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Graphene on wrinkled hexagonal boron nitride

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Abstract

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By Simon NIELSEN

Since its discovery in 2004 graphene has quickly become the most studied material of all times, mainly because of its incredible properties. Many believe graphene to be the material of the future that will revolutionize all sorts of technologies. The discovery also started a wide research movement for other two dimensional materials, one of which is hexagonal boron nitride (hBN). This one is of particular interest since it is an ideal substrate for graphene, enhancing its already incredible properties. As any other 2D material neither graphene nor hBN are completely flat because some sorts of corrugations and irregularities simply can not be avoided. To exploit in the best manner possible the potential of these materials it is therefore important to understand the impact of such irregularities. In this thesis we have studied the wrinkling process by thermal treatment of hBN flakes on different substrates. We have tried to understand how these wrinkles can be linked to thermal strain $\epsilon = \alpha \Delta T$ with α the thermal expansion coefficient (TEC) and T the temperature. By applying thermal treatments with different parameters to the hBN flakes, we have proposed a scenario for the wrinkling process that is plausible with our observations, trying to identify the key parameters in the process. We also created stacks of graphene on hBN and of encapsulated graphene between two hBN flakes to study the effect the thermal treatment would have on these stacks. The different samples were characterized by optical microscopy, Raman spectroscopy and Atomic Force Microscopy.

*There is nothing noble in being
superior to your fellow man.
True nobility is being superior to
your former self.*

— Ernest Hemingway

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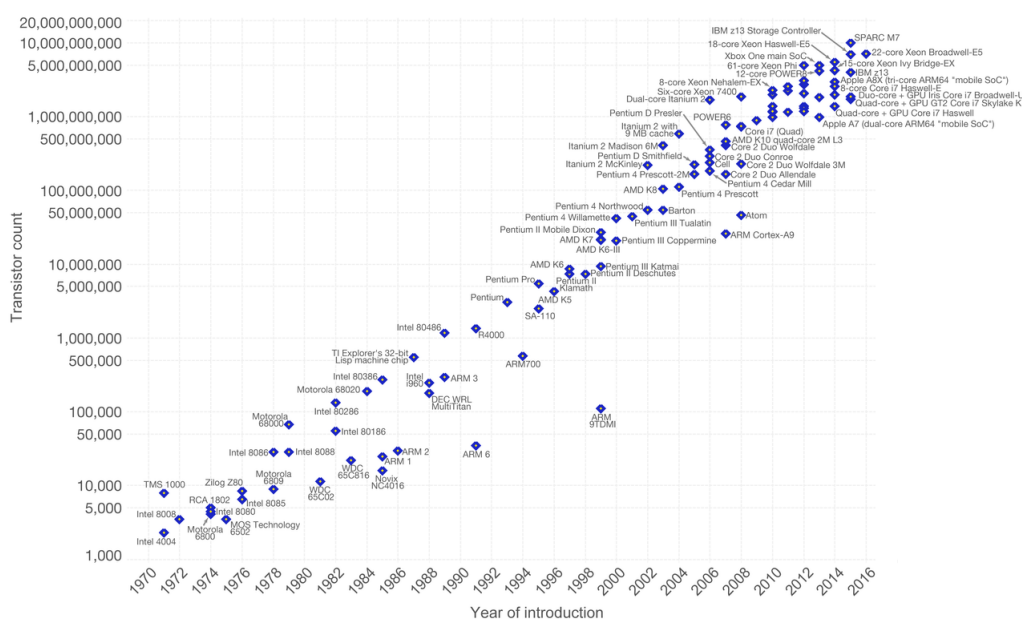
Introduction

In nowadays solid-state physics, great focus is directed towards the emergence of two-dimensional (2D) materials and their astonishing properties. The emergence of many new technologies relies on these materials and some of them are expected to be a real revolution in our modern day world. The domains that will be impacted by these new technologies are numerous but one of those that is the most talked about is probably the one of electronics. Since the 1960's the sector of electronics has been in constant growth so much so that there even has been made a law about it called Moore's law.

Moore's Law – The number of transistors on integrated circuit chips (1971-2016)

OurWorld
in Data

Moore's law describes the empirical regularity that the number of transistors on integrated circuits doubles approximately every two years. This advancement is important as other aspects of technological progress – such as processing speed or the price of electronic products – are strongly linked to Moore's law.



Data source: Wikipedia (https://en.wikipedia.org/wiki/Transistor_count)

The data visualization is available at [OurWorldinData.org](https://ourworldindata.org). There you find more visualizations and research on this topic.

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Figure 1.1: Moore's law [1]

In today's society it has become very difficult to imagine a world without electronic devices as our smart phones, our computers or our tablets which are all devices we use on a daily basis. But it has not always been like that and one of the events that instigated the revolution of electronics was the invention of transistors in the 1940's. Their inventor even received the 1956 Nobel Prize of physics. The transistor is the fundamental building block of modern electronic devices. It consists of a semiconductor material that is used to amplify and/or switch electronic signals and electrical power. It was quickly discovered that a great number of transistors could fit on one single electronic chip in what is called integrated circuits. Then, progress in the electronics field became the downsizing of transistors in order to fit as many transistors as possible on a single chip so that devices would become both

smaller and more powerful. It was then observed by Gordon Moore in 1965 that the number of transistors per chip doubled every year which he corrected to every 18 months afterwards. This is called Moore's law. A graph depicting the evolution of the number of transistors per chip is shown in Figure 1.1. As can be seen, the prediction of Moore's law is pretty accurate and it has actually dictated the evolution of electronic devices for the last 50 years by fixing the expectations of the industry. The problem being that the size of silicon transistors is beginning to reach a minimum and it will therefore no longer be possible for the electronics sector to continue its growth which many believe would have a huge negative impact on our modern society and economy. This is why it is necessary to find new materials to develop smaller types of transistors and that is where the new 2D materials come into play and could have an important role in the upcoming years.

The domain of electronics is of course only one example of the potential usefulness of 2D materials but there are countless others such as medicine, addressing the modern days environmental issues, biosensors, energy storage, composite materials,... The fact is that these materials are numerous, that they have a lot of interesting properties and that they can often be combined to optimize these properties. This is why they are an important subject of studies in nowadays science.

In this thesis we will devote our attention to two materials that are hexagonal boron nitride and graphene. We will be interested in one particular phenomenon which is the appearance of wrinkles at the surface of these materials under specific conditions. The reason why we are going to try to understand this phenomenon is that it might have an important impact on the properties of the materials and that such corrugations are very difficult to avoid in 2D materials. It is therefore important to understand this kind of irregularities of the materials if they are to be used in futur technological advances. We will first introduce the two materials and their properties before explaining different ways wrinkles can appear at their surface and discuss how the properties can be affected by strain induced by these wrinkles. Based on our observations and on previous works on the matter we will then suggest a scenario for the wrinkling process and try to highlight the different parameters that are essential to it.

State of the art

We will start off this thesis by describing the two dimensional materials we have used and the Van der Waals heterostructures that can be made out of these. Then we will show different ways for wrinkles to appear in both materials and describe existing models that have been made to explain the wrinkle formation. Finally we will say a few words on the effects that strain in a graphene sheet can induce as this is what has motivated this thesis.

2.1 Structures

Two-dimensional crystals

Sometimes also referred to as single-layer materials, 2D materials are crystalline materials consisting of a single layer of atoms. These are called the elemental 2D materials and they can be combined to form multilayer 2D materials often called van der Waals heterostructures. Even though the latter are not two-dimensional per se, their characteristics and properties are similar to the ones of 2D materials which is why they are considered as being part of that family. We will explore these structures further on in the next section.

The reasons why this kind of materials are of great interest are numerous. First of all they have uncommon mechanical properties due to their 2D crystal structure including high in-plane stiffness and strength but extremely low flexural rigidity. Just like thin membranes, they may be deformed by out-of-plane bending or by in-plane stretching which make their elastic properties include both in-plane and bending moduli.[34] On the other hand the inelastic mechanical properties of these materials such as strength and toughness depend strongly on the presence of defects or impurities and how those evolve during deformation.

Secondly, since 2D materials have the largest surface to volume ratio of any type of materials, surface forces like friction and adhesion are expected to play an important role in the manipulation of 2D materials. A great amount of researches have been carried out to try to measure those interfacial properties. We won't go into details about these here but a rather complete review is to be found in [34].

All the interest around those types of material really started with the discovery of graphene by Andre Geim and Konstantin Novoselov in 2004.[35] This was not of course the first time graphene was discussed since it had been theoretically predicted already in 1947 but it was the first time anyone actually managed to create a graphene sheet. The discovery even got the two scientists the Nobel Prize in 2010.

Simply put, graphene is a monoatomic layer of carbon and thus the thinnest material known to mankind with a thickness of only 0.07 nm, the average diameter of a carbon atom. It has an hexagonal structure with bond lengths of 0.142 nm which is shown in the left pannel of Figure 2.1. It is also important to know that it can be made into various forms and shapes. The most used ones are the ones that can be seen in Figure 2.1 on the right. We see a simple graphene sheet, a few graphene layers forming graphite, a carbon nanotube and a fullerene molecule. In this thesis we will only be interested in graphene sheets and graphite.

