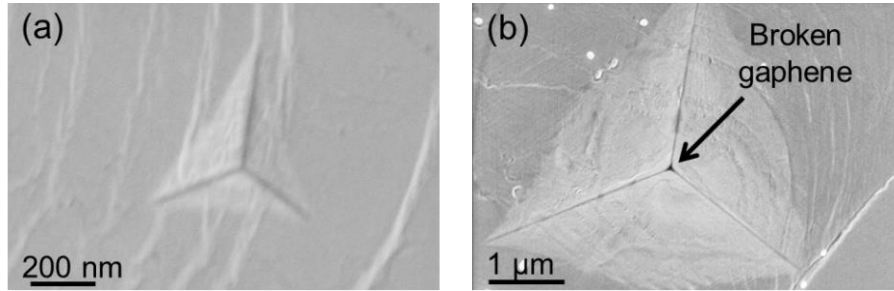


Figure 36: SEM images of Cu/graphene surface after (a) 100 nm deep nanoindentation and (b) 500 nm deep nanoindentation

6.2.3 Discrete dislocation dynamics simulations

To fully understand the mechanisms by which the dislocations move and interact during nanoindenting Cu in the presence and the absence of graphene, discrete dynamic dislocation (DDD) simulations have been performed through collaboration. The 3D DDD set up has been described in several references (Fivel, 2008; Verdier et al., 1998). It combines a DDD code (TRIDIS) which solves for the dislocation kinetics and equilibrium and a FE code (CASTEM) in order to correct for the image forces, allowing treating a full boundary value problems. The nanoindentation test is simulated by forcing a rigid spherical punch to penetrate through small displacement increments inside the solid. After each displacement increment, several iterations are needed to reach a state of equilibrium for the dislocations in the box. The Cu substrate is described through its elastic constants assuming elastic isotropy ($E = 112$ GPa, $\nu = 0.324$). For the graphene layer, a purely elastic ($E = 1000$ GPa, $\nu = 0.19$) row of elements is introduced sharing common nodes with the Cu solid assuming perfect adhesion with the Cu solid. The validity of this assumption of good adhesion for the case of CVD grown graphene on Cu has been verified by the results in section 6.1.

The Cu films in the experiments have undergone a long heat treatment as explained which leads to recovery and a microstructure almost exempt of initial dislocations. The clean and long pile ups in the AFM images (Figure 35) confirm that the indentation takes place inside a pristine or near pristine single crystal. The DDD framework requires the introduction of the dislocation sources in order to initiate the dislocation process. Empirical choices had to be made guided by the physics of the problem. MD simulations of nanoindentation in (111) oriented Cu crystal (Chang et al., 2010; Fivel, 2011) have shown that nucleation occurs through the inoculation of a first defect below the surface, just beneath the indenter, which then degenerates into several prismatic loops. These prismatic loops correspond to three interstitial loops built on the three $\langle 110 \rangle$ directions which are not included in the surface plane (see Figure 37). The size of the loops is defined by the radius of the contact area, R_c , at a given penetration depth. Note that the presence of prismatic loops for low penetration indentation has been confirmed experimentally for FCC metals by TEM observations in 316L stainless steels (Fivel et al., 1998).

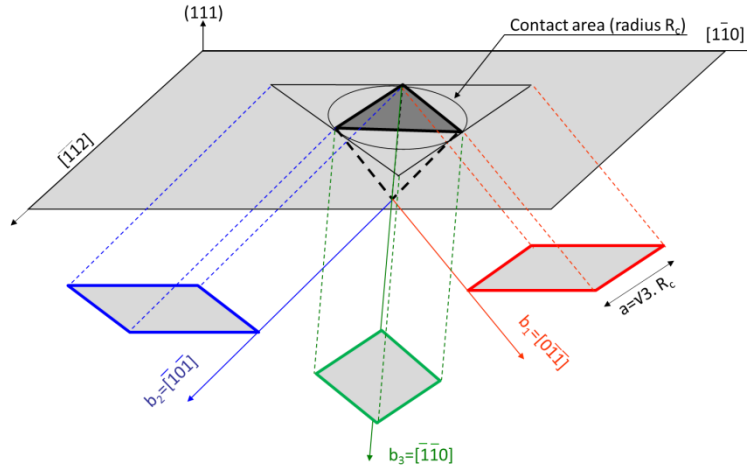


Figure 37: Geometry of the nucleation process as determined from MD simulations in the case of (111) spherical indentation.

In a previous study (Chang et al., 2010; Fivel, 2011), this nucleation process has been successfully introduced in the DD code and spherical indentation on a (111) Cu single crystal was performed. It was found that the dislocation microstructure evolution followed two regimes. The introduced interstitial dislocation loops are initially just gliding on their cylinder similar to the MD simulation predictions. Since the loop size is proportional to the contact radius, the loops get larger with the penetration depth and, at some point; their size gets large enough to allow Frank-Read mechanism to operate on each arm of the loop leading to a dislocation avalanche and a large increase of the dislocation density. After this stage, the dislocation density is large enough to perfectly accommodate the spherical shape of the indenter without any need of more dislocation nucleation. Hence, in the present study, we will use the same scheme to initiate the plasticity mechanisms with a specific focus on the strain burst induced by the dislocation nucleation process. The main difference with the previous study are: (i) the radius of the indenter tip is now 40nm in order to match with the experiments; (ii) the nucleation process is triggered at a pre-defined penetration depth 5, 10, 15 or 20nm in order to check the effect of the penetration depth on the size of the strain burst and up to that load, the response is purely elastic; (iii) the nucleation mechanism consists of introducing a large enough number of prismatic loops so that the evolution is already in the avalanche regime; (iv) in the case of the Cu/graphene specimen, an impenetrable surface (a facet) is introduced at the interface between the Cu substrate and the graphene layer; (v) for each introduced interstitial prismatic loop, there exists an equivalent vacancy loop located on the same cylinder but closer to the graphene layer in the case of Cu/graphene and outside the simulated volume in the case of Cu in order to ensure the consistency in the calculation of the surface steps as demonstrated in (24). After the introduction of the prismatic loops, the system is relaxed and the penetration depth is increased by small steps of typically 0.5 nm each time followed by relaxation. The relaxation condition is checked on the rate of change of the indentation force: equilibrium position is assumed when the force did not change by more than 0.1%

between 10 consecutive dislocation dynamics computation steps. A convergence analysis has been carefully performed to ensure that the response is independent of the way the loading is applied, and of the number of introduced prismatic loops. This led to the number of prismatic loops introduced to be equal to 8 sets of three interstitial loops and their corresponding 24 vacancy loops.

Figure 38 shows the predicted load penetration curves for bare Cu and Cu/graphene (experimental and predicted curves are superimposed in the figure). For the Cu, the pop in length agrees with the experimental measurements not only in the magnitude of the excursion but also in the variation of the excursion with increasing penetration depth. The relaxation by the pop in event converges into a unique elastoplastic master curve, whatever the load at which the pop in occurs. The behavior is completely different in the presence of the graphene layer in agreement with the experimental response, the pop in remains independent of the load and has a constant length. After the plasticity event, the indentation load increases considerably.

Figure 39 shows the dislocation arrangements for both systems at different instants of the indentation in the case of a nucleation process triggered at 10 nm depths. For a given indentation position, there is a clear difference in the shape of the dislocation microstructure. The plastic zone, corresponding to the zone with the highest dislocation density, is contained in a sphere in the case of Cu whereas it expands as half a sphere in the case of Cu/graphene system with a larger volume. This difference in the dislocation arrangement is correlated to the indentation force, which is found to be much higher in the presence of the graphene layer as shown in Figure 40. At the surface, the features are also very different. Slip steps are clearly visible in the case of bare Cu indentation whereas the surface relief is smooth when the graphene layer is introduced in excellent agreement with the AFM images (Figure 35).

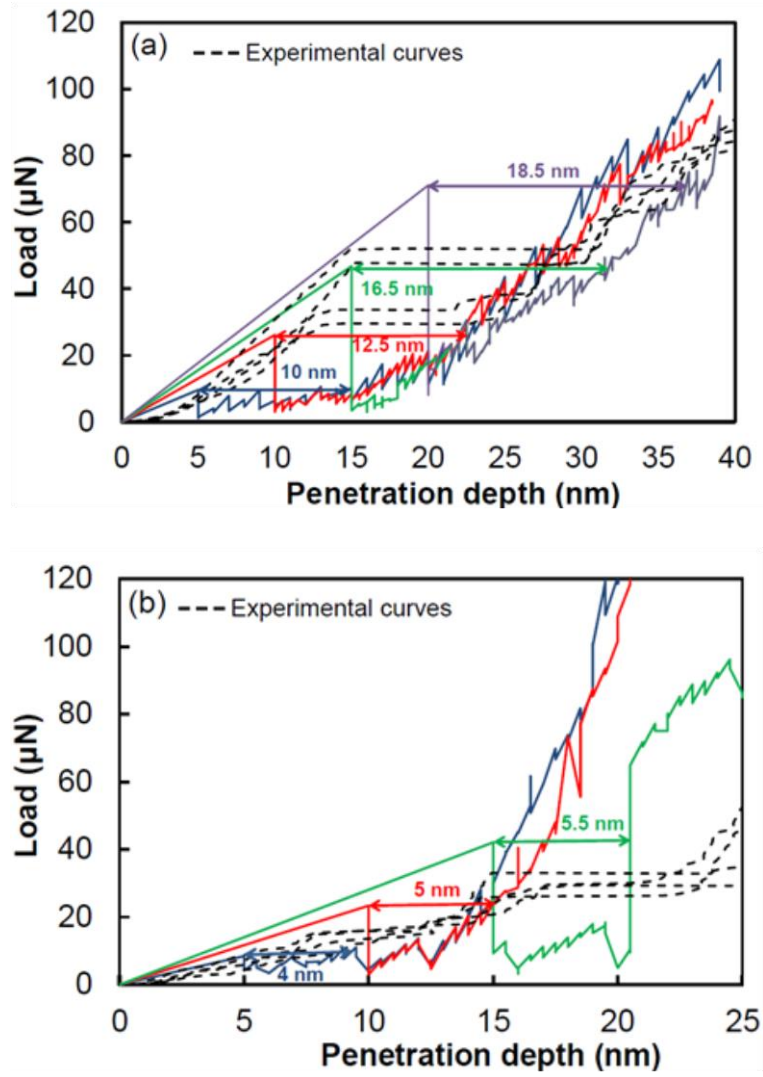


Figure 38: DD Simulations predicted load-displacement curves in the case of (a) Cu and (b) Cu/Graphene. Pop-in length is illustrated onto each curve for different critical displacements. Experimental curves are superimposed for quantitative comparison.

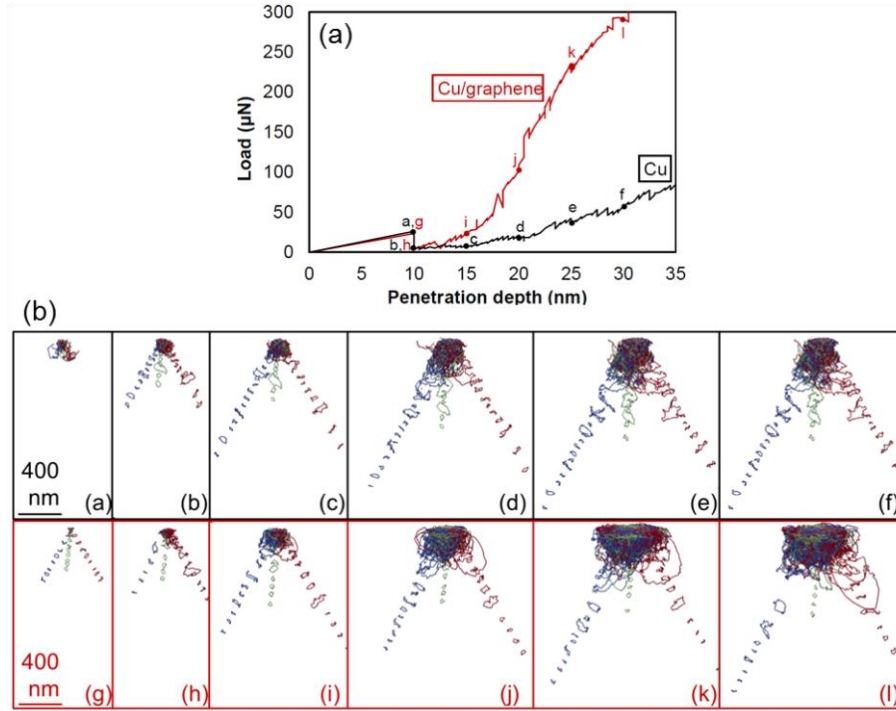


Figure 39: (a) DDD Load-penetration curve for bare Cu and Cu/graphene for when plasticity is triggered at 10 nm depth, (b) Dislocation arrangements for Cu and Cu/graphene at different instants of indentation pointed on the load-penetration curve

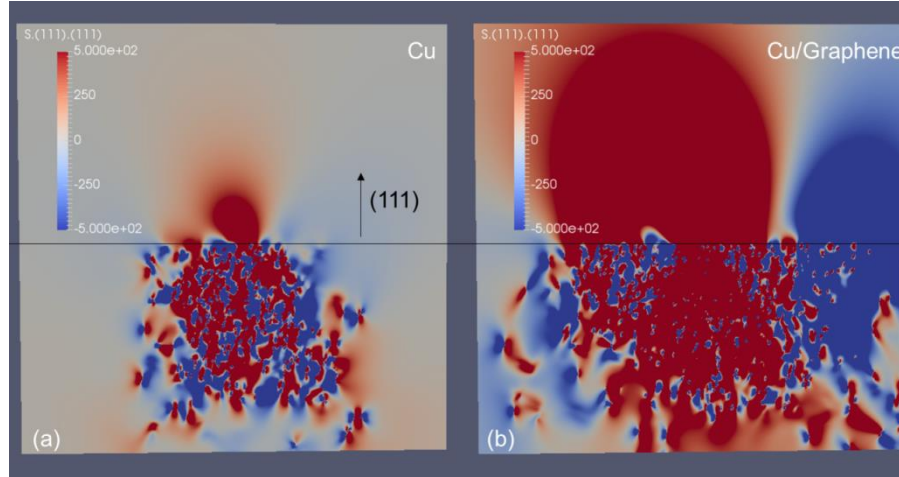


Figure 40: Normal stress zone in MPa after nanoindentation inside (a) Cu and (b) Cu/graphene. Note a higher long range normal stress zone in Cu/graphene

6.2.4 Discussion on the graphene plastic constraint effect

The experimental evidence and DDD simulations can now be discussed together to let emerge a complete picture of the observed effect of graphene on plastic indentation of Cu. The major differences observed between the plastic response of bare Cu and Cu/graphene are: i) the length of the pop-in in the Cu/graphene system is smaller compared to bare Cu; ii) the length of the pop-in in Cu is directly proportional to the critical load at which plastic deformation takes place, while it is independent of the load in the Cu/graphene system; iii) the surface around the indent is smooth in the Cu/graphene system with no dislocation slip traces and a smaller pile up compared to bare Cu.