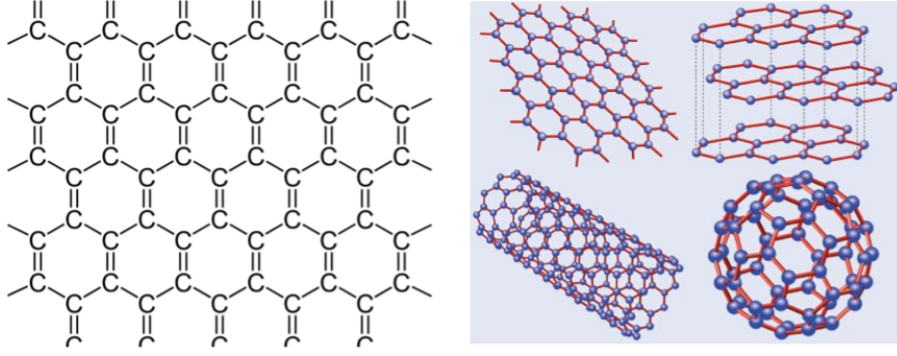


Figure 2.1: The structure of graphene [2] and different examples of shapes given to graphene [3]

Since its discovery, graphene has become the most studied 2D material and it seems to be the one with the most incredible properties. The electrons travelling in graphene behave as massless Dirac fermions and are described by a two-dimensional analogue to the Dirac equation rather than the Schrödinger equation. This explains its very particular dispersion relation $E = \hbar v_F |\vec{k}|$ where E is the energy, v_F the Fermi velocity and $\vec{k}$ the wavevector. The dispersion relation is illustrated by the famous Dirac cone given in Figure 2.2a. It is considered a zero-gap semiconductor since its conduction and valence bands meet at the Dirac point, located at the edge of the Brillouin zone as we see in Figure 2.2a. and b. The carrier density at the Dirac point is non-existent but the carrier mobility will still be high even though the density has vanished. The carrier mobility exceeds $15\,000\text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$ at room temperature which is quite remarkable. Graphene also exhibits an excellent thermal conductivity of approximately $5300\text{ W.m}^{-1}.\text{K}^{-1}$ and an exceptional strength with a Young's modulus of 1 TPa. More detail about the properties of graphene can be found in [34] and [36].

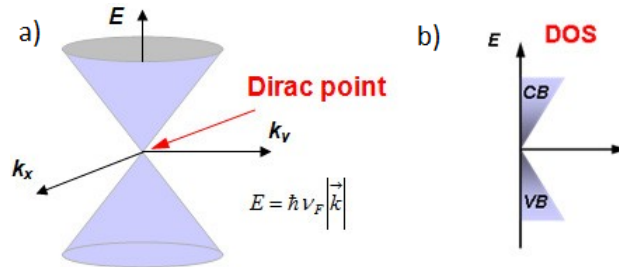


Figure 2.2: Illustration of the Dirac cone (a.) and the density of state (b.) of graphene [4]

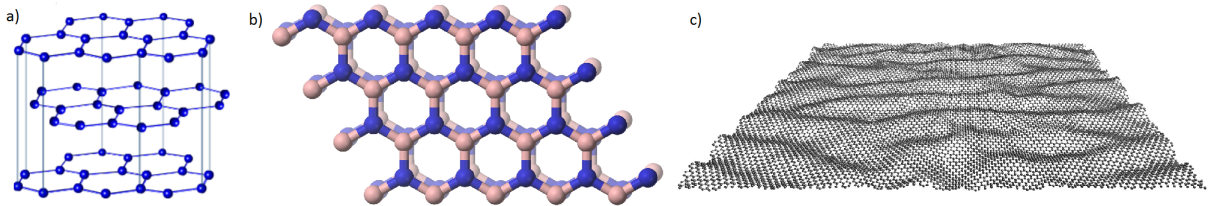


Figure 2.3: **a.** Illustration of a graphite flake composed of three graphene sheets. [5] **b.** Cartoon of two hBN layers held together by adhesion forces. The blue spheres represent boron atoms while the pink spheres are symbolizing the nitrogen atoms. We see that the boron atoms of one layer align with the nitrogen atoms of the other layer and vice versa. [1] **c.** Modelization of the actual topography of a so-called "perfectly flat" two-dimensional graphene layer. [6]

Another important 2D material is the hexagonal boron nitride that we will further refer to as hBN. It is the most stable crystalline form of boron nitride and it has a layered structure just as graphite. In each layer, the boron and nitrogen atoms are held together by covalent bonds while the layers

are bound by cohesive forces. Van der Waals forces seem to play an important role in the interlayer adhesion but other phenomena like surface roughness and water capillarity also intervene [34]. Unlike graphene, hBN is a wide band gap semi-conductor which actually makes it more of an insulator. hBN shows great thermal stability with a melting temperature of 2973°C and a noteworthy property of hBN is its negative thermal expansion coefficient of $\alpha = -2,7 \cdot 10^{-6}/^{\circ}\text{C}$. This particular characteristic will reveal itself as essential within the work frame of this thesis. An illustration of three-layered graphite and of bilayered hBN can be seen in Figures 2.3a and b respectively. An interesting detail is the fact that the boron atoms of one layer align with the nitrogen atoms of the other layer and vice versa.

As we have described them, 2D materials seem completely flawless and it all sounds a little too good to be true. Sadly it is. In fact, no material is a 100% flat not even graphene. The surfaces of 2D materials are actually filled with different sorts of corrugations. The sheets are buckled, wrinkled, crumbled or all of those at the same time. An example of what a real graphene sheet looks like is given in Figure 2.3c. These corrugations have important consequences since they are able to modify the properties, mechanical as well as electronic, of the 2D materials. In the case of graphene for example these irregularities can act as doping defects and charged impurities leading to Dirac points deviated out of the Brillouin Zone. The corrugations can also lead to suppression of electron transport, mobility and weak localization and they may create a band gap in the electronic structure changing graphene into a semi-conductor. [12] From a mechanical point of view, the elasticity, the strength and the surface properties might be altered as well. All these possible changes due to corrugations are the reason why it is important to study their effect and, since they can't be avoided, we have to understand how the different corrugations are created in an attempt of controlling them eventually.

Van der Waals heterostructures

An important concept to master in order to understand the following chapters are the van der Waals heterostructures. As we briefly mentionned, there are many different two-dimensional crystals besides graphene and a way of investigating them is to create heterostructures. To put it simply, these structures are made by stacking different two-dimensional crystals as can be seen in Figure 2.4 that shows an example of a van der Waals heterostructure made by stacking 5 different monolayer materials. This process is often compared to building with Lego blocks and it has been shown that these atomic scale Lego works exceptionnaly well. In fact, strong covalent bonds insure the stability of the obtained stack whereas weaker van der Waals forces are sufficient to hold the layers together, which also explains the name of the heterostructures.

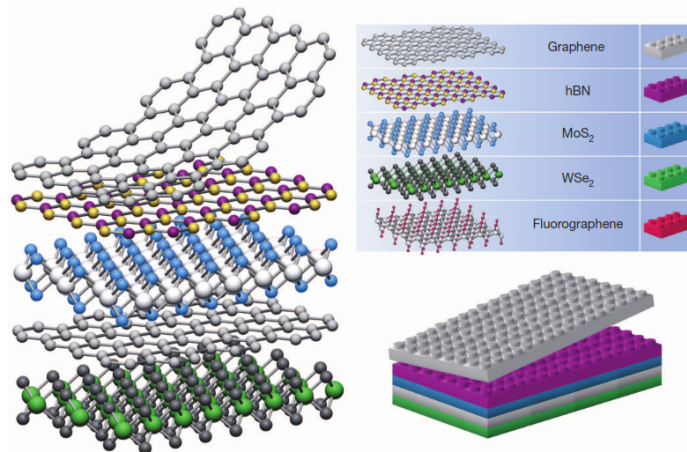


Figure 2.4: Example of a van der Waals heterostructure. It is illustrated how layers of different materials can be stacked onto each other as building blocks for a new structure. [7]

It is worth noting that far from all the van der Waals heterostructures that can be imagined will actually survive if created. Still, the creation of heterostructures are an important tool to study the materials involved in the stacks. The example that interests us here in particular is the stacking of monolayer graphene onto a thin hBN crystal.

It has been found [8] that the hexagonal boron nitride has an extremely smooth surface with very little dangling bonds and charge traps (compared to silicon oxide, in particular). This means that when graphene is exfoliated or transferred onto hBN, the number of scattering points due to the contact is almost non-existent, so that one can in theory reach "quasi-epitaxial" situations, where the graphene crystal lattice is not perturbed by the lattice of the underlying substrate. Furthermore, hBN has a lattice constant and a crystal structure which are similar to the ones of graphene (1.7% mismatch). All this means that by exfoliating it or transferring it onto hBN, it is possible to achieve high quality graphene with properties that are not limited by the contact with the substrate. In [8] the authors report on a mechanical transfer technique illustrated in Figure 2.5. The results obtained when measuring the resistivity in their device is given in Figure 2.6.