As the tip penetrates the material, dislocations start to develop at a load allowing the critical shear strength to be attained locally beneath the indenter. An avalanche of dislocations is created with collective effects and interactions that drive some dislocations deeper in the bulk and some dislocations to the surface to escape in order to accommodate the tip

displacement, therefore causing the pop-in observed in the load-displacement curve. The presence of graphene on the surface of Cu blocks the escape of dislocations through the surface. Instead, the dislocations pile up at the interface causing the development of a strong back stress shutting down the dislocation source and preventing more dislocations from being created. This causes an overall decrease in the number of dislocations involved in the process, thus an overall decrease in the length of the pop-in. Furthermore, the linear relationship between the pop-in length and the load at which the pop-in occurs in the case of Cu is an expected behavior for a metal and is confirmed by DDD simulations. As the load at which the plastic flow initiates increases, the stored elastic energy in the material increases, and so a higher number of dislocations is created to dissipate this stored energy. However, in the case of Cu/graphene the pop-in length is constant regardless of the load at which plasticity occurs as has also been shown by simulations. This can be explained by considering that any activated source of dislocations will be shut off by the back stress from the dislocations piling up at the interface between Cu and graphene, and therefore, no matter how high the load at which plasticity starts is, the number of dislocations reaching the surface will be constant. Our DDD simulations showed an exceptional quantitative validation for the nanoindentation experiments, this enabling further clarification of the deformation mechanisms in Cu. It was illustrated that in the presence of graphene, indeed pop-in length remains constant independently of the depth at which the dislocation activity is triggered. This good agreement between experimental and modelling results further justifies the assumptions made to treat the graphene layer as impenetrable to dislocations.

The DDD simulations show that the dislocations arrangement is completely different when comparing Cu with and without graphene coating. For bare Cu, the plastic volume is contained in a sphere, while for Cu/graphene, the plastic volume takes the shape of a large half-sphere, indicating a larger volume of active plasticity inside Cu. The load increases dramatically in

Cu/graphene after the first plasticity event, which shows that an alternative mechanism of deformation should start at this point. A detailed analysis of the internal stress field induced by the dislocations shows that stress component normal to the free surface has a much longer range in the Cu/graphene system compared to bare Cu. Therefore, for Cu/graphene, a larger plastic deformation volume is contained inside the material itself laterally and in the depth to accommodate the penetration of the tip.

The absence of slip bands around the indent confirms that the presence of a single atom graphene layer on top of Cu blocks dislocations from escaping the surface in agreement with previous work on metal-graphene layered pillars in which dislocations could not traverse graphene (Kim et al., 2013). Pile up height reflects the volume of the deformation region at the surface, and a higher pile up for Cu indicates more dislocation activity at the surface. While, the formation of slip bands around the indent also confirms the same phenomenon. The smooth surface around the indent on Cu/graphene indicates that no dislocations escape the surface during the nanoindentation process. Scanning electron microscopy (SEM) of the indentation regions shows no evidence of graphene fracture, and DDD simulations also confirm this smooth surface morphology of Cu/graphene.

The DDD simulations assume perfect adhesion between graphene and the underlying Cu film which is essential to block dislocations and build up a sufficient back stress. Therefore, the adhesion between graphene and the underlying metal plays an important role in determining the extent to which the graphene layer can act as a dislocation barrier. Similar arguments have been proposed by Kim *et al.* attributing the higher strength of Ni-graphene pillars than Cu-graphene pillars to the higher interfacial shear strength between graphene and Ni than between graphene and Cu (Kim et al., 2013).

Conclusion: A single layer graphene coating can modify the plasticity under the contact significantly for indentation depth more than 1000 times larger than the graphene layer thickness. This results from the extremely high impenetrability of graphene which resists extreme stress generated by the dislocations accumulated at the interface. The result is a delocalization of the plasticity process by forcing much more homogenous organization of the dislocations inside the material. A good adhesion between graphene and the substrate is important to make use of this property. These results have potential impacts on applications requiring good resistance to erosion or scratch resistance while preventing oxidation. Indeed, resistance to erosion will be improved both by plasticity delocalization as well as by lower contact induced roughness. Moreover, given the 2D nature of graphene and its remarkable mechanical strength, this very strong constraint on plasticity reinforces the interest in the use of graphene inside metallic matrices as a strengthening component.

PART III:
CHARACTERIZING FREE
STANDING GRAPHENE
FILMS

Chapter 7: Deflection of suspended graphene membranes

7.1 Samples preparation

In order to fabricate suspended circular graphene membranes, a 300 nm SiO_2 layer is first grown on a Si wafer and e-beam lithography is used to pattern circular holes on the surface with different diameters. PMMA is spin coated on the surface, then exposed to the electron beam, and developed leading to exposed circular SiO_2 areas, which are then etched using a SF_6 plasma, before stripping the PMMA using acetone to obtain circular holes in the SiO_2 layer.

After performing this process, it was found out that a small optimization was required. When the exposed SiO_2 is etched by SF_6 , it was found that the PMMA mask is also etched with a higher etch rate than SiO_2 , which resulted in etching the entire SiO_2 layer, not only the exposed circular areas. To fix this issue, a Cr layer is deposited first on the SiO_2 , and then the PMMA is spin coated, exposed and developed. The Cr layer is then etched using a Cl_2 plasma, followed by etching the SiO_2 using SF_6 , and finally the remaining Cr layer is removed by a further step of Cl_2 plasma. Graphene is transferred over the patterned holes by the same technique explained in section 2.1.2. Figure 41 shows a schematic of the process to fabricate the suspended graphene membranes.

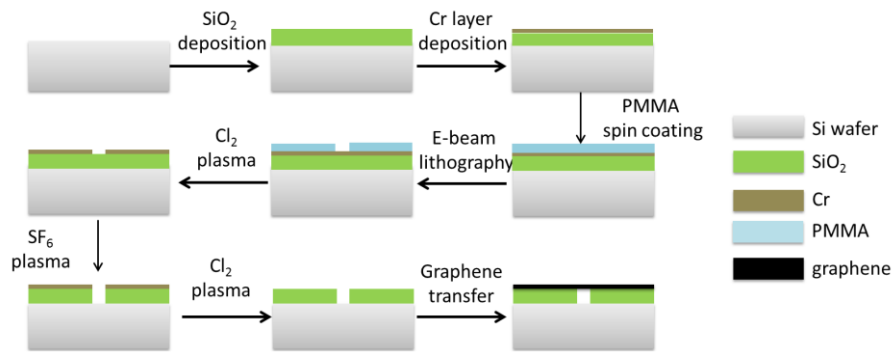


Figure 41: Schematic of the process to fabricate suspended graphene membranes

Optical images of the resulting graphene transferred on the etched SiO_2 holes are shown in Figure 42. The graphene appears to be well transferred with only few little cracks in the sheet. Raman spectra were taken on the sample. These spectra show that not all the graphene membranes are well suspended. Figure 43 shows the Raman spectra of a suspended membrane, compared to the supported graphene on SiO_2 . It is clear that the intensity ratio between the 2D and the G peaks (I_{2D}/I_G) is much higher for suspended graphene. It is safe to assume that the graphene membrane suspended on each hole is a single domain, taking into account that the size of graphene domains is $\sim 50\ \mu\text{m}$ on average, while the hole diameter is $\sim 1\ \mu\text{m}$.

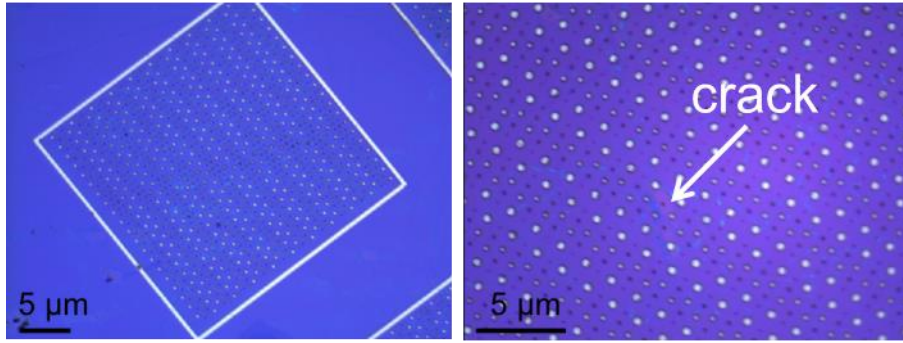


Figure 42: Optical images of transferred graphene on SiO_2 to fabricate suspended graphene membranes

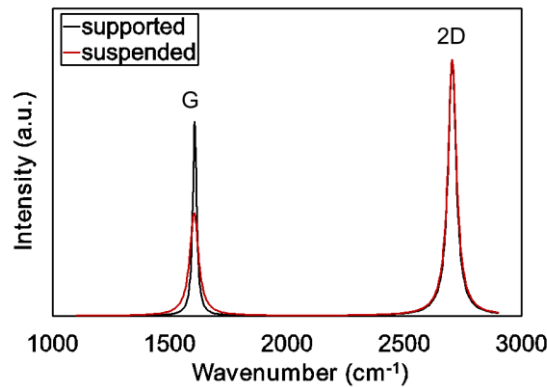


Figure 43: Raman spectra of suspended vs supported graphene

7.2 AFM tests and results

A scan has been performed by AFM in peak force tapping mode in order to determine which membranes are suspended and eligible for the deflection tests. The images were taken in order to determine the topography and the phase composition of the surface, which indicates if the membranes are well suspended. Figure 44 shows both AFM images of one area of the sample. From the topography image (Figure 44a), the suspended membranes are determined to be located where there is no contrast between the surface and the membrane. While, from the phase composition image (Figure 44b), the suspended membranes are the ones involving a clear phase contrast between the surface and the membrane. It is also observed from the AFM images that the smaller the membrane diameter is, the higher the probability is to obtain a well suspended graphene beam. Figure 44c shows the height profile of a suspended graphene membrane with a 1 μm diameter and the membrane appears to be sticking to the wall for a depth of around 25 nm.

This process is repeated on different areas of the sample and few membranes are selected to perform the load-displacement tests. The load-displacement tests are performed by selecting a point in the center of a membrane to exert an increasing load with a preselected maximum value, while the displacement is recorded for each load level. The tip used for this measurement is a diamond tip, with a radius of 18 nm as measured by SEM. The spring constant of the cantilever is calibrated by pushing on a SiO_2 surface with known properties and was found to be 42.65 N/m.

The raw data from the AFM measurements are then collected and treated to obtain the required load-displacement curves. From the measurements, the cantilever displacement (z) and the cantilever deflection (d) are obtained. As explained in section 3.4.2, the force and membrane deflection are then calculated from these values. Figure 45a shows an example of a raw z - d curve obtained from the AFM measurement on the suspended graphene membrane in Figure 44. Note that the unloading curve is chosen

for analysis to ensure no contribution from any plastic effects. The data must first be treated in order to set a correct zero point for the curves. This is done as following; the values d_0 and z_0 are illustrated in Figure 45a, and are subtracted from the raw data to obtain a corrected curve as shown in Figure 45b.

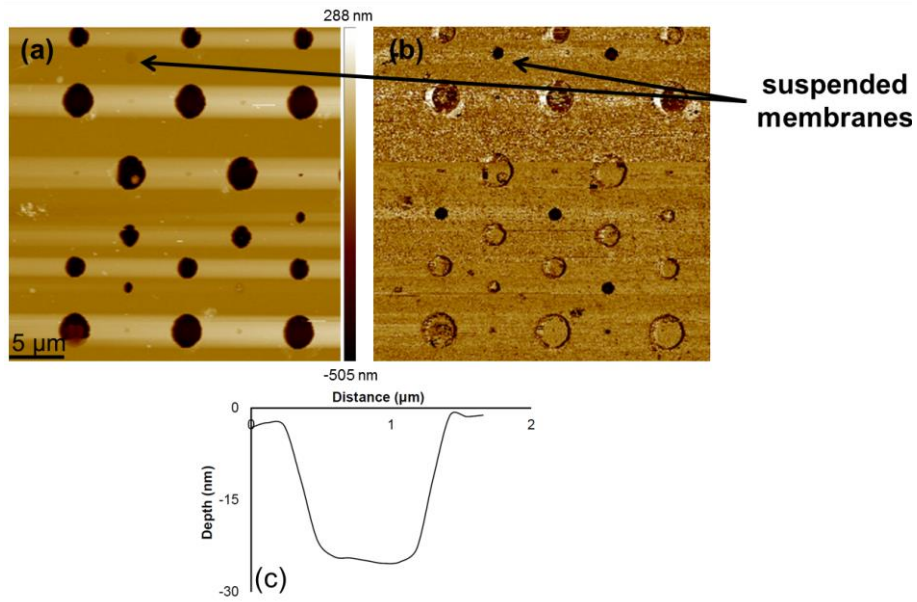


Figure 44: AFM images of the surface to determine suspended membranes, images taken for (a) topography and (b) phase composition of the surface

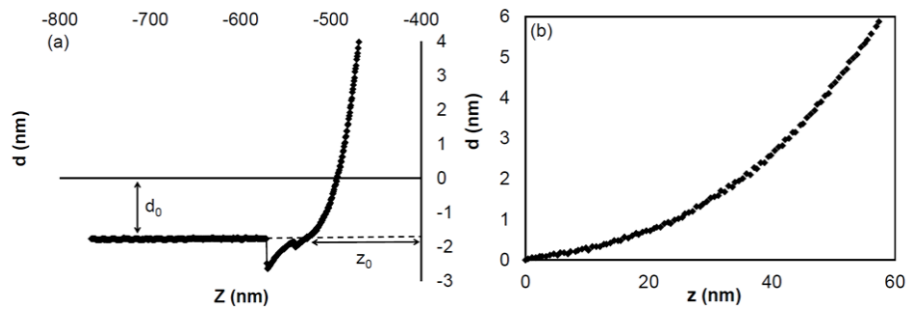


Figure 45: z - d curves obtained from AFM measurements (a) before and (b) after treating to set the zero point

The force and membrane deflection are then calculated through the relationships; $F = k_c * d$ and $\delta = z - d$, where F is the force, k_c is the cantilever spring constant, and δ is the membrane deflection. Performing this procedure on the data in Figure 45b, the load-displacement curve of a graphene membrane is obtained as shown in Figure 46.

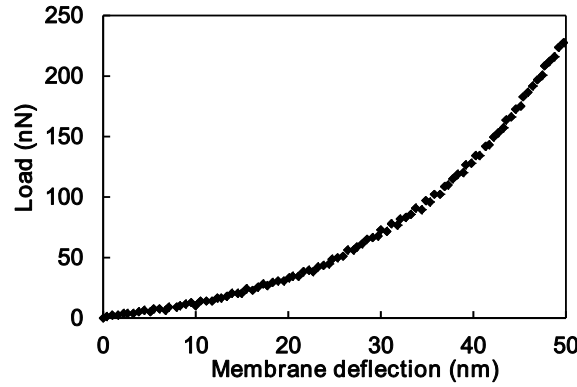


Figure 46: Load-displacement curve from AFM deflection on a suspended graphene membrane

Equation 7 is then used to fit the load-displacement curve with the pre-tension and the Young's modulus as fitting parameters. By fitting the curve in Figure 46, the pre-tension is found to be equal to 0.33 N/m, and the Young's modulus to be 356 N/m. Since, graphene is a 2D material; the 2D Young's modulus is the best parameter describing its mechanical stiffness. In order to obtain the bulk Young's modulus of graphene, the 2D modulus can be divided by graphene's thickness which is around 0.34 nm, which would give a value of ~ 1.05 TPa. This measurement procedure is repeated several times on different membranes and with different maximum set load values. Overall, 19 different datasets were obtained and 19 different values for the modulus and the pre-tension were acquired and are shown in Table 3, and the average 2D modulus is calculated to be 348 N/m, with an error of ± 54 N/m; corresponding to a bulk modulus of $1 \text{ TPa} \pm 160 \text{ GPa}$ showing a perfect agreement with literature (4), and suggesting that our CVD produced graphene is of excellent quality. The variation in the values

obtained for the modulus could be attributed to the different surface conditions or the possible defects present in each membrane.

Table 3: Fitting values of pre-tension and 2D Young's modulus of graphene membranes as-measured by AFM load-displacement curves

Dataset #	Pre-tension (N/m)	2D modulus (N/m)
1	0.3295	356.4
2	-0.08431	358.6
3	-0.21	350.6
4	1.081	333.1
5	-0.06612	338
6	-0.02624	407.1
7	0.2754	237.1
8	0.1165	321.5
9	0.1721	290.3
10	-0.02572	346.6
11	-0.2835	290.6
12	-0.2793	414.9
13	-0.3417	474.5
14	-0.7926	366
15	-1.332	266.3
16	-0.7963	376.1
17	0.1955	357.4
18	0.1594	387.2
19	2.061	340.5

AFM membrane deflection tests also enable the measurement of the membrane fracture strength. Three suspended membranes were loaded until the point of fracture, which appears on the load-displacement curve by a sudden drop in load as illustrated in Figure 47. The 2D fracture stress for a circular membrane under a spherical indenter is given by the following equation (Lee et al., 2008); $\sigma^{2D} = \left(\frac{FE^{2D}}{4\pi R}\right)^{\frac{1}{2}}$, where F is the load at which the membrane breaks, E^{2D} is the 2D Young's modulus, and R is the tip radius. Applying this model on the three fractured membranes, the average fracture stress obtained is found to be 51 ± 10 N/m, leading to a corresponding bulk value of intrinsic strength of 151 ± 29 GPa; again in agreement with the values reported in literature (Lee et al., 2008) and confirming the high mechanical quality of our CVD grown graphene.

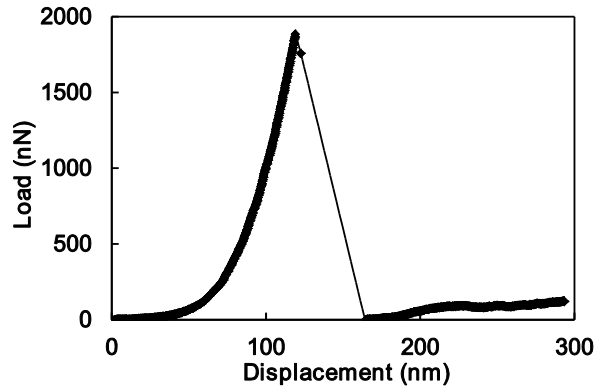


Figure 47: AFM load-displacement curve for a graphene membrane illustrating the membrane's fracture point

Conclusion: AFM membrane deflection tests have been performed on CVD grown graphene at UCL. The mechanical properties measured are in excellent agreement with literature, and confirm the mechanical quality of the graphene. These properties measured are useful for the design of micro and nano mechanical devices involving graphene in some capacity. Moreover, by validating the utilization of this technique at UCL, the effect of different processing or environmental conditions on graphene's mechanical properties can be studied. For example, etching, lithography, or other clean room fabrication steps.

Chapter 8: On-Chip tensile testing devices of suspended graphene beams

8.1 Process development engineering

This on-chip tensile testing device is a technique developed at UCL. The goal of this technique is to apply uniaxial stress on thin films by utilizing the residual stress developed during thin films deposition. The concept behind this technique was explained in section 3.4.3. As mentioned, this technique has been successfully used to characterize aluminum thin films (Coulombier et al., 2010), polysilicon films (Mulay et al., 2015), silicon nanowires (Bhaskar et al., 2012; Passi et al., 2012, 2011), palladium thin films (Idrissi et al., 2011), and metallic glass films (Ghidelli, 2015).

To accommodate a single layer graphene into this process, several technical and processing issues have to be addressed. As shown in Figure 12, the process flow of these devices can be described as follows:

1. Deposition of a sacrificial layer on a substrate;
2. Deposition of the actuator material thin film;
3. Patterning the actuator thin film into beams by means of lithography and dry etching;
4. Deposition of the test material (sample) thin film;
5. Patterning the sample thin film into beams by means of lithography and dry etching;
6. Wet etching of the sacrificial layer in order to release the structure, so that the actuator beam applies load on the test beam;
7. Drying by using critical point dryer (CPD).

In order to use graphene as the sample material, every step and material has to be selected in a way to avoid damaging the graphene during processing.

8.1.1 Sacrificial layer and graphene processing

8.1.1.1 Sacrificial layer material selection and etching

First, the sacrificial layer material was considered. In earlier work with other materials, a 1 μm thick PECVD SiO_2 film was selected as the sacrificial layer. The motivation for choosing PECVD SiO_2 was the easiness of HF acid etching, so the releasing step can be quick and highly selective. However, graphene can only be deposited on metallic surfaces; which means that graphene has to be transferred on SiO_2 films with this sacrificial layer option. As discussed before in section 2.1.2, the transfer process is one of the critical limiting steps of graphene processing, this is due to the defects it creates in graphene films, including cracks, folds, and polymer residues on its surface. Ideally, this transfer process should be avoided if possible to maintain the quality of the CVD-grown graphene. Since, graphene can be grown on Cu thin films as described in section 5.1, this Cu film can be considered as the sacrificial layer. The etch rates of Cu films were tested by using ammonium persulfate (APS) solutions with 20% concentration and found to be around 1 $\mu\text{m}/\text{min}$ (Figure 48).

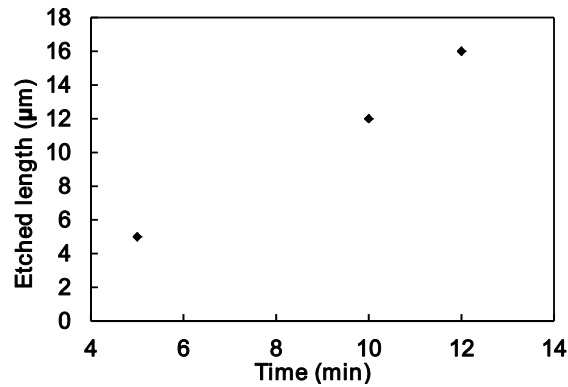


Figure 48: Cu thin films etch rate by 20% APS solution

8.1.1.2 Graphene beams patterning

Using Cu as the sacrificial layer has another implication on the processing steps. Since graphene is directly grown on Cu, the order by which the actuator and sample materials are deposited will have to be altered. In our case, the graphene will be first deposited on Cu thin films and patterned, followed by deposition of the actuator.

Patterning of graphene beams is performed by photolithography as described in section 4.1.3. Upon performing the above described process, it was noticed that a large amount of residues remained on the graphene beams. It has been previously shown that photoresists leave larger amount of residues on graphene compared to PMMA which is used in electron beam lithography (Fan et al., 2011). Moreover, the step of etching graphene under O₂ plasma causes crosslinking and material re-deposition on the photoresist which makes it harder to remove by weaker solvents like acetone, while a stronger solvent (e.g: piranha) cannot be used because it will etch the graphene film. Therefore, the solution proposed is that before spin coating the photoresist on the top of graphene, a PMMA layer is spin coated to act as a buffer between the graphene and the photoresist. After the photoresist is exposed and developed, the PMMA layer will be etched by O₂ plasma along with the graphene. For the final step of stripping the photoresist, a stronger solvent than acetone has to be used while making sure the graphene is not etched by it. By trial, it was found that the best candidate solution is PG remover from MicroChem. Corp. which is an NMP (1-Methyl-2-pyrrolidon) based solvent. Figure 49 shows a diagram explaining the steps of graphene photolithography, while Figure 50 shows a SEM image of graphene beams after photoresist stripping by acetone and by PG remover.

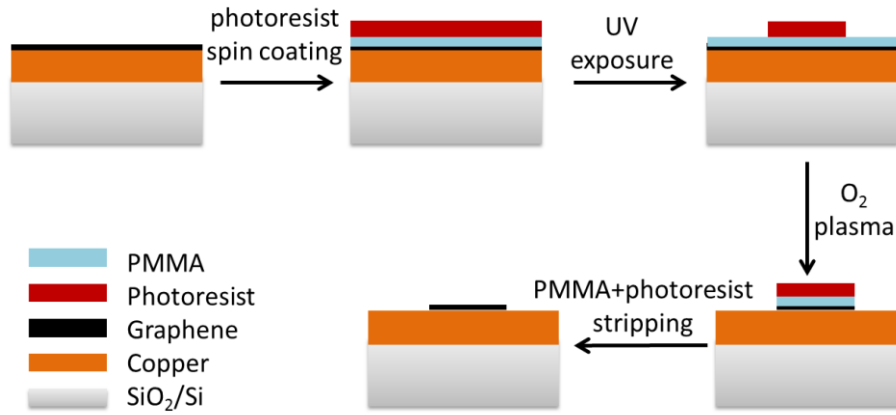


Figure 49: Schematic describing the photolithography process of graphene beams

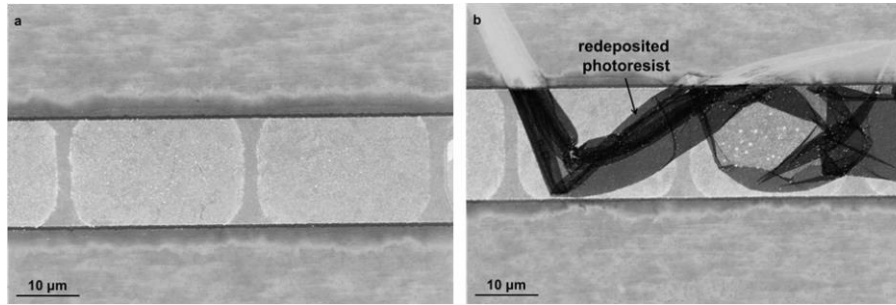


Figure 50: Result of graphene photolithography after photoresist stripping using a) PG remover and b) acetone

After patterning graphene beams, one final step was taken in order to ensure good adhesion between the graphene beams and the actuator beams. It is known that graphene surface energy is low as discussed in section 6.1. Therefore, increasing the surface energy is important so that the actuator and the sample beams are well connected after the structure release. Previous reports have shown that a low power plasma treatment is beneficial to increase graphene's surface energy (Shin et al., 2010). Therefore, several tests have been performed to find the right plasma conditions to increase graphene's surface energy while not causing any damage to the graphene film. Oxygen plasma powered by 2 W and 5 W

were tested on graphene, and Raman spectra were taken before and after the treatment, to check for graphene damage. Figure 51 shows the Raman spectra before and after 2 W and 5 W plasma treatments for 15 seconds. Using 5 W plasma creates a lot of defects and causes damage to the sp^2 -carbon atoms structure in graphene, as indicated by the high intensity of the D peak at 1350 cm^{-1} and the decreased ratio between the intensities of the 2D(2700 cm^{-1}) peak and the G peak (1600 cm^{-1}). However, using 2 W plasma does not seem to induce any defects in graphene, and the graphene structure remains as before the plasma treatment. Therefore, these conditions were favored to use for graphene's surface treatment.