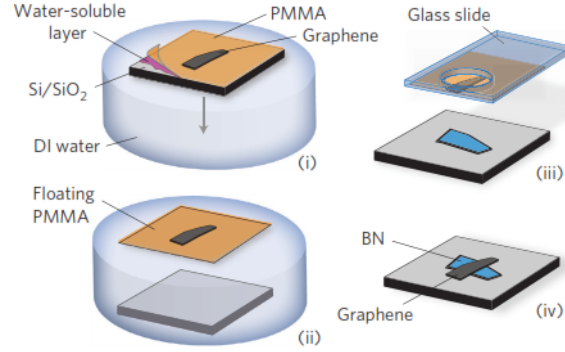


Figure 2.5: Illustration of mechanical transfer of graphene onto hBN. **i.** A graphene sheet is exfoliated onto a polymer stack including a water-soluble layer and a PMMA layer. The device is then floated on the surface of a deionized water bath. **ii.** The water-soluble polymer dissolves and the Si/SiO_2 substrate sinks to the bottom of the bath. **iii.** The PMMA membrane is adhered to a glass slide. Then by using an optical microscope, the positions of the graphene sheet and the hBN flake of interest are located. **iv.** The graphene and hBN sheets are precisely aligned and the two can be brought into contact. [8]

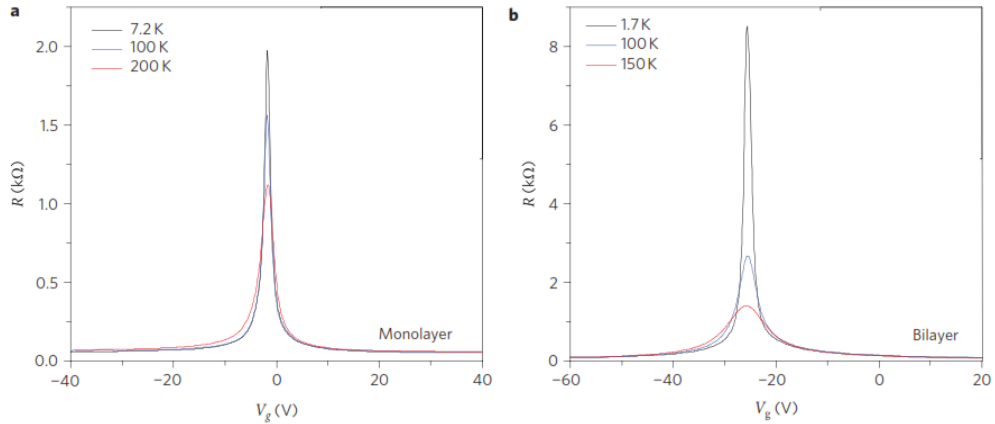


Figure 2.6: Resistance of graphene monolayer (**a.**) and bilayer (**b.**) sheets on hBN as a function of back gate voltage V_g and temperature [8]

Graphene is first exfoliated onto a polymer stack consisting of a thin layer of PPMA and a thicker Si or SiO₂ layer separated by a water-soluble layer. This device is then floated on the surface of deionized water as illustrated in Figure 2.5i. Once the water-soluble layer dissolves, the Si/SiO₂ wafer sinks and we obtain a floating PMMA layer as in Figure 2.5ii. The PMMA membrane is then adhered to a glass slide shown in Figure 2.5iii and by using an optical microscope to locate the graphene flake on the suspended polymer film, it is possible to align the graphene sheet and the target hBN flake and finally place the graphene within a few micrometers of the target position. During this transfer process, the target substrate is heated at 110°C in order to eliminate any water adsorbed to the surface of either the graphene or the hBN flake. The heating also facilitates a good adhesion between the PMMA and the substrate. Once the transfer is done, the PMMA is dissolved using acetone and the obtained result is shown in Figure 2.5iv. To perform measurements, one will then have to place electrical contacts on the sample by using standard electron beam lithography. Finally, the sample is annealed in flowing H₂/Ar gas at 350°C in order to remove any residue and obtain as clean samples as possible.

Figures 2.6a and 2.6b display the resistance in a typical monolayer or bilayer graphene sheet respectively. Here the resistance is a function of backgate voltage V_g and temperature. In both cases, the resistivity peak is extremely narrow, especially at low temperatures, and occurs at nearly zero gate voltage. This indicates that the transferred graphene on hBN device hosts a two-dimensional charge carrier system of high quality. Furthermore, the obtained mobility in monolayer graphene is $\mu_C \sim 60000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is three times better than graphene-on-SiO₂ devices. In the case of bilayer graphene, the mobility was found to be comparable to the best suspended graphene devices and almost an order of magnitude greater than bilayer graphene on SiO₂. Further detail on these results can be found in [8].

The quality of these results confirms that hBN has revealed itself as an ideal substrate for the study of electronic properties in graphene. In fact, the average length an electron can travel freely in a given material is defined as the *mean free path*

$$l = \mu \frac{h}{2e} \left(\frac{n}{\pi} \right)^{1/2} \quad (2.1)$$

where μ is the carrier mobility, n the carrier density, h is Planck's constant and e the electron charge. This means that if the carrier mobility in a graphene sheet is good enough, the mean free path of the electrons can become greater than the dimensions of the sample. In that case, the movement of the electrons will simply obey classical mechanics and will no longer be diffused by impurities or other forms of imperfections. Such electronic behaviour is called Ballistic Transport (illustrated in Figure 2.7b) in opposition to the more common Diffusive transport shown in Figure 2.7a. To summarize, one can easily obtain ballistic transport in graphene which greatly facilitates the detection of charged particles since it is way easier to control the electronic paths. To do so, one could for example use magnetic focusing in order to control an electron beam in a graphene sheet. This has been done in [37] and [38].

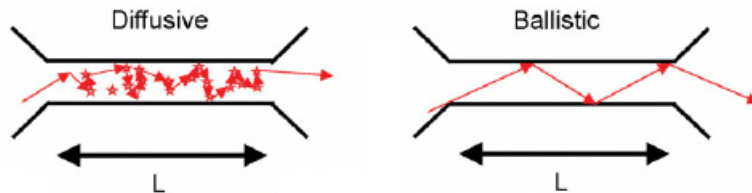


Figure 2.7: Illustration of the difference in electronic movement between diffusive (a.) and ballistic (b.) transport [9]

This being said, we can go back to the importance of the morphology of the substrate on which graphene is exfoliated which is probably the most important parameter in view of optimizing the charge carrier mobility. Tuning the h-BN substrate morphology also offers a new lever arm that can

be used to fine-tune all the charge carrier parameters in the transferred layer (e.g. : strain in graphene can also be used to open a bandgap, which is desirable in some cases). In this work, the starting point was to study the effects of wrinkles in a graphene sheet on its properties. To do so we decided to create stacks of graphene on hBN then to create wrinkles in these stacks. The advantages being firstly that the properties of the graphene sheet will be optimal when it is deposited on hBN and secondly that it is possible to create controlled wrinkles in hBN using a thermal treatment as we will explain in the next sections.

2.2 Wrinkles in two-dimensional structures

Wrinkles in graphene

Even though graphene seems to be the new miracle material it is not perfect and irregularities in a graphene sheet are inevitable. Ripples and wrinkles are most certainly part of the reality of graphene and these are expected to have a strong influence on the electronic properties by inducing effective magnetic fields and changing local potentials. [11] These effects will be described in detail further on. It is however possible to try to control the formation and orientation of such corrugation as it has been shown by [11].

To do so they used suspended graphene as schematically shown in Figure 2.8. The substrate in blue has been dissolved where the metallic contacts in red did not protect it, leaving only the graphene to create a bridge between the two gates. This of course represents the theoretical form of suspended graphene that one hopes to achieve even though the end result rarely looks so perfect.

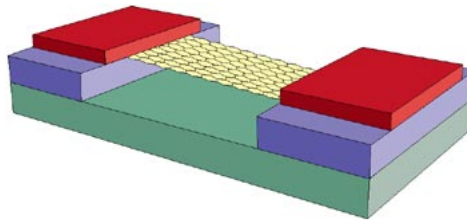


Figure 2.8: Suspended graphene. Metal electrodes (red) contact a single graphene sheet (yellow) that is fully suspended over a silicon substrate (green). The spacer layer (blue) would have been etched away locally. [10]

It was observed that periodic ripples appeared at the creation of the suspended graphene sample. These ripples can be caused both by longitudinal tensile strain and by in-plane shear strain and it was shown that they can be produced by applying a thermal treatment to the graphene membranes. This suggests that the ripples in graphene can be controlled and used in strain-based electronics. When the samples of suspended graphene are annealed from room temperature to 600°K then cooled back down to room temperature a certain pattern in their behaviour can be observed. This can be seen in Figures 2.9a which show Scanning Electron Microscopy (SEM) images of a suspended graphene membrane at different stages of the annealing process.

We see that at 600°K the graphene sheets seem flat and then when the samples are cooled down the ripples appear. Some of the membranes also experience a longitudinal buckling effect as in Figure 2.9c where the graphene sheet seems to have sagged down towards the substrate after the annealing. In [11] they showed that the amplitude of the ripples were depending on the maximum annealing temperature as shown in Figure 2.9b which therefore gave them a way of controlling the rippling effect.

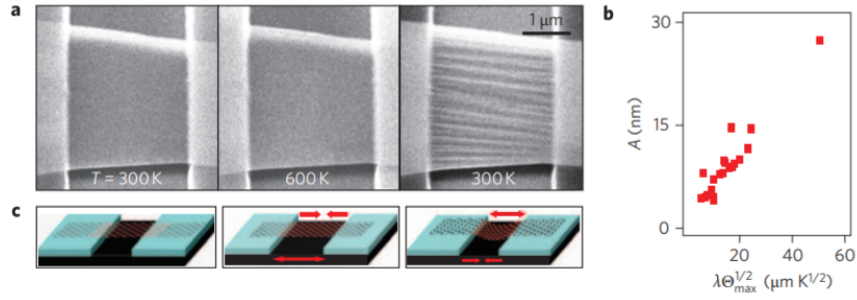


Figure 2.9: **a.** A graphene sheet before, during and after annealing at 600°K. **b.** Amplitude of the wrinkles dependence on maximum annealing temperature. **c.** Cartoon of a suspended graphene sheet before, during and after annealing at 600°K.[11]

But this is only one of many ways in which wrinkles can be created in a graphene sheet. While most of them are natural, the formation of wrinkles can also be stimulated by various mechanisms. Let's first devote our interest to the naturally occurring corrugations.

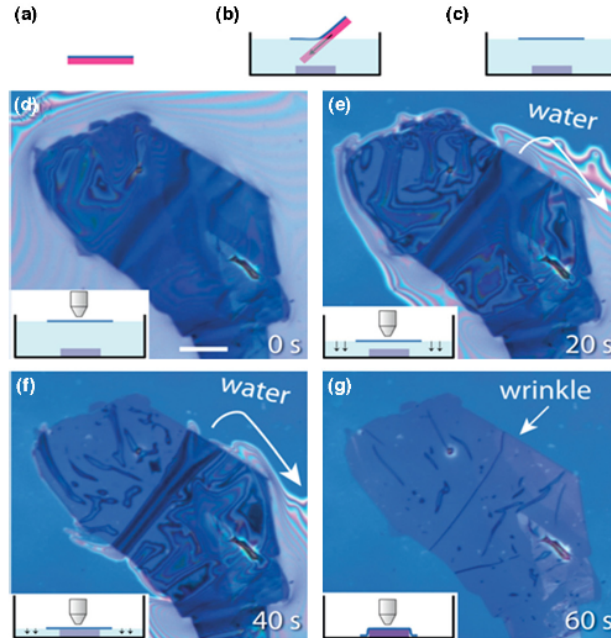


Figure 2.10: Wrinkles formation under wet transfer process. **a.** A graphene sheet (blue) on its original substrate (pink) and covered by a polymer. **b., c.** Removal of the polymer-graphene film from first substrate. The film then floats on water above the second substrate. **d-g.** Wrinkle formation during the transfer seen through an optical microscope. One can see that as the water is drained from the interface between the graphene sheet and the new substrate it creates corrugations that serve as water drain channels. Once all the water is drained the remaining corrugations form the wrinkles. The insets in **d-g.** show the evolution of the graphene-substrate separation distance. [12]

The first mechanism that leads to wrinkles is typically the transfer process from the metal on which the graphene is grown onto the silicon substrate used to support the graphene sheet afterwards. To realize such a transfer, one usually has to start by depositing a layer of polymer onto the graphene-on-metal in order to protect the graphene. This can be done by spin-coating the polymer on the sample. The metal catalyst is then dissolved before transferring the graphene sheet onto the desired substrate before dissolving the polymer.[12] This is shown in Figures 2.10.a-g. Since this is a wet transfer technique, the liquid between the graphene and the substrate will have to be drained. This is very important for the formation of wrinkles because these will form along the liquid drain

channels. Once again, this can be observed in Figure 2.10.

Another way for the wrinkles to form lies within the growth of graphene itself in a chemical vapour deposition process (CVD). CVD is a chemical process usually used to create thin solid films on a substrate by a chemical reaction of vapour-phase precursors. We won't go into the details of the technique but a complete overview can be found in [39]. What's important to remember is that the substrate is heated during the deposition because it helps reduce unwanted gas-phase reactions that can lead to particle formation. This also means that once the deposition is over, the substrate will have to cool down. It is during this cooling phase that wrinkles might appear.

In this case, the wrinkles essentially originate from the high temperatures used in the CVD technique and from the fact that the thermal expansion coefficients (TEC) of graphene and the substrate on which it is grown are very different. There is also an important contribution from the non-ideal substrate surface : usually, laminated foils are used for graphene growth, with large corrugations coming from the lamination process, as well as from the copper foil microstructure (grains and crystalline defects). In particular, when graphene is grown on a metallic substrate, chances are high that one will be able to observe high densities of wrinkles because the TEC of graphene is negative while the TEC of metals is positive. This means that when the graphene-on-substrate is cooled down in the last step of the CVD process the graphene will be expanding while the substrate will tend to shrink which results in the formation of wrinkles as illustrated in Figure 2.11a. It has been observed though [12], that in this process, wrinkles only seem to appear along one of the axis while along the other axis the graphene simply bends as in Figure 2.11b. In Figure 2.12a one can observe an image of such wrinkled CVD grown graphene obtained with an Atomic Force Microscope (AFM) and Figure 2.12b displays the topographic profile corresponding to the red line in Figure 2.12a. This kind of height profile is a powerful tool in the characterization of wrinkles and the calculations of their aspect ratio.

It is important to notice that this kind of wrinkle formation can also occur in an epitaxial graphene growth on silicon as this process also uses high temperatures and therefore the graphene will tend to expand during the cooling phase of the process.

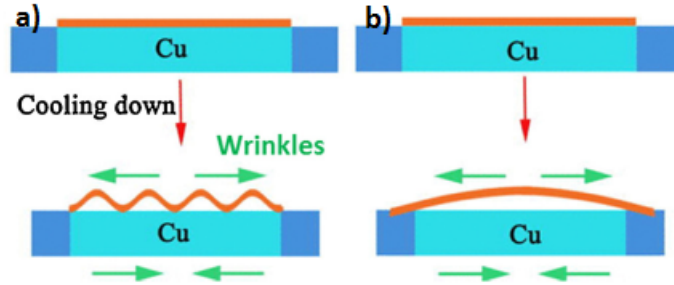


Figure 2.11: Formation of wrinkles in the cooling down process of CVD grown graphene. The wrinkles form in the x -direction (a.) while the graphene sheet simply bends in the y -direction (b.) [12]

Finally, the morphology of the substrate on which graphene is transferred can strongly affect its properties but can also lead to the formation of wrinkles. An example is shown in Figure 2.13. In this case, a thin graphite flake (14nm) has been transferred onto a $\text{In}_{0.75}\text{Ga}_{0.25}\text{As}$ substrate (inset of Figure 2.13) and linecuts have been made in the substrate as well as in the graphite flake to see the topological profiles of both. As we can see, the graphite tends to follow the morphology of the substrate and at some points the irregularities of the substrate are even magnified in the morphology of the graphite flake. Even though this example is using a graphite flake, it has been shown [14] that a simple graphene sheet and few-layer graphene (FLG) sheets act the same way when transferred onto a substrate.

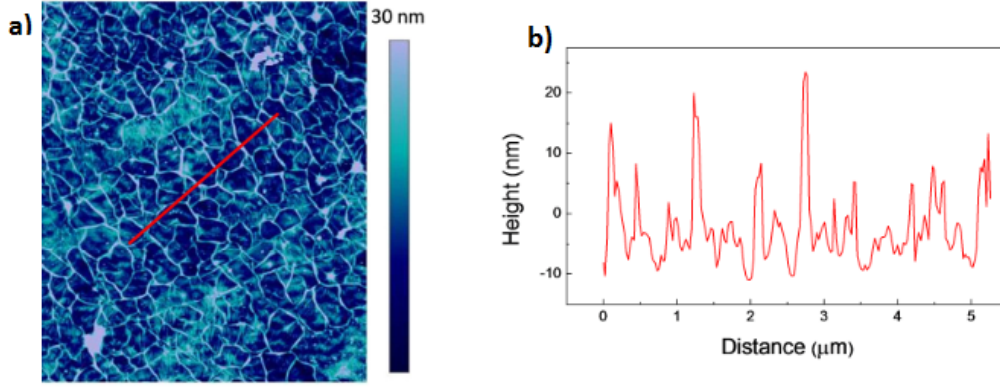


Figure 2.12: AFM image of a wrinkled graphene sheet after a CVD process. The profile in **b.** follows the red line in **a.** [13]

This phenomenon will be of the uttermost importance in this thesis. In fact, the goal is to study graphene transferred onto wrinkled hexagonal boron nitride (hBN) and study the wrinkles thereby created in the graphene as well as the electronic properties of the wrinkled graphene. We will therefore first try to understand the wrinkle formation in hBN.