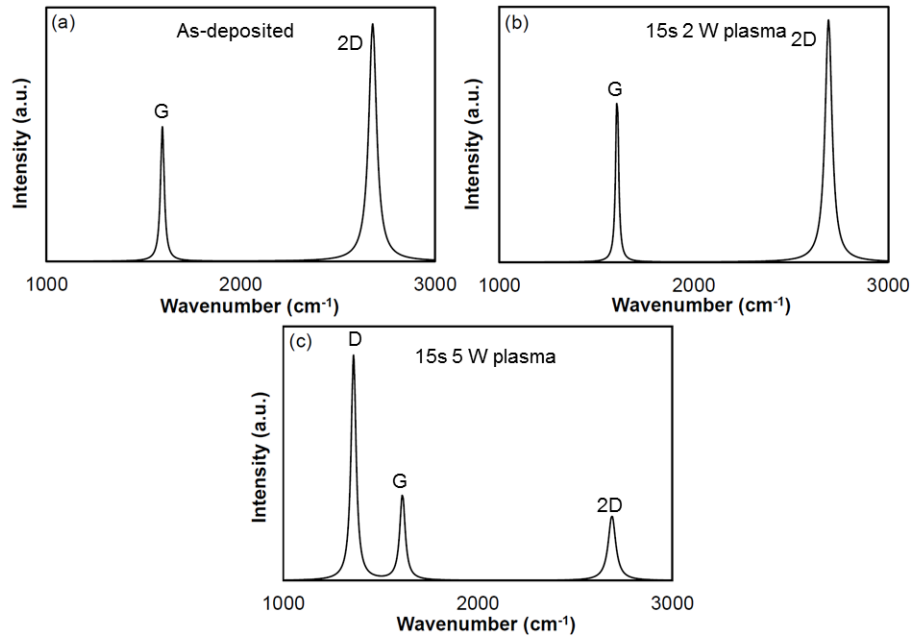


Figure 51: Raman spectra of (a) graphene as-deposited on Cu, (b) graphene after being treated for 15 seconds by 2 W plasma, and (c) graphene after being treated for 15 seconds by 5 W plasma

8.1.2 Actuator material selection and patterning

8.1.2.1 Choice of material

Low pressure chemical vapor deposited (LPCVD) Si_3N_4 has been found to be the optimum choice of actuator material for earlier works. First, it contains a high residual stress of around 1 GPa when deposited on a Si wafer, providing enough mismatch strain to relax and pull on the sample beams. Nanoindentation measurements have indicated a Young's modulus of around 270 GPa for LPCVD Si_3N_4 . Therefore, the mismatch strain of LPCVD Si_3N_4 is calculated to be around 0.3%. Other reasons that motivated the use of LPCVD Si_3N_4 ; its high etch selectivity with PECVD SiO_2 , which facilitated the final release step, and finally, being an amorphous material which minimizes the stress gradient over the film thickness, thus avoiding out of plane bending.

In this work with graphene as sample material, another actuator material has to be used. Since, the sacrificial layer in this process is a Cu thin film; the high temperature ($\sim 800^\circ\text{C}$) at which LPCVD Si_3N_4 is deposited would risk the melting and evaporation of the Cu film. Cu has a melting point at around 1085°C , and for thin films, the melting temperature significantly decreases below this value due to the higher surface to volume ratio. Instead, plasma enhanced chemical vapor deposited (PECVD) Si_3N_4 was selected as the actuator material. PECVD technique utilizes the high energy of electrons in the plasma to dissociate the reactive gas and form the film on the substrate just by controlling the pressure. This leads to the possibility of depositing the required films at much lower temperatures than by using LPCVD. PECVD Si_3N_4 is also amorphous and by optimizing the deposition conditions, highly stressed layers could be deposited. However, few considerations have to be taken into account in order to enable the use of PECVD Si_3N_4 as the actuator material. First, since the nitride layer will be deposited on top of graphene/Cu surface, the deposition conditions must avoid damage of the graphene while producing Si_3N_4 with high enough mismatch strain. In order to deposit a highly stressed PECVD Si_3N_4 layer, certain conditions have to be

met; first, during deposition a low ratio of Si:N has to be maintained. Secondly, the power inside the chamber during deposition must be kept low. Third, the pressure inside the chamber has to be higher than 1 Torr. Habibpour et al. (Habibpour et al., 2011) have shown that conditions similar to those mentioned above do not cause any degradation to graphene. Therefore, a recipe was selected with the following parameters; SiH_4 , NH_3 , and N_2 flows of 40, 30, and 1500, respectively, a pressure of 1.25 Torr, 25 W plasma and 350 °C deposition temperature.

After deciding on a recipe, it has to be confirmed that graphene does not suffer any degradation during the nitride deposition. Raman spectra were taken for a CVD grown graphene film on Cu thin film before and after the nitride deposition. Since, the deposited nitride is an amorphous material; it is transparent to the 540 nm laser used in our Raman spectroscopy and the graphene underneath could be directly probed. Figure 52 shows no significant change of the Raman spectra before and after deposition. There is just a slight change in the intensities ratio of the 2D and G peaks, but it is due to the interference with the deposited nitride layer, while the absence of a D peak suggests that no defects are created in the graphene lattice.

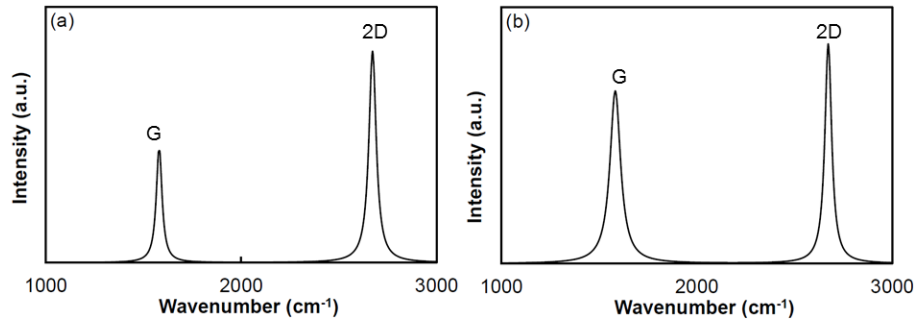


Figure 52: Raman spectra of graphene (a) before PECVD Si_3N_4 deposition, and (b) after PECVD Si_3N_4 deposition

8.1.2.2 Estimation of actuator mismatch strain

To check for the mismatch strain in PECVD Si_3N_4 to confirm its capability of loading the graphene sample beams, two techniques are used. First, free

beams of PECVD Si_3N_4 are fabricated. Figure 53 shows a schematic of the process. The idea is that when the nitride film is deposited, internal stress will develop and if a beam is patterned such that it is anchored on one side and free on the other, this internal stresses will cause the free side to relax and therefore either contract (in case of internal tensile stress) or expand (in the case of internal compression stress).

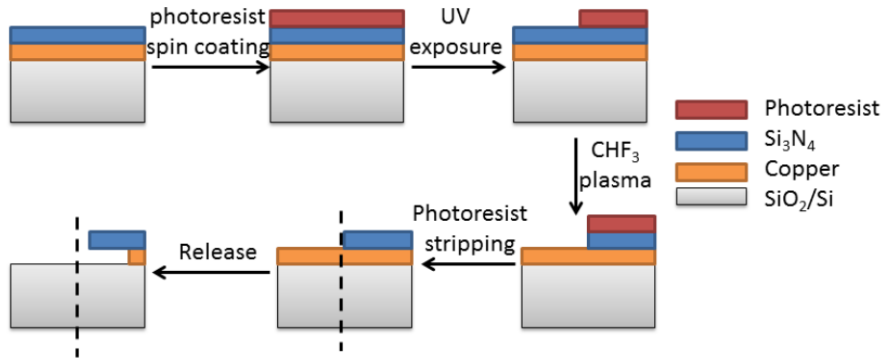


Figure 53: Schematic of the process of fabricating free Si_3N_4 beams

The displacement of the free beam will indicate the mismatch strain inside the sample as discussed in section 3.4.3, by the formula

$$\varepsilon_{mis} = \frac{-u_{free}}{L_i^a}$$

where u_{free} and L_i^a are the free beam displacement and the initial beam length, respectively.

This method theoretically provides the best way to characterize the mismatch strain in the actuator beams. However, in practice, some internal stress gradient is always present even in amorphous materials. This leads to out of plane bending of free beams especially for longer ones, which makes it impossible to accurately measure the in-plane displacement. Figure 54 shows SEM images of a released array of free Si_3N_4 beams. It is clear that the longer the beam is the higher out of plane bending it undergoes. From

the shorter beams shown clearly in Figure 54b, the displacement is measured as shown in Figure 54c, and the measured displacement is plotted against the beam length in Figure 55. It is noticed from this plot, that the displacement is not exactly linear with the beam length as should be expected which indicates the described out of plane bending even at short beams which overestimates the measured displacement as the beam length increases. From the measured displacements, the mismatch strain is estimated to be between 0.35% for the shortest beam with length of 100 μm . However, this value is probably overestimating the mismatch strain as well, therefore, in order to avoid any out of plane displacement, another array of free beams is released, but was dried in air and not in CPD, so that the beams stick to the substrate and prevent any out of plane bending. Figure 56a shows an SEM image of the released array, and the displacement is plotted for all beams in relationship to their lengths (Figure 56b). It is observed, that in this case the relationship between the measured displacements and the beams lengths is almost linear as shown by the fitting line on the plot. From the slope of this curve, the mismatch strain is calculated to be around 0.23%.

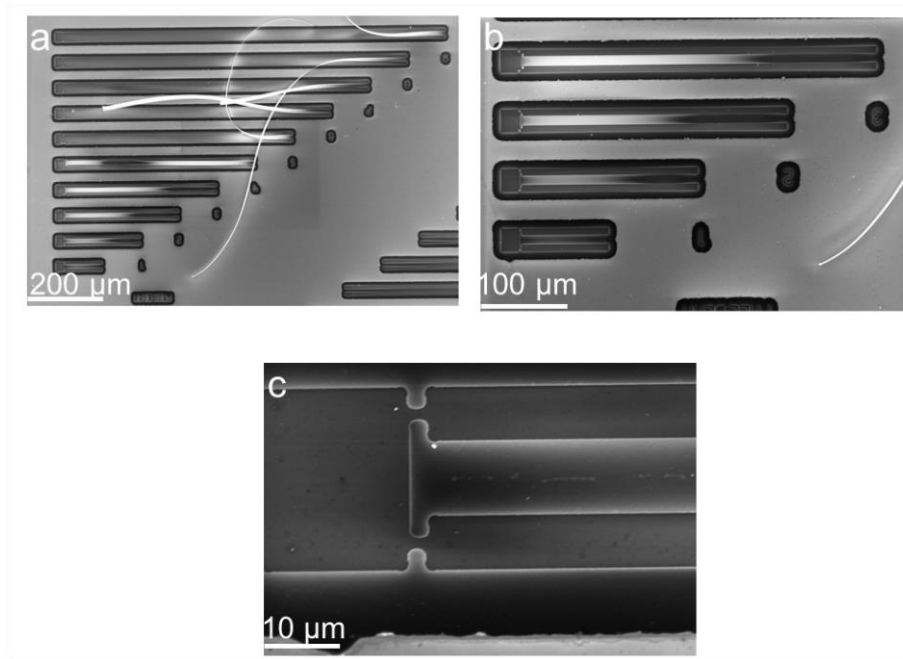


Figure 54: SEM images of released free Si_3N_4 beams with different magnifications

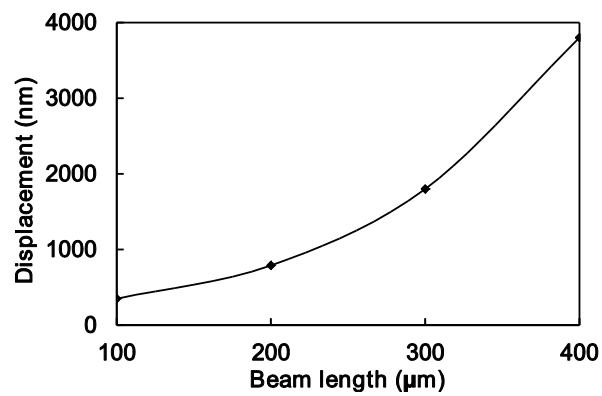


Figure 55: Measured displacement against beam length for free Si_3N_4 beams

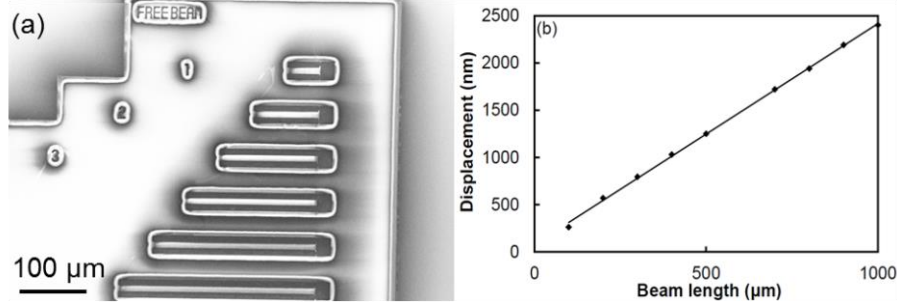


Figure 56: a) SEM image of free nitride beams dried in air to avoid out of plane bending, b) measured displacements plotted against the beams lengths

This value is not accurate enough though, also due to the inaccuracy of the measured displacement by the SEM. Therefore, another alternative to the free beams is used which is the “self-actuated beams”. Self-actuated beams are in principle micro tensile testing devices with the actuator and the specimen beams are fabricated from the same material. In this case, self-actuated beams of Si_3N_4 are fabricated and released. To calculate the mismatch strain from such structures, the forces in the actuator and the sample beams are calculated at equilibrium so that:

$$F = S_a E_a \left(-\frac{u}{L_i^a} - \epsilon_{\text{mis}} \right) = S_t E_t \left(\ln \left(\frac{L_i^t + u}{L_i^t} \right) - \epsilon_{\text{mis}} \right) \quad (16)$$

Through the above equation, the mismatch strain can be linked to the geometrical parameters as follows:

$$\epsilon_{\text{mis}} = \frac{S_t \ln \left(\frac{L_i^t + u}{L_i^t} \right) - S_a \frac{-u}{L_i^a}}{S_t - S_a} \quad (17)$$

So, just by knowing the length, width, and thickness of the material in addition to measuring the displacement after release, the mismatch strain in the Si_3N_4 film can be calculated. Figure 57 shows an example of a released array of self-actuated beams of 100 nm thickness nitride, the actuator is tapered with an effective width of 10 μm, and the sample beam's length is 50 μm. Figure 58 shows a plot of the measured displacement against the actuator length. From those structures, the

mismatch strain is calculated for each device, and the average mismatch is estimated to be around 0.29%, which is in agreement with previous works performed at UCL with similar condition (Table 4). It is noticed that the mismatch strain calculated from the self-actuated devices is a little less than the one calculated by suspended free beams and a little more than the one calculated by the sticking free beams. This indicates that indeed even in the shortest suspended beams, there is some out of plane bending which leads to the measured displacement to be overestimated, while not using CPD to stick the beams to the underlying substrate leads to measuring displacements smaller than reality.

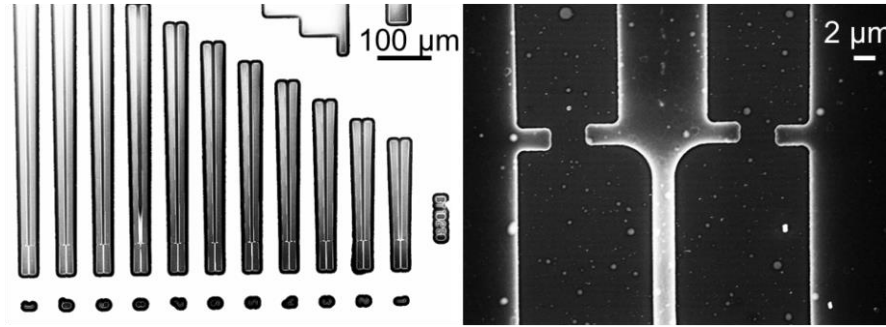


Figure 57: Self-actuated structures of nitride beams

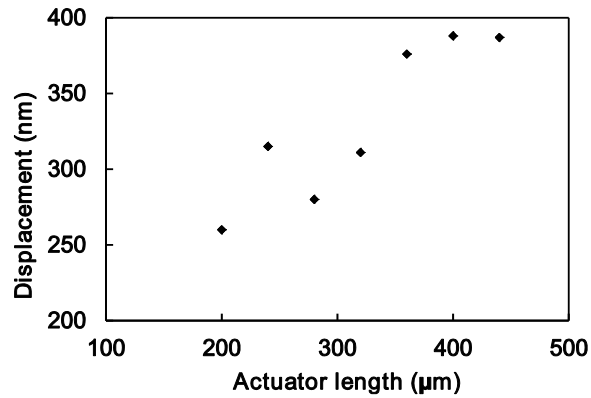


Figure 58: measured displacement vs actuator beam length of self-actuated Si_3N_4 devices

Table 4: Parameters and mismatch strain calculated for previous PECVD nitride trials performed at UCL

SiH ₄ (5%) [sccm]	NH ₃ [sccm]	N ₂ [sccm]	P [W]	p [Torr]	T [°C]	ϵ_{mis}
500	35	665	60	1.5	300	0.0025
40	30	1500	25	1	350	0.00253
40	40	1490	25	1	350	0.0023
40	50	1480	25	1	350	0.00239
40	30	1500	25	1.25	350	NA
40	30	1500	25	1.5	350	NA
40	30	1500	25	1	300	0.00226
40	30	1500	25	1	400	NA
40	30	1500	25	1.75	350	0.00287
40	30	1500	25	2	350	0.00285
40	30	1500	100	1	350	0.00116

8.1.2.3 Etching and patterning the actuator beams

After verifying the suitability of using PECVD Si₃N₄ as an actuator material with a mismatch strain of 0.29% similar to this of LPCVD Si₃N₄, the issue of patterning the nitride layer into the desired beam structures is addressed.

Photolithography is used to make the desired shapes. However, etching the Si_3N_4 remains a problem in the presence of graphene. Normally, the best way of etching would be using a dry etching method like using CHF_3 plasma etching for fabricating free beams. Plasma etching is very beneficial in applications that require very good directional etching, the etching is performed only along the thickness of the layer, and the structures under the photoresist are not attacked along their width or length. However, with the presence of graphene under the nitride layer, it is very critical to be able to control the etching time so that it stops exactly after etching the nitride layer so that it does not attack the graphene underneath, as even a very small error would result in the graphene being exposed to the plasma and etched. This however proved not to be possible in practice. Therefore, an alternative method of etching the nitride has to be considered. One alternative is using wet etching, and HF acid is considered as the ideal candidate. In order to successfully control etching PECVD Si_3N_4 by HF, a very low concentration is required since the etch rate is too fast. Therefore, 2% HF is used and the etch rate is tested to be around 10 nm/second. Moreover, with this low concentration, the issue of graphene fluorination is avoided, since it has been shown that using HF concentrations of more than 3% would cause fluorination of graphene (Nebogatikova et al., 2014). Figure 59 shows SEM images of free Si_3N_4 free beams etched by using 2% HF.

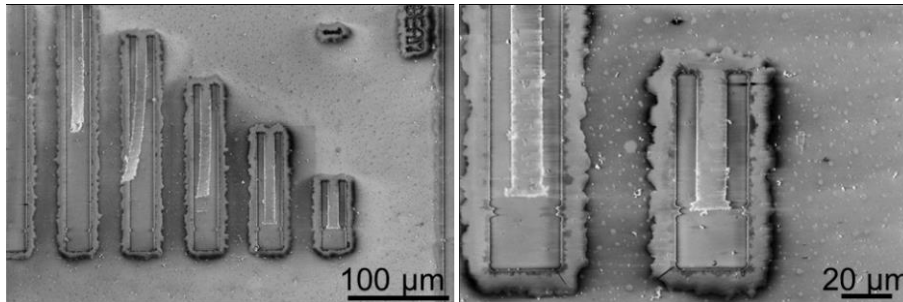


Figure 59: SEM images of free nitride beams etched by 2% HF

It is clear that Si_3N_4 is indeed etched and the beams are successfully patterned, however, by stripping the photoresist; it became clear that the

beams are significantly etched along their width and length. The cursors at the side of the beams are not well defined as in the case of plasma etching. Moreover, a higher stress gradient develops in the beams due to the etching of the beams' edges which causes inhomogeneity in the structures, therefore, even higher out of plane bending takes place in Si₃N₄ beams etched by HF.

Another solution to fix this issue is using a combination of plasma etching and HF etching. The idea is to use plasma etching to etch down the Si₃N₄ layer down to a thickness of around 10 nm, and then etching the rest by HF. This minimizes the time of the sample being exposed to HF down to around 1 second. Figure 60 shows the result of etching the nitride layer using this technique. It is seen that this technique yields better results than only using HF; the cursors are better defined, and although the issue with the out of plane bending is still there, SEM images show a slight improvement. Consequently, patterning the actuator by CHF₃ plasma followed by 2% HF remains the most promising option.

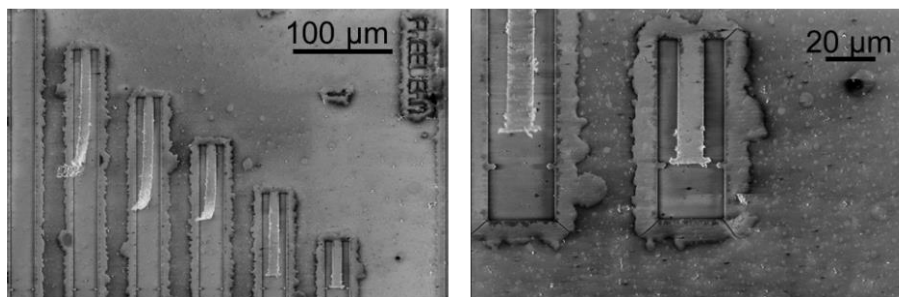


Figure 60: SEM images of free nitride beams patterned by CHF₃ plasma + 2% HF

8.1.3 Releasing of suspended graphene beams

One of the main issues faced while fabricating the micro tensile testing devices for graphene is the ability to release the structures in a way that would allow the actuator to pull on the graphene sample beam while keeping the integrity of the graphene beams. This step has to be accomplished through carefully controlling the sacrificial layer etching (Cu)

and protecting the graphene structures during the wet release process. Several devices have been reported where graphene beams have been suspended (Bharadwaj et al., 2014; Levendorf et al., 2009), and it was shown that the presence of a photoresist layer on top of graphene during etching the underlying Cu layer is mandatory to keep the graphene integrity during release. Tests have been performed on CVD grown graphene on Cu thin films for the release procedure, and it was indeed clear that the presence of a protective resist layer protects graphene from extensive damage. Figure 61 shows a schematic of the process to obtain suspended graphene beams.

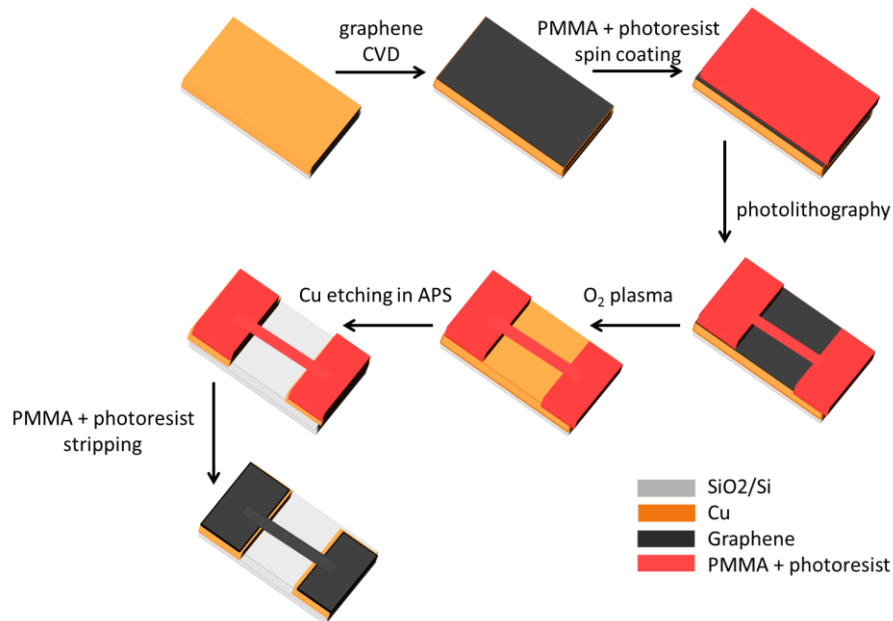


Figure 61: Schematic of the process steps to fabricate suspended graphene beams

The Cu sacrificial layer was etched by a 20% solution of APS, followed by rinsing, and stripping the resist layer by PG remover before finally using CPD for drying. CPD is important to avoid the damage of graphene by stiction which occurs due to the capillary forces between the structures and the underlying surface due to the presence of liquid. Figure 62 shows an

example of released suspended graphene beams grown by CVD on a Cu thin film. The main observation from this test is that the longer the graphene beams are, the higher the probability they will be damaged during release. According to our experience, beams with dimensions larger than 5 μm have very low yield after release.

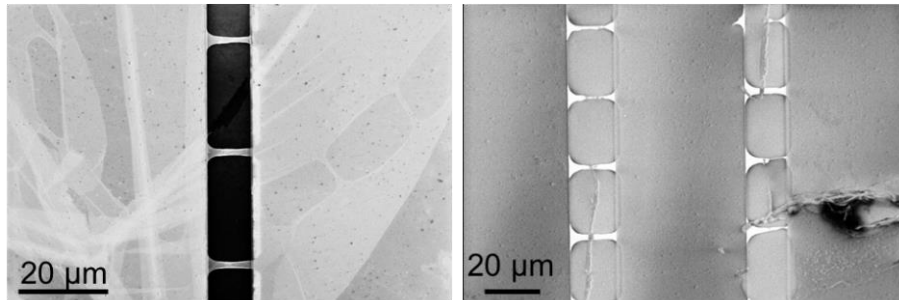


Figure 62: Example of released suspended graphene beams

8.2 Initial results

8.2.1 Geometrical design

After testing and validating the materials and process steps as described above, the geometry of the devices has to be considered. The mechanical properties of the actuator beams are well known through other characterization techniques as described previously, with mismatch strain of 0.29%, and a Young's modulus of around 140 GPa. The mechanical properties of graphene can be acquired from the AFM loading tests as explained in section 0, so the Young's modulus is taken to be 1 TPa, and the mismatch strain of graphene is assumed to be negligible (Averaging the pre-tension values in Table 3 would result in a mismatch strain value of 0.04%). These values were used to obtain an estimation of the correct geometries needed for the actuator and the sample beams. The parameters that need to be fixed are:

1. Sample thickness, width, and length
2. Actuator thickness, width and length

Equation 7 is used to calculate the expected strains and displacements in graphene beams for each geometrical design of the actuator. Finally, it has been found that an actuator of 100 nm thickness, with widths ranging from 5 to 15 μm , and lengths ranging from 50 to 500 μm would satisfy all the conditions described.

Figure 63 shows an example for estimating the strain and displacement of an array of 1 μm wide and 10 μm long graphene beams being pulled on by a 100 nm thick and 5 μm wide Si_3N_4 beams for different actuator lengths. According to this data, a maximum strain of around 14% can be expected, and the displacements should be large enough for measurements by SEM.