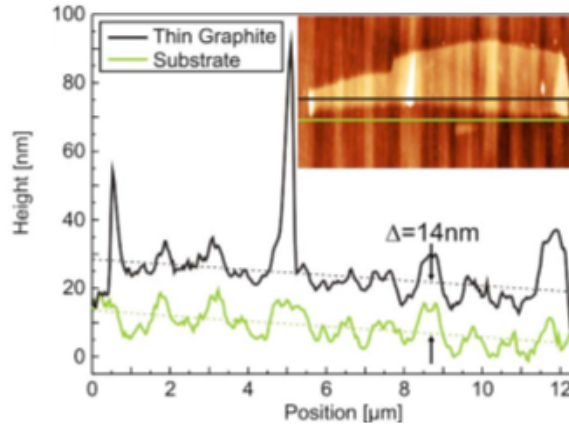


Figure 2.13: Linecuts through a thin (14nm) graphite flake and the substrate on which it has been transferred ($\text{In}_{0.75}\text{Ga}_{0.25}\text{As}$). The inset is an AFM image of the graphite flake. [14]

Wrinkles in hBN

The wrinkles in hBN flakes can be created just as the wrinkles appearing in CVD grown graphene. The thermal expansion coefficient (TEC) of hBN is positive along the c-axis while it is negative in the plane contacting the silicon substrate. By annealing the hBN-on-substrate one then expects a flattening of the hBN flake as the sample is heated but when it cools down afterwards the substrate applies a tensile stress on the hBN flake which causes it to form wrinkles. Here lies the main difference between the wrinkles created in graphene and in an hBN flake. While the wrinkles in graphene only appeared in one direction of the plane, those in an hBN flake form origami-type structures as shown in Figure 2.14. This type of junctions formed between wrinkles will be called origami-type junctions following the name given in [15].

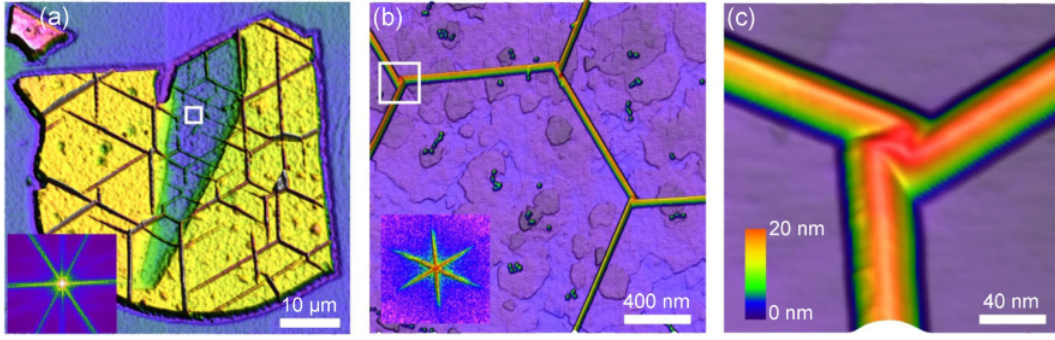


Figure 2.14: AFM images of an hBN flake after Rapid Thermal Annealing (RTA). **b.** and **c.** are zoomed images of the white square in **a.** and **b.** respectively. The insets in **a.** and **b.** are the FFT images of the flake topography. [15]

The h-BN flakes that were used to obtain the results shown in Figure 2.14 were prepared by standard mechanical exfoliation, using commercial hBN powder (Sigma-Aldrich). The exfoliated flakes were transferred onto a doped Si substrate with a thin layer (300 nm) of silicon oxide on top, and annealed at 1,000°C for 25 minutes in a quartz tube. The heating and cooling rates for crystallographic wrinkle production were 50 and 8°C/min, respectively. AFM characterization of the samples was carried out on Bruker MultiMode 8 and Park XE-70 microscopes operating in PeakForce and intermittent contact modes, respectively. [15]

After discovering this kind of wrinkle patterns, the researchers asked themselves whether or not the orientation of the wrinkles had anything to do with hBN lattice. To test this, they employed a procedure of decoration of the hBN lattice with self-assembled octadecylphosphonic (OPA) molecules. The basic idea of the procedure is that by letting the OPA molecules self-assemble (under certain conditions) on top of an hBN flake they should form ripples oriented along the armchair direction. Further details on the technique can be found in [15]. In Figure 2.15 we see the resulting AFM phase image of an annealed hBN flake decorated with self-assembled OPA molecules. The wrinkle, in red, clearly exhibits an origami-type junction and the ripples created by the OPA molecules can easily be identified as the black lines covering the image. The inset in Figure 2.15 is a Fast Fourier Transform image that reveals the 5nm periodicity of the OPA ripples expected from theoretical calculations. [15] Since the ripples are parallel to the wrinkle in the lower right of the image and since they are theoretically oriented along the armchair direction, so should this wrinkle. Furthermore, the armchair structure has a C_3 symmetry and so do the threefold wrinkle junction which means that the two other wrinkles forming the junction also are in the armchair direction. Same goes for the ripples in the upper left part of the image since they form a 120° angle with the dominant ripple domain.

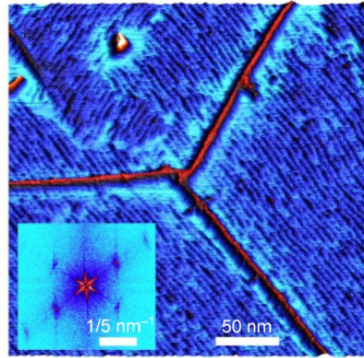


Figure 2.15: AFM phase image of an annealed hBN flake decorated with self-assembled OPA molecules. The inset is the FFT image of the topography of the flake. [15]

When they found these crystal oriented wrinkles with origami-type junctions, the authors of [15] also developed a model to explain their formation. It is pictured in Figure 2.16. A schematic of a possible origami-folding pattern is shown in Figure 2.16a. The black lines indicate regions in which wrinkles may form and their junctions form triangles that are considered as the unit cell of an origami pattern while the shaded zone indicates three wrinkles forming an origami junction. The smallest unit cell possible is the one shown in Figure 2.16b. that we will call the b-cell but as shown in Figures 2.16c. and d., the origami pattern unit cell can be composed of multiple b-cells and have a variety of sizes. This model predicts origami pattern of many different heights and widths. Figure 2.16e. shows an origami pattern using the b-cell as unit cell which makes it the smallest wrinkle origami possible. To put it in another way, this model predicts crystallography oriented size-scalable wrinkles combined by origami junctions which describes the experimental AFM images obtained in Figure 2.14 pretty accurately.

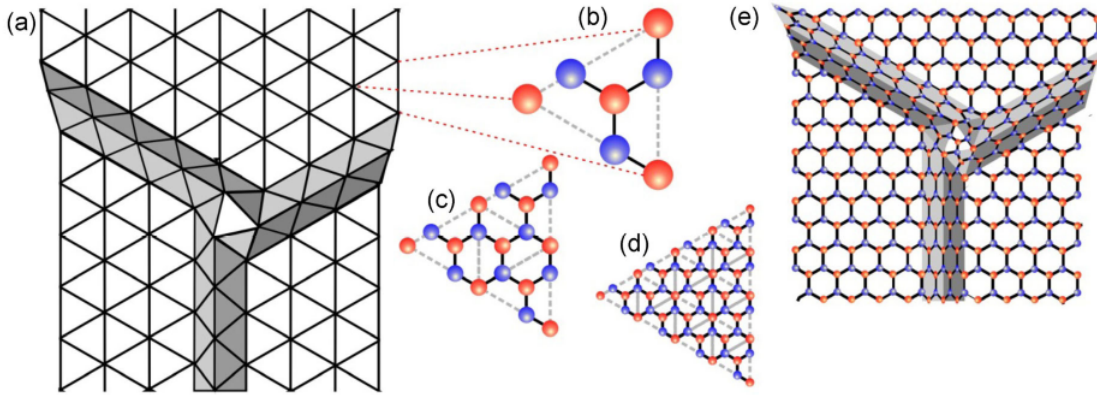


Figure 2.16: Model for origami-type junctions in annealed hBN. **a.** Schematic image of the proposed folding of an hBN flake. **b.**, **c.** and **d.** Different sizes of the triangular unit cell of the model. **e.** Illustration of proposed model for the smallest possible origami-type junction. [15]