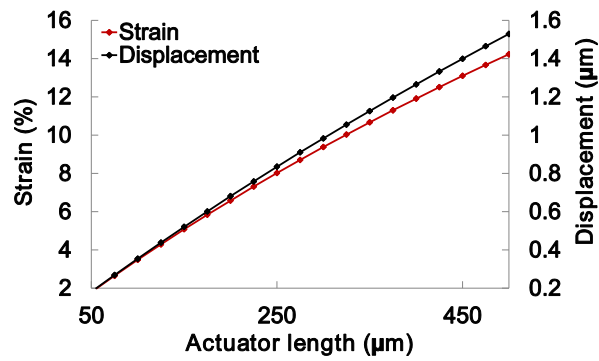


Figure 63: Calculation of the expected displacements and strains in an array of testing devices

8.2.2 Processing first devices

After estimating the strain values, different geometries of actuators and sample beams are designed and the corresponding lithography masks are fabricated. Afterwards, the first trials of fabricating the tensile testing devices have been performed according to the processing steps previously described (full process flow illustrated in Figure 64).

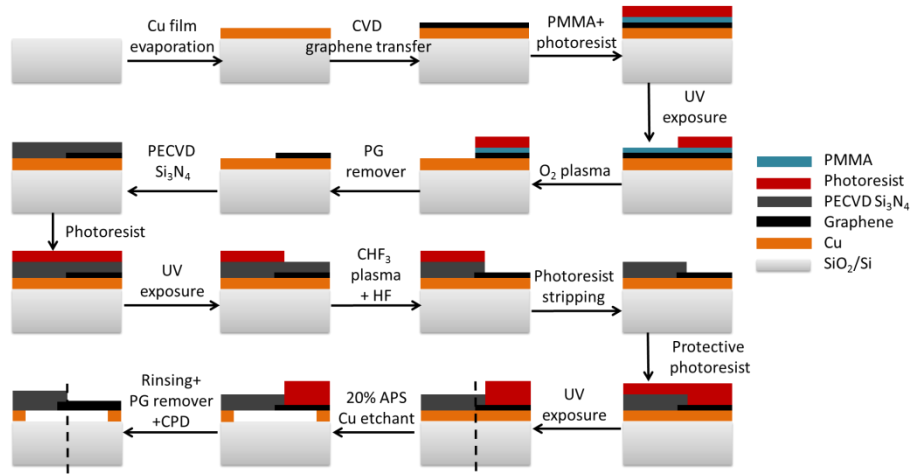


Figure 64: On-chip tensile testing micro devices process flow

SEM images were taken of the devices before and after release. Figure 65 shows the devices just before releasing them. The Si₃N₄ and graphene beams are well patterned except for the cursors which, as discussed before, is a result of the HF attacking the nitride layer in the horizontal direction. The next step after this stage is depositing a new layer of photoresist and exposing it with the same mask used to pattern the graphene beams in order to protect the graphene beams during the release step. The remaining photoresist from the previous step has to be stripped before coating the new layer, so that the thickness of the photoresist all over the wafer remains the same, and therefore, avoid obtaining different exposure levels on the wafer during the lithography step.

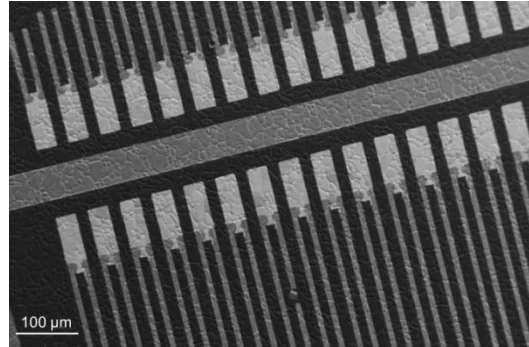


Figure 65: Tensile testing devices before etching Cu sacrificial layer to release the structures (dark color: Si₃N₄, grey background: Cu, bright color: graphene)

Figure 66 shows SEM images of released devices. It is clear that the process has not been successful in these first trials. As shown in the SEM images, the graphene beams are broken, twisted and disconnected from the actuator beams in some cases. Also, the Si₃N₄ beams do not show any displacements after release, and by careful investigation, it is observed that the Si₃N₄ beams are broken and cracked at several locations, and therefore no load is actually applied on graphene beams.

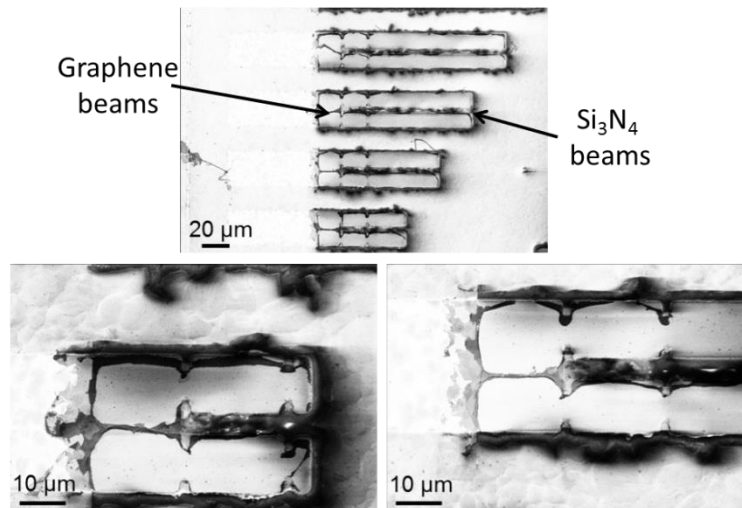


Figure 66: SEM images of released graphene micro tensile testing devices

8.2.3 Analyzing and optimizing the process

In order to further optimize the process, some hypotheses were considered for the failure of the first trials. First, the issue of graphene beams being broken and twisted is considered; there could be 2 reasons for this observation: First, graphene is not well protected by the photoresist layer during the release of the devices. This could arise from the fact that graphene beams sizes range between 1 and 5 μm and almost always in practice there exist some misalignments during photolithography. This means that the photoresist protective layer may not be covering the graphene beam after lithography or at least may be only partially covering it. Figure 67a shows a schematic describing this problem. The best solution for this problem is to design the protective layer to have larger area than the graphene beams in order to compensate for any misalignment as illustrated in Figure 67b.

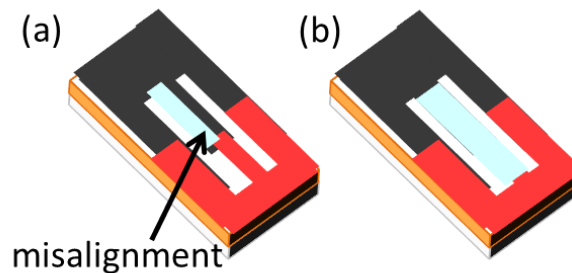


Figure 67: Schematic of a) the original protection layer showing misalignment with the graphene beam, b) the modified design by using a wider protection beam to compensate for any misalignment

The second reason for graphene damage during the process is the fact that the graphene beams are only supported by graphene anchors. Figure 68 shows high magnification SEM images for released graphene beams, and it is clear that the anchors experience a lot of tearing and damage, which lead to the graphene beams collapsing. To fix this issue, a new design is proposed where having graphene anchors is avoided. Instead the devices

are designed so that two Si_3N_4 beams pull on a graphene beam from both ends. This will apply uniaxial stress on the graphene beams in both directions, and meanwhile, graphene will be supported on both sides by the nitride and will not depend on graphene anchors. Figure 69 shows a schematic illustrating the difference between the two designs. For calculating the stress and strain in the graphene beams, equations 7 & 14 are still used, but in this case, the actuator length will be taken as the sum of lengths of both Si_3N_4 beams.

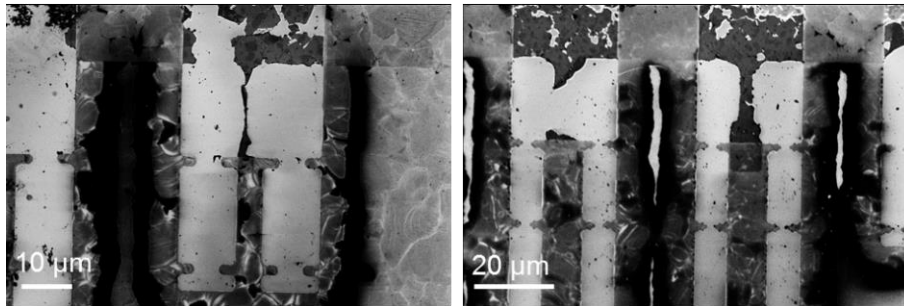


Figure 68: High magnification SEM images of released graphene micro tensile testing devices (note: the tears and damage in the graphene anchors)

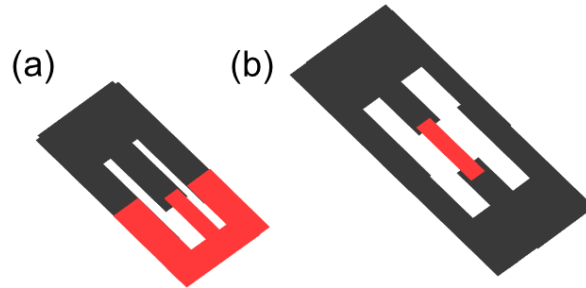


Figure 69: Schematic of the a) original design of the devices, b) optimized design; the graphene beam is now pulled on both sides by the Si_3N_4 beam, instead of being supported by graphene anchors which would be damaged during the process.

Another problem noticed from the released devices is that the PECVD Si_3N_4 beams contain a lot of cracks. This causes the actuators to collapse and therefore no load is applied on the graphene beams. A test was performed

with a PECVD Si_3N_4 layer deposited on as-deposited copper film and on an annealed copper film. Free suspended beams were fabricated as described in Figure 53. Optical microscope images clearly show a huge difference between both samples. Figure 70a shows the beams deposited on as-deposited Cu. The Si_3N_4 beams have a good quality, no cracks, and a magnified image shows clearly the displacement obtained by releasing and relaxing the internal stress. Oppositely, Si_3N_4 beams deposited on annealed Cu show severe damage and no beams appear to be well released (Figure 70b).

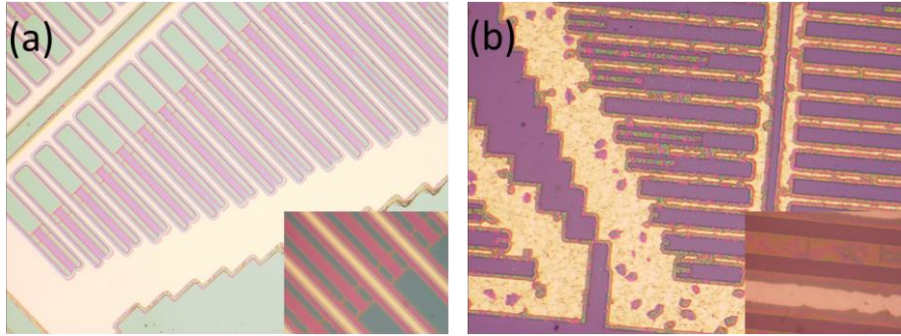


Figure 70: Si_3N_4 free actuator beams deposited on a) as-deposited Cu film and on b) annealed Cu film.

This could be explained by considering the following; the Cu film grains are significantly larger after the CVD growth of graphene, since it is grown at very high temperatures close to 1000 °C. Figure 71 shows an SEM image for Cu film surface after graphene growth, the average grain size is around 20 μm . This grain growth of Cu increases the roughness of the surface, and because PECVD is a conformal deposition process, so when the nitride layer is deposited, it follows the morphology of the Cu surface and breaks due to its high roughness.

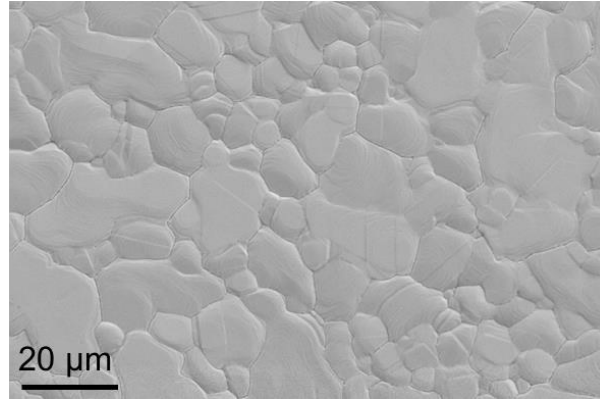


Figure 71: Cu surface after graphene growth by CVD (average grain size is 20 μm)

PECVD Si_3N_4 is not a high quality nitride, so its fracture strain is small compared to LPCVD Si_3N_4 for instance. Moreover, it is expected that as the area of the beam increases, it would break at even lower strains due to the increase of defects. Indeed, self-actuated PECVD Si_3N_4 tensile testing devices (as shown in Figure 57) show that for beams of width as small as 1 μm, and length as small as 25 μm, the fracture strain is as low as 1% (Figure 72), and decreases as the beam length increases.