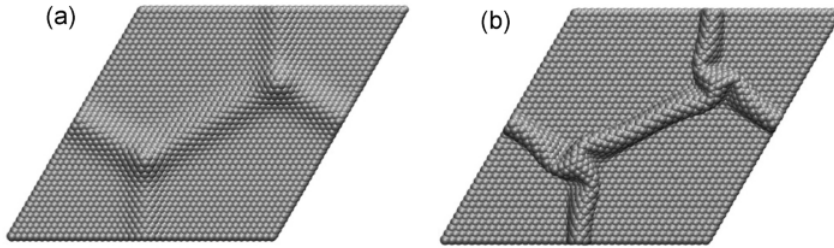


Figure 2.17: Molecular dynamic simulations of wrinkle formation. The simulation starts from a single biaxially compressed hBN layer (**a.**) on top of unstrained layers. After 120 ps, the final stable wrinkle structure (**b.**) is obtained. One can easily observe the symmetry breaking between the initial and final states of the wrinkles. [15]

To test the validity of the model, they carried out molecular dynamics simulations using a periodic supercell approach. A honeycomb lattice formed by a shallow ripple was used as initial condition (Figure 2.17a.). The height of the wrinkles then increases as their shape is modified and the strain in the planar part of the hBN is gradually relaxed. After approximately 120 ps the final form of the simulation is obtained as shown in Figure 2.17b. Once again the origami structure as described in the experimental results and in the model is obtained. It is noteworthy though that there is a break of symmetry between the initial and the final structure of the simulation. In fact, as both cases have C_3 symmetry, only the initial image also has mirror symmetry along the large diagonal of the

junction. This symmetry is broken by the simulation and can't be found in the final junction. But as the symmetry of the experimental junctions is also C_3 without the mirror symmetry, the simulation matches the experimental results perfectly which tends to indicate that the model is correct.

2.3 Mechanical models

Here we will present a couple of analytical models that proceeds to explain the wrinkling of a 2D material under compressive strain.

Atomic-based continuum theory

This first model proceeds to explain wrinkling through a numerical simulation using an atomic-based continuum theory. One major issue in the practical use of wrinkled graphene is to determine the locations of said wrinkles. This model also proposes a way of controlling the location of wrinkles based on the idea that there exist patterns of weaker graphene-substrate adhesion and that the wrinkle network geometry can be traced back to those patterns.

The model considers a $500 \times 5000 \text{ nm}^2$ graphene sheet supported by a substrate undergoing lateral deformation as shown in Figure 2.3.

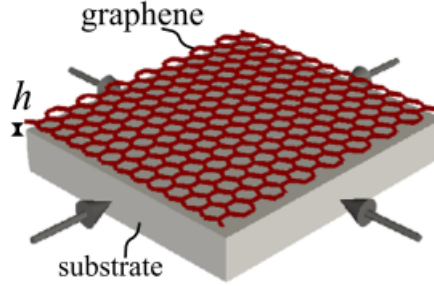


Figure 2.18: Simulated graphene sheet (red) on silicon substrate (grey). The arrows indicate the lateral deformation and h is the graphene-substrate distance. [16]

In this continuum theory model, the graphene is described by a surface parametrization given by

$$\vec{x}(u, v) = (x(u, v), y(u, v), z(u, v)) \quad (2.2)$$

and the elasticity of the modelled graphene is described by an hyper-elastic potential $W(\vec{C}, K)$ where $\vec{C}$ is the in-plane strain and K is the curvature of the surface. This leads to a total elastic energy

$$U_{el}(\vec{x}) = \int_{\Omega_0} W(\vec{C}, K) dS_0 \quad (2.3)$$

where S_0 is a reference stress-free planar state.

To apply strain they then reduce the lateral dimensions of the substrate by λ_x and λ_y so that the normalized total area of the substrate becomes

$$\epsilon_c = 1 - \lambda_x \lambda_y. \quad (2.4)$$

In the simulations, they apply strain incrementally by using an iterative process in which λ_x and λ_y becomes $\lambda - x, k = (\delta\lambda_x)^k$ and $\lambda_y, k = (\delta\lambda_y)^k$ where $\delta\lambda_x$ is the incremental stretch ratio along x . The equilibrium configuration at step $k + 1$ can then be derived by modifying the previous equilibrium configuration $\vec{x}_k(u, v)$ using $(\delta\lambda_x x_k(u, v), \delta\lambda_y y_k(u, v), z_k(u, v))$ in order to define an initial step consistent with the boundary conditions. [16]

Once the graphene and the strain are modelled, one has to take into account the interaction between the graphene sheet and the substrate. First one has to consider the total adhesion energy given by

$$U_{adh}(\vec{x}) = \int_{\Omega_0} \nu(z) dS_0 \quad (2.5)$$

where $\nu(z)$ is the non-bonded adhesion energy density per unit surface and can be expressed as [16]

$$\nu(h) = -\gamma \left[\frac{3}{2} \left(\frac{h_0}{h} \right)^3 - \frac{1}{2} \left(\frac{h_0}{h} \right)^9 \right] \quad (2.6)$$

where γ is the adhesion energy and h_0 is the equilibrium separation.

Two key parameters in this model will be to model stripes of weaker adhesion and describe dry friction between graphene and substrate. The stripes will be used to control the wrinkle patterns and can be described by modulating the adhesion energy

$$\gamma(x, y) = \bar{\gamma} \left(1 - e^{-dist(x, y; l)^2 / c^2} \right) \quad (2.7)$$

where $dist(x, y; l)$ is the distance between a point (x, y) and the closest line in the weaker adhesion pattern l and c is fixed at 1 nm.

The other interaction between graphene and substrate to take into account is the tangential force that is modelled as dry friction. The work of friction then takes the form [16]

$$U_{fr, k}(\vec{x}) = \int_{\Omega_0} \tau_0 \kappa(s_k(u, v)) dS_0 \quad (2.8)$$

where τ_0 is the interfacial shear strength, s_k is the incremental lateral sliding relative to the substrate

$$s_k^2(u, v) = [x - \delta \lambda_x x_k(u, v)]^2 + [y - \delta \lambda_y y_k(u, v)]^2 \quad (2.9)$$

and $\kappa(t)$ is a differential approximation to $|t|$ such that

$$\kappa(t) = \frac{1}{\beta} (e^{\beta t} + e^{-\beta t}), \quad \beta > 0. \quad (2.10)$$

As $\beta \rightarrow +\infty$, $\kappa(t) \rightarrow |t|$ but in the calculations they chose $\beta = 200$ nm.

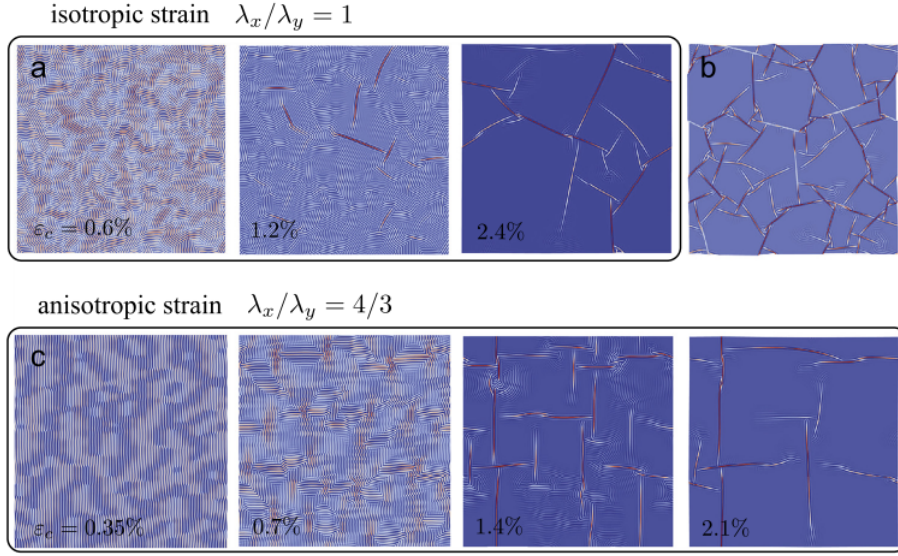


Figure 2.19: Results of the simulations of spontaneous wrinkles in supported graphene under biaxial compression ($\tau_0 = 0.3\text{MPa}$, $h_0 = 4.5\text{nm}$ and $\gamma = 0.45\text{J/m}^2$) using the atomic-based continuum theory. **a.** Evolution of the buckling pattern under different degrees of isotropic strain - 0.6%, 1.2% and 2.4% - **b.** The density of the wrinkles pattern is higher for a higher friction ($\tau_0 = 1.8\text{MPa}$). **c.** Evolution of the wrinkling pattern under different degrees of anisotropic strain - 0.35%, 0.7%, 1.4% and 2.3% -. In this case we see the wrinkles aligning with the two main directions of strain. [16]

We now have a total work function $U_{tot}(\vec{x}) = U_{el}(\vec{x}) + U_{adh}(\vec{x}) + U_{fr,k}(\vec{x})$ which can be discretized into finite elements. For simulations, the $500 \times 500 \text{ nm}^2$ substrate is also subdivided into finite elements leading to 3×10^6 degrees of freedom. This allows the model to predict the appearance of spontaneous wrinkles when the substrate is under strain. The strain can be applied in two different ways: either isotropically which basically means that $\lambda_x = \lambda_y$ or anisotropically where $\lambda_x \neq \lambda_y$. Both possibilities are shown in Figure 2.19.