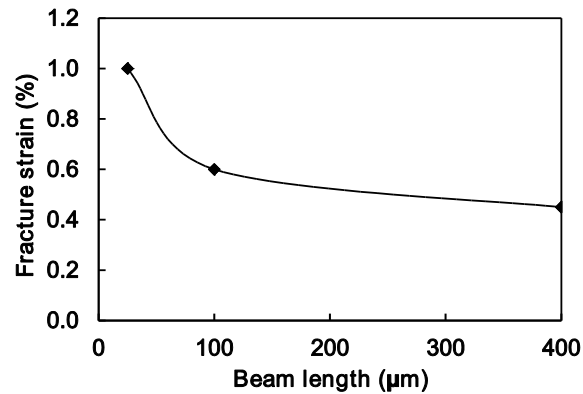


Figure 72: Fracture strain of Si_3N_4 beams as a function of the beams length

This proves to be a critical problem for completing the process, and even films with thickness as low as 350 nm (minimum thickness possible for CVD

process) still undergo a large grain growth at those high temperatures. In order to optimize the process, either a different sacrificial layer or a better quality actuator material should be used. Both options have been investigated and finding a different actuator material proved to be complicated. As previously discussed, LPCVD Si_3N_4 is not feasible due to its deposition conditions. Other materials investigated included metallic thin films; Cr, Pd, Ti, and Ni. However, this did not succeed due to the low adhesion between these metallic thin films and the Cu sacrificial layer, which caused the films to be delaminated upon starting the process. Consequently, a different sacrificial layer has to be found. Graphene can only be grown on metallic surfaces by CVD, most commonly, Cu, Ni or Pt. Therefore, it is not possible to use a sacrificial layer on which graphene can be directly grown, because all metallic surfaces will undergo grain growth during CVD which would lead to fracture of the actuator beams. Therefore, another layer has to be used where graphene could be transferred on top of it. SiO_2 was considered, however, etching it would have been a problem due to poor etching selectivity with PECVD nitride. Another option was to use a Si sacrificial layer and XeF_2 dry etching for release; this would also avoid the issues with the wet release damaging graphene. However, our tests show that even short exposure times to XeF_2 , graphene turns into fluorographene. Alternatively, it is proposed to use as-deposited Cu films as the sacrificial layer; using as-deposited Cu films has the advantage that most of the processing steps developed so far will remain the same.

8.3 Results of modified process

Based on the observations made from the initial process results, the process is repeated including the corrections discussed in section 0.3. Graphene is first transferred on top of an as-deposited Cu film, the transfer step is performed as per Figure 1, but instead of transferring on SiO_2 , the graphene is transferred on a Cu thin film with a thickness of 1 μm . Graphene is grown by CVD on a Cu foil; spin coated with a 300 nm PMMA layer, and then the Cu foil is etched using FeCl_3 solution. Afterwards, the graphene/PMMA film is moved to several water baths for rinsing. A lot of

care has to be taken in this step, because any remaining residues of FeCl_3 will lead to the etching of the Cu film after the transfer. The graphene/PMMA film is then transferred on top of the Cu film, and left to dry. Finally, the substrate is heated at 105 °C for 5 minutes followed by dropping fresh PMMA on the surface, before removing the PMMA layer with acetone. Figure 73 shows an SEM image of the transferred graphene; the film appears to be of good quality with mostly a single layer graphene with small bilayer islands forming.

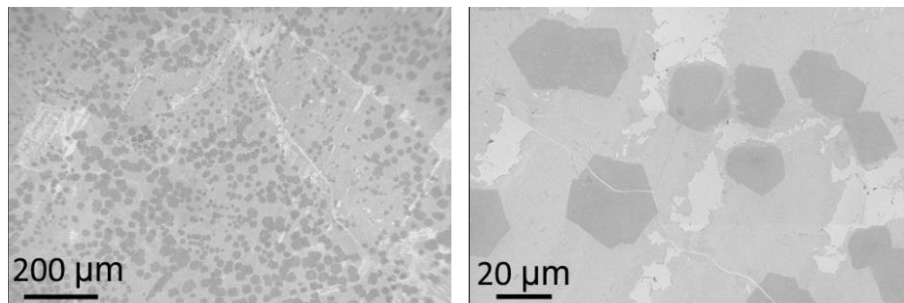


Figure 73: SEM images of graphene transferred on Cu thin film

The following steps of the process are performed as explained before. The graphene is patterned into beams by photolithography using a PMMA/photoresist layer. PECVD Si_3N_4 is deposited and patterned by photolithography and a combination of dry and wet etching into the actuator beams. Finally, another photoresist layer is deposited and patterned as beams with larger dimensions than graphene beams to act as a protective layer during release. Figure 74 shows SEM images for the optimized devices before release.

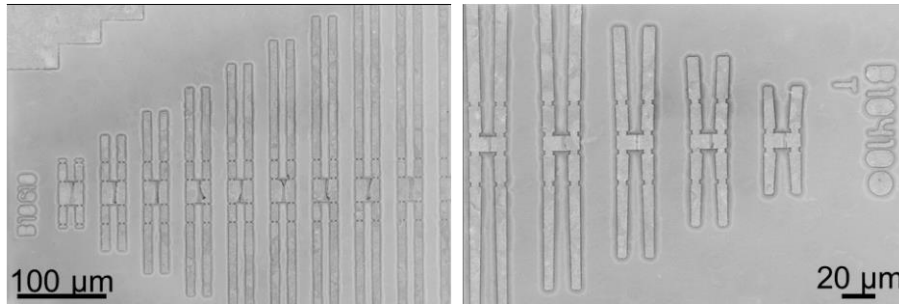


Figure 74: SEM images of optimized tensile testing devices before being released

The release is then done by 20% APS solution, followed by rinsing in DI water, and the protective photoresist layer is stripped using PG remover, before drying using CPD. SEM images were taken for the released samples. Figure 75 shows a few examples of successful devices. The graphene beams appear to be suspended and connected to the actuator beams. However, all over the wafer, the yield remains very low for the devices.

The design is done so that an array of devices with different geometries would lead to a stress-strain curve of the test material. So, many devices have to be successful in the same array, or at least few devices with different geometries have to be successful. However, in our case, usually a single device is found successful in each array; most commonly, being the devices with the shortest actuator length. This makes estimating the fracture strain of graphene not possible for instance.

This could be explained due to the fact that as the Si_3N_4 beams are longer, the more out of plane bending they undergo as previously shown. Moreover, HF etching of Si_3N_4 further increases this out of plane bending due to the inhomogeneity it creates when it attacks the edges of the beam. Graphene as explained in chapter 3 has a very low bending stiffness; therefore, a graphene beam will collapse if the actuator beams undergo a large out of plane bending. Ultimately, this leads to only the devices with the shortest actuator beams to be successful. Indeed, further investigation of some of the working devices has shown that the displacements measured are much larger than expected, and this could be attributed to

the out of plane bending even at the devices where graphene is still present.

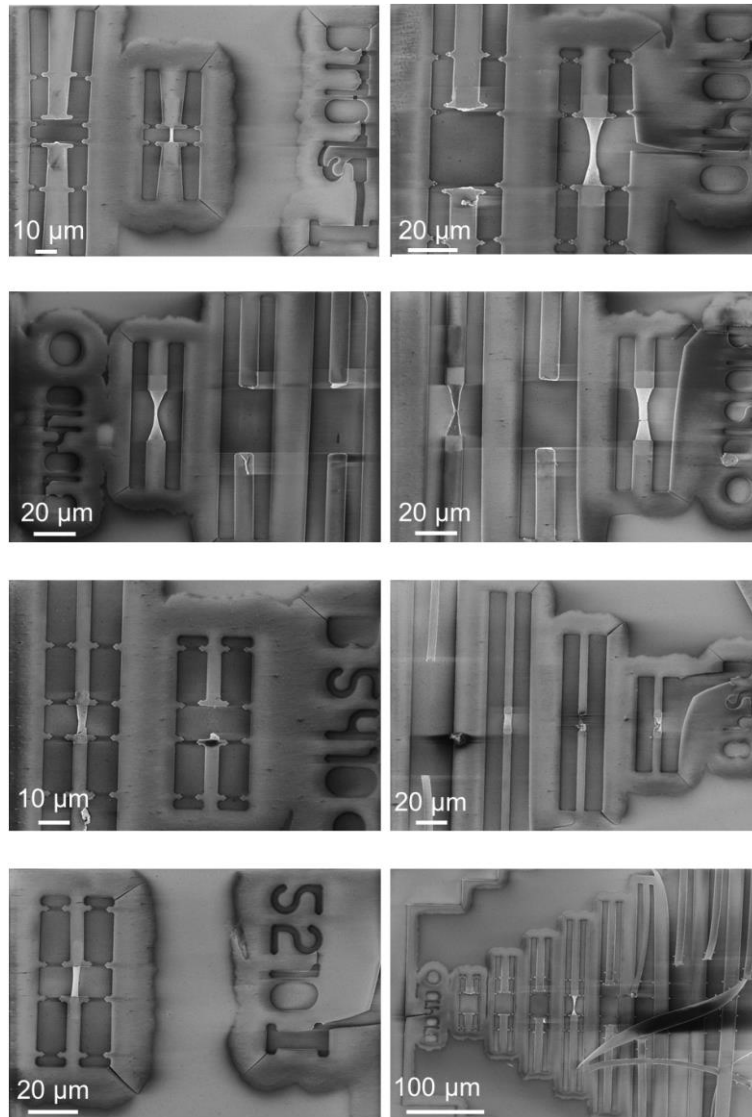


Figure 75: SEM images of example functional micro tensile testing devices on graphene after release

Figure 76 shows a magnified image of one working device, with a graphene beam having a width of $1\text{ }\mu\text{m}$ and a length of $5\text{ }\mu\text{m}$. The actuator beams in this case have a width of $10\text{ }\mu\text{m}$, and the length of each beam is $25\text{ }\mu\text{m}$. The measured displacement by SEM for this structure is 300 nm for each actuator beam. This measured displacement is too large for an actuator beam with such a length similar to what was shown in Figure 55, which indicates that there is some out of plane bending even in such small beams with graphene still attached to the actuators.

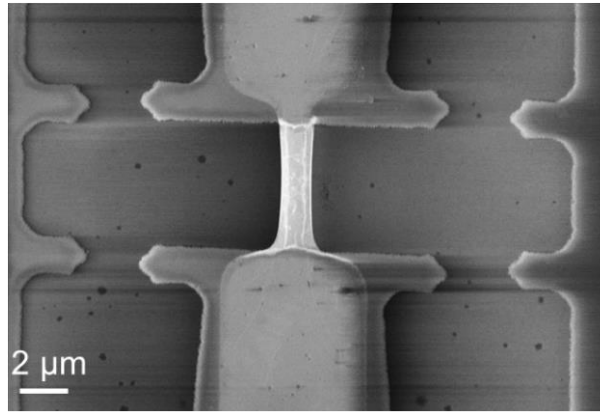


Figure 76: A zoomed SEM image of a working micro tensile testing device

Estimating the stress and strain of graphene from those working devices proved to be a complex task. First, the working devices all have very small actuators, which means that the displacements taking place are too small to measure by SEM, on the other hand, in some beams there are visible displacements, however those displacements are larger than expected due to the contribution of out of plane bending. Instead, the displacement, stress and strain in each beam of the working devices is calculated using equation 16 of the force equilibrium between the sample and the actuator beams, in addition to the known properties of the actuator, and by assuming a graphene's Young's modulus of 1 TPa based on the AFM membrane deflection tests in chapter 7. This method only takes the previously known inputs from design (widths, lengths, thickness),

Chapter 8: On-Chip tensile testing devices of suspended graphene beams

characterizing the actuator (Si_3N_4 modulus & mismatch strain) and AFM measurements (graphene's modulus), and uses it to get an idea about the expected values of displacement, stress, and strain in each graphene beam.

Table 5 shows the calculated values of displacement, strain, and stress, and according to those calculations, and as shown, the maximum value of strain attained in one of the working devices is around 4.8%.

Table 5: Displacements, stress and strain values calculated for graphene beams based on successfully released on-chip tensile testing devices

Actuator length (μm)	Actuator width (μm)	Sample length (μm)	Sample width (μm)	Displacement (nm)	Strain	Stress (GPa)
50	10	5	1	142	0.028	28
100	10	10	1	214	0.0212	21.2
50	10	10	4	139	0.0138	13.8
200	10	10	4	493	0.0481	48.1
50	10	8	6	134	0.0166	16.6
50	10	10	6	136	0.0135	13.5
100	5	10	4	192	0.019	19
150	5	8	4	326	0.04	40
50	5	10	2	139	0.0138	13.8

Another possibility to further study the strain in the graphene beams would have been the use of Raman spectroscopy. It is well known that Raman signal of graphene can be significantly affected by strain in graphene. However, in most of these devices, Raman spectroscopy could not be accurately performed, and no meaningful results were possible to obtain due to two different reasons. First, In order to set the laser focus for the Raman measurement, it is done by an optical microscope, while suspended

graphene is hardly visible under optical imaging. Moreover, the suspended beams have very small dimensions which are at the limit of the laser spot resolution, which further complicates focusing on the right area. Secondly, all the processing steps and SEM imaging of the graphene induces doping, disorder, and changes to the graphene lattice structure. This makes it very complicated to single out the effect of strain from the Raman spectra obtained.

As shown in Table 5, it has been found that the maximum strain applied by one of the working devices is the one with an actuator beams with length of 100 μm each, and a width of 10 μm , and a graphene beam with length of 10 μm and width of 4 μm , leading to a strain of around 4.8%. This device is shown in Figure 77a. It is worth noting that the edges of the graphene beam are folded due to the mechanical instability resulting from graphene's 2D nature and this is the reason of the distorted shape appearing in Figure 77a (similar to a suspended sheet of paper). Raman spectrum taken at the center of the beam is shown in Figure 77b compared to graphene which is in contact with the nitride actuator beams and therefore considered free of strain. The Raman spectra show that the released beam is a little bit red shifted, and a clear splitting of the G band takes place which could all be attributed to strain the graphene lattice as reported by literature (Mohiuddin et al., 2009; Ni et al., 2008; Pérez Garza et al., 2014). The smaller red shift than expected might be due to the fact that graphene under the nitride beam is also strained, or due to the interference between graphene and the nitride layer on top. Moreover, the presence of a D peak coupled with the small I_{2D}/I_G ratio indicates presence of high disorder in graphene or a damaged graphitic atomic structure.

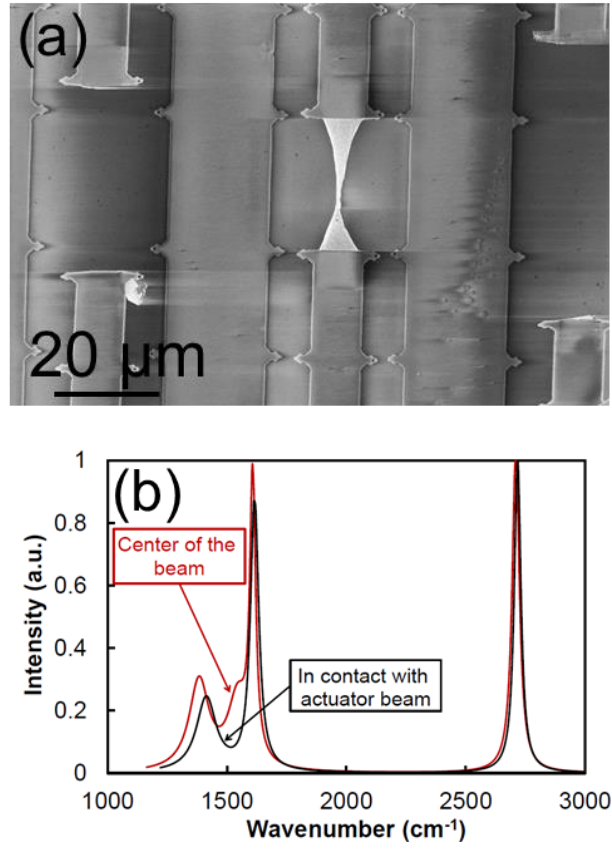


Figure 77: (a) SEM images of example functional micro tensile testing devices on graphene after release, (b) Raman spectra taken at the center of the released graphene beam and at the edge still connected to the Si_3N_4 actuator beam

Conclusion: A fabrication process to obtain on-chip tensile devices of single layer graphene has been developed. The actuator and sacrificial layer materials have been selected in a way to avoid damage to the graphene layer during fabrication. Moreover, processing steps have been carefully developed in order to maintain graphene integrity throughout the process. The process has shown the potential to fabricate suspended graphene beams under strain. Proof-of-concept results have been obtained and are expected to be of great impact on many applications that would require graphene under strain. Furthermore, this technique developed at our group has the potential to be used for in-plane uniaxial tensile testing characterization not only of bulk thin film materials, but could also be extended to 2D materials. Further work in this topic must address the possibilities of using different actuator materials with no or negligible stress gradient to avoid out of plane bending of the actuator beams. Finally, the next step would be performing this process on CVD grown graphene directly on Cu thin films, where the Cu thin films are then used as the sacrificial layers, in order to avoid the initial graphene transfer process. More specifically, monocrystalline Cu thin films are expected to be more practical to avoid the stresses generated in deposited actuator layers due to the Cu film's grain growth during the high temperature CVD process.

PART IV :
CONCLUSIONS AND
PERSPECTIVES

Chapter 9: Conclusions & outlook

In this work, several techniques have been developed and used to characterize the mechanical behavior of graphene. The different results were investigated and analyzed leading to exploring several novel properties of graphene and its potential applications as a coating or as a reinforcing component in composites. Additionally, the processing capability of graphene into a fully scaled microfabrication process has also been explored.

Two different configurations of graphene have been studied involving, graphene/substrate systems and freestanding graphene films. Nanoindentation experiments along with numerical simulations have been used to explore the properties of graphene on a substrate and the role of the graphene-substrate interactions. Freestanding graphene membranes have been probed by AFM tip deflection tests, while freestanding beams have been integrated into a full fabrication process for micro mechanical devices. The main conclusions of these two tests are provided hereafter.

Mechanical response of graphene/substrate systems

Nanoindentation data of CVD grown graphene on Cu thin films have been compared to the measurements performed on bare Cu films. Although, it appears virtually impossible to deconvolute mechanical properties of graphene by this method due to its atomically thin nature, carefully investigating the results coupled with numerical simulations have unraveled some unique effects. The presence of graphene has resulted in significant modification of the elastic and plastic deformation response of the Cu film.

Nanoindentation of Cu/graphene has demonstrated the role of graphene in eliminating the adhesion between the indenter tip and the indented surface. Our study has also shown that the presence of graphene modifies the elastic response of Cu to nanoindentation to a near ideal response as illustrated by the load-displacement curves, following almost perfectly Hertz law. This is to our knowledge a completely original result. The results

also show a higher elastic load bearing capacity of graphene coated Cu. The atomistic phenomenon leading to this result has been studied and was found to be due to the absence of adhesion between the surface and the tip. The first reason has been validated by MD simulations, and through further experiments, it was found that the interactions between the graphene and the underlying substrate play a crucial role in this phenomenon. The fact that graphene is CVD grown on the surface of Cu, means that the interactions between graphene and Cu in this case are so strong that the indenting tip is not able to deform or bend graphene. On the other hand, when graphene is transferred onto a substrate, the interaction is not as strong, which allows the tip to bend and deform graphene leading to increased surface adhesion. However, the intrinsic adhesion strength between the transferred graphene and the substrate can be used to modify the response, as demonstrated by the difference between graphene transferred on Cu and on SiO₂. These results open the door to nanoindentation being a characterization tool for the quality of graphene transfer, in the sense that it can be used to test the quality of the interface between graphene and the substrate, highlighting the importance of a clean and a reproducible graphene transfer process for fully utilizing this property of graphene. More tests on different graphene/substrate systems would also be beneficial in order to completely understand this phenomenon and to find more interesting systems with different levels of surface adhesion depending on the required application. Friction tests also could be performed in order to study the effect of graphene/substrate interaction on the friction coefficient of graphene.

Nanoindentation tests have also demonstrated, for the first time, a significant effect of graphene on the plasticity onset and dislocations activity in Cu. First, it was shown that the presence of graphene although initially leads to a stiffer response, it later softens and the yield takes place at a lower load. However, the major plasticity burst characterized by the “pop-in” in the load-displacement curve is strongly reduced by the presence of graphene, suggesting a reduced number of dislocations involved in this

plasticity event. Moreover, it has also been shown that, in the presence of graphene, the number of dislocations generated in Cu is independent of the applied load in contrast to the expected response of Cu where the number of dislocations increases with increasing applied load. AFM images and DDD simulations validate this effect and confirm that the plasticity under the contact is significantly modified for indentation depth more than 1000 times larger than the graphene layer thickness. Furthermore, the DDD simulations explain the dislocations mechanism taking place in Cu when coated with the highly impenetrable graphene layer. The result is a delocalization by forcing much more homogenous organization of the dislocations inside the material. These results have potential impacts on applications requiring good resistance to erosion or scratch resistance while preventing oxidation. Moreover, given the 2D nature of graphene and its remarkable mechanical strength, this very strong constraint on plasticity reinforces the interest in the use of graphene inside metallic matrices as a strengthening component.

Understanding the role that the adhesion between graphene and the substrate has on the dislocation barrier property of graphene is crucial in order to be able to use graphene with different metals as a strengthening component. This could be achieved by transferring graphene on metallic surface with different levels of adhesion and performing nanoindentation tests. However, the metallic surfaces have to be nearly free of pre-existing dislocations with grain sizes large enough to easily generate dislocations in them; this is important as shown by the response of graphene transferred on as-deposited Cu films.

Mechanical response of freestanding graphene films:

Another objective of this work was to characterize freestanding graphene beams using the concept of micro tensile testing devices developed at the UCL. In order to do so, a process was developed to fabricate the required devices. Moreover, in order to validate the mechanical quality of CVD graphene produced at the UCL for the purpose of device design, AFM

membrane deflection tests were performed on suspended graphene membranes. This technique was selected due to its simple sample preparation requirements, and due to its accuracy in determining graphene's mechanical properties, being the standard most common mechanical characterization technique to study graphene. AFM loading tests revealed that our graphene is indeed of high quality with a Young's modulus of ~ 1 TPa.

Accommodating graphene in the micro tensile testing devices required a lot of process optimization; from the selection of the sacrificial layer to the optimization of the final release step. In this work, we have shown a proof of concept results of the devices to be used in characterizing 2D materials. However, as has been shown, the yield of the devices is low. Since this type of devices requires a lot of data in order to be able to correctly determine the test material's properties, a low yield is an issue which prevents the complete characterization of graphene. The reasons for this low yield and graphene failure can be divided into three categories:

1. The cracks in graphene even before processing begins resulting from fabrication and transfer;
2. The failure of graphene beams during the release step due to the nature of the process;
3. The issues with the actuator having out of plane bending due to stress gradients developed in the process.

The first issue could be fixed by using Cu films onto which graphene can be directly grown as a sacrificial layer as described in section 8.1.1, however, a better quality actuator with a higher fracture strain than PECVD Si_3N_4 has to be used in order to withstand the stresses developed by the Cu surface growth and large grains after annealing. Alternatively, growing graphene on a single crystal Cu film is a very promising idea. Secondly, the release step has to be further optimized; in this work, we have shown that a good protection of graphene beams during release is mandatory for its success. However, there still remain issues with the manual handling of the released

samples in etchant and rinsing baths. Dry release would be an ideal choice; however, the right conditions have to be selected in order not to damage the graphene structure by the drying gases as in the case of using XeF_2 .

Finally, the issue of stress gradients in the actuator has to be addressed. When using this technique to test bulk materials (e.g: Al, Pd,..etc.), the issues of stress gradients and out of plane bending are not as crucial. This is because of the ability of the sample beams in this case to hold the actuator beams in position and prevent them from bending. However, in the case of graphene or other 2D materials, their bending stiffness is too small, and therefore cannot withstand the out of plane bending of the actuator beams. As explained in section 8.1.2, the patterning of the actuator with HF also plays a role in increasing this out of plane bending. This step can be avoided by reversing the order by which the graphene and the actuator materials are deposited, which would enable etching the actuator material only using plasma. However, this will raise another technical difficulty of transferring graphene onto patterned actuator beams and then processing it. Moreover, even plasma-etched actuator beams show out of plane bending, therefore, an in-depth study of the origins of the stress gradients in PECVD thin films deposited at UCL has to be performed in order to find ways to prevent them from developing. Another possibility would be using these devices in studying multi-layered 2D materials, since as the number of layers increase, the bending stiffness of the beam is also expected to increase, and therefore increasing the chances of the sample beam being able to withstand the out of plane bending of the actuator.

Furthermore, different techniques with easier processing requirements can be explored in order to apply uniaxial load on graphene beams. One promising technique is the Push-to-Pull (PTP) device, which is a MEMS-fabricated device which can be used in conjunction with a pico or a nanoindenter for in-situ mechanical characterization of 2D materials (Lu et al., 2010). Graphene beams can be fabricated and released on a Si frame, and then the Si frame can be placed on the PTP device, where the frame

can then be broken by focused ion beam (FIB), leaving the graphene beam free on the PTP device where a uniaxial load is applied.

Eventually, it would be of great interest to use the micro tensile testing devices technique to study metal-graphene composites. In this work, it has been demonstrated that graphene strengthens the Cu response to plastic deformation; however, the plasticity starts at lower loads due to the low cross-plane stiffness of graphene (section 6.2). Using the micro mechanical testing devices, in-plane loading could be applied on metal-graphene composites to study the effect of graphene's high elastic modulus (confirmed in chapter 7), on the metal elastic and plastic response. It is expected that a significant strengthening would be observed given the ability of graphene to block dislocations movement, and by making use of its exceptionally high in-plane stiffness.

Scientific resume

List of papers

1. M. Hammad, J.-J. Adjizian, C.-H. Sacré, B. Huet, J.-C. Charlier, J.-P. Raskin, T. Pardoen, Adhesionless and near-ideal contact behavior of graphene on Cu thin film, Carbon. 122 (2017) 446-450.
2. M. Hammad, M. Fivel, B. Huet, C. D’Haese, B. Nysten, J.-P. Raskin, T. Pardoen, Single layer graphene controlled indentation plasticity mechanisms in Cu. Submitted.
3. M. Hammad, B. Huet, T. Pardoen, J.-P. Raskin, Design, fabrication and development of on-chip tensile testing devices of suspended graphene beams. Submitted.

Conferences

1. M. Hammad, J.-P. Raskin, and T. Pardoen, “Nano-Indentation of Cu/Graphene Bilayer System”. 14th European Mechanics of Materials Conference - EMMC14, Aug 27-29, 2014, Gothenburg, Sweden.
2. M. Hammad, M. Fivel, C. H. Sacre, H. Idrissi, C. D’Haese, D. Schryvers, B. Nysten, J.-P. Raskin, and T. Pardoen, “Nanoindentation of Cu/Graphene Bilayer System”. 2014 Materials Research Society Fall Meeting & Exhibit, Nov. 30 – Dec. 5, 2014, Boston, Massachusetts, USA.
3. B. Huet, M. Hammad, J.-P. Raskin, “Wafer Scale Transfer of Graphene Grown on Cu Thin Films”. 2014 Materials Research Society Fall Meeting & Exhibit, Nov. 30 – Dec. 5, 2015, Boston, Massachusetts, USA.
4. M. Fivel, M. Hammad, H. Idrissi, J.-P. Raskin, T. Pardoen, “3D Dislocation Dynamic Simulations of Nanoindentation: Application to Cu/Graphene Bilayer System”. 2015 Materials Research Society Fall Meeting & Exhibit, Nov. 29 – Dec. 4, 2015, Boston, Massachusetts, USA.

5. T. Pardoën, M. Hammad, M. Fivel, H. Idrissi, D. Schryvers, C. D'haese, B. Nysten, J.-P. Raskin, "Single Layer Graphene Controlled Indentation Plasticity in Cu". 2016 Materials Research & Society Fall Meeting & Exhibit, Nov. 27 – Dec. 2, 2016, Boston, Massachusetts, USA.
6. M. Fivel, M. Hammad, H. Idrissi, J.P. Raskin, T. Pardoën, "3D Dislocation Dynamics Simulations of Nanoindentation: Application to Cu/graphene Bilayer System". Dislocations 2016, Sep. 19-23, 2016, Purdue University, West Lafayette (IN), USA.

Students supervision

1. Master thesis supervision : Loïc Henneçon. Aug. 2015.
"Graphene resonators: Extraction of mechanical properties"
2. Clean room project supervision. 2013-2015.
"Micro and Nanofabrication Techniques (UCL, cours LELEC 2560)"

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