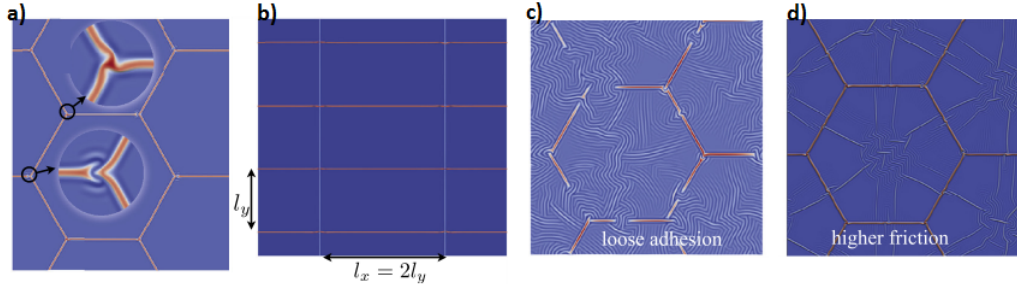


Figure 2.20: Illustration of the simulated controlled wrinkles using patterns of weaker adhesion. **a.** shows the wrinkles forming a honeycomb pattern under isotropic strain while **b.** shows a rectangular wrinkling pattern under anisotropic strain. In **c.** we see that the wrinkles fail to connect if the adhesion is too loose. In that case wrinkles do not form in every strip of weaker adhesion. In **d.** we observe that by tuning the friction to higher values supplementary wrinkles appear outside of the desired honeycomb lattice. This highlights once again the importance of the adhesion and friction factors. [16]

In the results shown in Figure 2.19 the stripes of weaker adhesion have been neglected since the first goal is to understand how the wrinkles form before trying to control their location. If we start by analysing the case with isotropic strain, we observe that there is a threshold strain

around $\epsilon_c = 0.6\%$ where the graphene sheet goes from a planar surface state to developing a small-amplitude rippling throughout the whole sample. As the compression increases ($\epsilon_c = 1.2\%$) the ripples seem to concentrate into localized short wrinkles partially releasing the rippling in the rest of the sample. According to the authors of [16] this is due to decohesion of the graphene-substrate interaction. As the strain continues to increase ($\epsilon_c = 2.4\%$) the wrinkles grow longer and begin to connect forming a network that divides the sample into smaller nearly flat areas. While some connexions between wrinkles are very complex it is nevertheless noteworthy that the vast majority of the junctions are T-shaped. According to [16], this is due to the fact that T-shaped junctions are energetically favourable compared to other types of junctions. Once the pattern of wrinkles is established, enhanced compression mainly increases the height of the wrinkles without significantly reorganizing the geometry of the pattern. However the wrinkles can be modulated in many ways. For example by modifying the frictional forces between graphene and substrate which determine the separation of the wrinkles. [16] In Figure 2.19b. this force has been significantly increased and we observe an enhanced density of shorter wrinkles dividing the sample into smaller subdomains. The wrinkling process in the case of anisotropic strain (Figure 2.19c.) is very similar to the isotropic case. Again we first see ripples appear then turn in to wrinkles which become more and more spaced out and connected while the rest of the sample goes back to a nearly flat state. The main difference being that with the anisotropic strain the ripples and wrinkles seem to be aligned with the principal directions of strain. Finally, according to [16] the resemblance between the simulations and the actual wrinkles observed in single and few-layer graphene is remarkable.

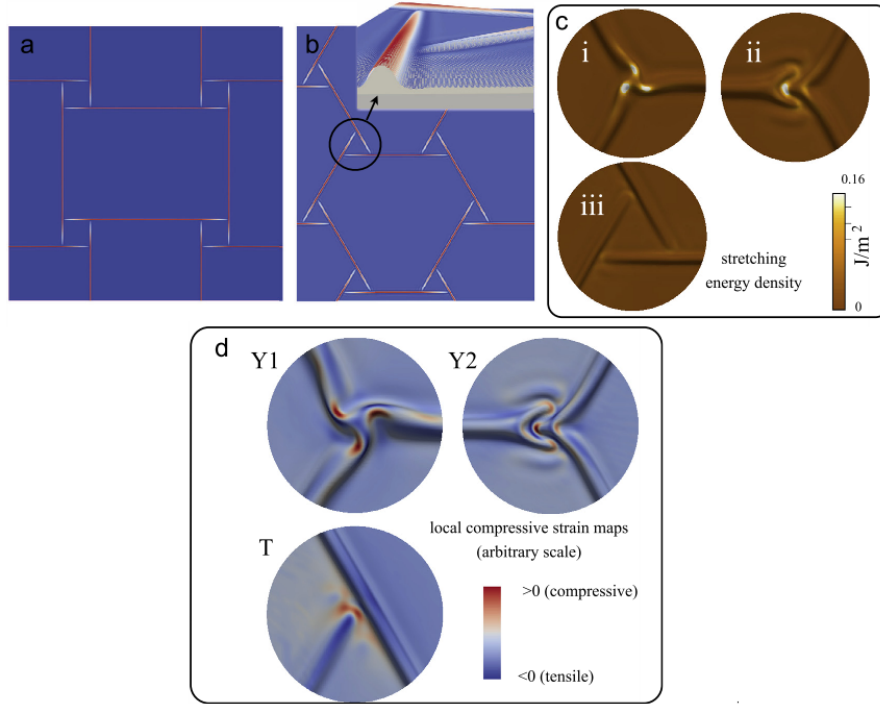


Figure 2.21: Illustration of the different types of wrinkle junctions. **a.** and **b.** show the two types of patterns featuring only the lower energy T-junctions. **c.** illustrates all three types of junctions found in the honeycomb pattern and their stretching energy density. **d.** displays the local strain of each of the three types of junctions. [16]

Once the random spontaneous wrinkles can be simulated, the model proceeds to figure out a way of controlling their formation. To do so they simulate stripes of weaker adhesion as mentioned above. In the case of isotropic strain they created a honeycomb lattice of weaker adhesion but since the wrinkles under anisotropic strain seemed to follow the strain directions they chose to use a rectangular stripe pattern in the anisotropic case. The results of these new simulations can be seen in Figure 2.20a. and b. We see that the wrinkles formed under isotropic strain (Figure 2.20a.) follow the honeycomb pat-

tern and develop two types of junctions, one of which is exactly similar to the origami-type junctions that were actually observed in hBN (Figure 2.14c.) which seems very promising for our project. Under anisotropic compression, the wrinkles first form in the direction of minimum stress and then match the targeted pattern as a second set of wrinkles develop (Figure 2.20b.). This has been tested for a large variety of parameters [16] and in most cases the wrinkles were conform to the desired patterns. Nonetheless there are cases where the wrinkle formation isn't under control. Two examples are given in Figures 2.20c. and d. In the first case the loose adhesion between graphene and substrate formed ripples that prevented the wrinkles from connecting to form the expected honeycomb lattice. In the other example, an excessive interfacial friction lead to the random formation of additional spontaneous wrinkles.

Finally, in order to verify whether or not T-junctions are lower energy configurations compared to other types of junctions (including the Y-junctions of Figure 2.20a.), they created wrinkle patterns that only exhibit this kind of junctions (Figures 2.21a. and b.). They then proceeded to measure the stretching energy density of both the T-junctions and the two types of Y-junctions and the result is given in Figure 2.21c. As predicted by the authors of [16], the T-junction configuration seems in fact to be energetically lowest and should therefore have a greater stability than the Y-junctions. They also measured the local types of strain in both the Y-junctions and the T-junction. The result is shown in Figure 2.21d. We will come back to this outcome later on.

Interlayer molecules model

The binding energy between a graphene sheet and a copper substrate consists, in this model, of the bending energy stored in the graphene and the adhesion energy representing the interatomic interactions between graphene and copper. If we use the notations in Figure 2.22c., the profile of the wrinkle can be assumed to follow [17]

$$y_s = \frac{1}{2}h(1 + \cos\left(\frac{\pi x}{W}\right)) \quad (2.11)$$

where h is the height of the wrinkle. The bending energy can then be written

$$E_b = \frac{Db}{2} \int_{-W/2}^{W/2} (y_s'')^2 dx = \frac{Dbh^2\pi^4}{16W^3} \quad (2.12)$$

with $D = 1.2$ eV the bending stiffness of graphene and b the length of the wrinkle along its axis. The adhesion energy E_a can be calculated as

$$E_a = bW\Lambda \quad (2.13)$$

with Λ the binding energy between graphene and copper. In the equilibrium state we then have

$$E_b - E_a = 0 \quad (2.14)$$

and using experimental data for the height, the length and the width of the wrinkles the obtained adhesion energy is $\Lambda \leq 0.0034$ J/m². By comparing this to values obtained for Γ by first hand calculations which range between 0.397 J/m² and 0.72 J/m² [17], we can easily see that there is a difference of two orders of magnitude between the results. This shows that the dimensions of the wrinkle obtained with atomic force microscopy (AFM) are not consistent with theoretical results.

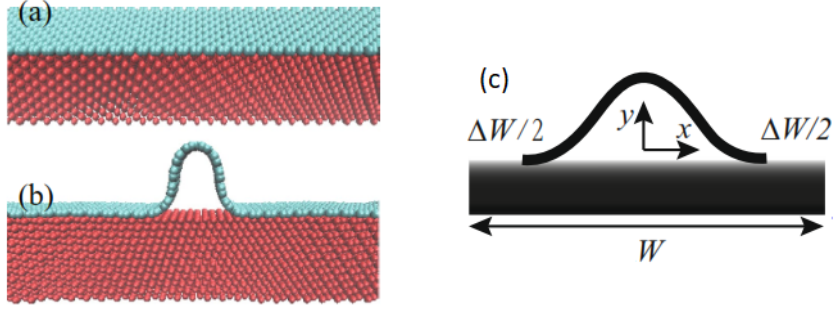


Figure 2.22: **a.** Molecular dynamic simulation of graphene ((blue) on copper (red) at 300°K. **b.** Molecular dynamic simulation of the same stack after compression. We see a typical wrinkle form in the graphene. **c.** Schematic representation of a wrinkle of width W . [17]

To understand this further, a one-dimensional molecular dynamic model is realized as shown in Figure 2.22a. and b. The blue plane represents the single layer of graphene while the red rectangle is the copper substrate. To simulate the wrinkles formed by differential thermal expansion, a pre-compressive strain is applied to the graphene layer, which was fixed in both ends by a horizontal spring, then the whole system is relaxed at a temperature of 300°K. While there should be a random uniform distribution of wrinkles, the MD simulations show that this is not the case due to weak binding that allows graphene to slip on the copper substrate. Neighbor wrinkles were observed to merge into larger wrinkles creating a large strain in the wrinkled part of the graphene and a small strain in the plane parts of the one layer sheet.

By varying the strain from $\epsilon = 12\%$ to $\epsilon = 65\%$, the MD simulations give the wrinkle profiles seen in Figure 2.23a. We see that as the strain increases, the wrinkle profile evolves into a mushroom-type profile meaning that its width starts to decrease as strain and height increases.

$$U(\theta, s, \alpha) = \int_{-W/2}^{W/2} \left(\frac{1}{2} D \left(\frac{\delta\theta}{\delta s} \right) - \Gamma \right) ds - \alpha \left(W - \Delta W - \int_{-W/2}^{W/2} \cos\theta ds \right) \quad (2.15)$$

where D is the bending stiffness of graphene, α is a Langragian multiplier. The first therm is the total free energy and the second therm is the boundary condition. As the ends of the wrinkle are fixed, we have $s = \pm W/2$ and $\theta = 0$ and knowing that the gradient $\Delta_{\theta,s} U(\theta, s, \alpha) = 0$, one finally gets the relation

$$\frac{\delta\theta}{\delta s} = \sqrt{\frac{2\Gamma(\cos\theta - \cos\theta_0)}{D(1 - \cos\theta_0)}} \quad (2.16)$$

The difference in length between the graphene sheet and the copper substrate ΔW , the width of the wrinkle ($W - \Delta W$) and its height d can be written

$$\Delta W = 4 \int_0^{W/4} (1 - \cos\theta) ds = 4 \sqrt{\frac{D(1 - \cos\theta_0)}{2\Gamma}} \left[\int_0^{\theta_0} \frac{1 - \cos\theta}{\sqrt{\cos\theta - \cos\theta_0}} d\theta \right] \quad (2.17)$$

$$d = \int_0^{W/2} \sin\theta ds = 4(1 - \cos\theta_0) \sqrt{\frac{D}{2\Gamma}} \quad (2.18)$$

$$W - \Delta W = \int_{-W/2}^{W/2} \cos\theta ds = 4 \sqrt{\frac{D(1 - \cos\theta_0)}{2\Gamma}} \int_0^{\theta_0} \frac{\cos\theta d\theta}{\sqrt{\cos\theta - \cos\theta_0}}. \quad (2.19)$$

This shows that the height of the maximum height of a wrinkle will be $d_{max} = 8\sqrt{\frac{D}{2\Gamma}}$.

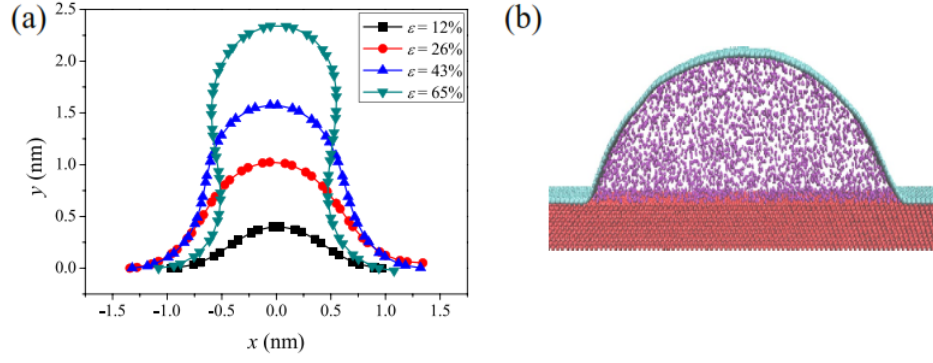


Figure 2.23: **a.** Typical shape of wrinkles in graphene formed under strain from 12% to 65%. **b.** Molecular dynamic simulation of the wrinkle morphology in graphene in presence of interlayer hydrogen molecules (purple) between the graphene (blue) and the copper substrate (red). [17]

These theoretical results fit nicely with the molecular dynamics simulations but some experimental results remain unexplained by this model. The authors of [17] therefore thought that another key mechanism had to come into play and they found that this element could be the existence of interlayer molecules. As graphene is impermeable even to hydrogen molecules, a lot of these can be trapped between a graphene sheet and the substrate. They therefore made new molecular dynamics simulations including various numbers of interlayer hydrogen molecules. The result of one of these simulations is shown in Figure 2.23b. They figured out that the height and width of the simulated wrinkle increased with the number of interlayer molecules and the new results were consistent with their experimental data.

2.4 Effect of strain on electronic properties

Graphene is able to sustain reversible elastic strain as large as 25% which is enormous compared to silicon that breaks around 1.5% of strain.[18] This actually makes the strain engineering of graphene highly possible which means its electronic properties can be tuned by applying mechanical strain to a graphene sample. It has been shown by tight-binding models and ab initio calculations that uniaxial strain shifts the Dirac cones away from K and K' below a threshold strain value ($\approx 20\%$), but opens a gap above this threshold. Figures 2.24 a and b respectively show the deformation of the Brillouin zone and the shifting of the Dirac cone in the $\mathbf{k}^*$ space of graphene under uniaxial strain. Shear strain has been found to have a similar effect but with a lower threshold value around 16% while biaxial strain, on the other hand, conserves the crystal symmetry of graphene thus the Dirac cones are not shifted nor is a band gap opened but instead the slopes of the Dirac cones are changed which impacts the Fermi velocity.

To understand the shifting of the Dirac cones, we will consider an in-plane uniform deformation described by a bidimensional strain tensor

$$\boldsymbol{\epsilon} = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} \\ \epsilon_{21} & \epsilon_{22} \end{pmatrix}. \quad (2.20)$$

In the deformed graphene sheet, real space vectors will be given by

$$\mathbf{r} = (\mathbf{I} + \boldsymbol{\epsilon})\mathbf{r}_0 \quad (2.21)$$

with $\mathbf{I}$ the unit matrix and $\mathbf{r}_0$ the vector in the unstrained graphene. As can be seen in Figure 2.24 the Brillouin zone of strained graphene will no longer be a regular hexagon. If we introduce a $\mathbf{k}$ space deformation

$$\mathbf{k}^* = (\mathbf{I} + \boldsymbol{\epsilon})^T \mathbf{k} \quad (2.22)$$

then the Brillouin zone will keep its hexagonal shape since

$$\mathbf{k} \cdot \mathbf{r} = \mathbf{k} \cdot (\mathbf{I} + \boldsymbol{\epsilon})\mathbf{r}_0 = (\mathbf{I} + \boldsymbol{\epsilon})^T \mathbf{k} \cdot \mathbf{r}_0 = \mathbf{k}^* \cdot \mathbf{r}_0 \quad (2.23)$$

The tight binding hamiltonian for the strained graphene then becomes

$$H(\mathbf{k}) = \sum_{j=1,2,3} t_j \exp(i\mathbf{k} \cdot \mathbf{a}_j) = \sum_{j=1,2,3} t_j \exp(i\mathbf{k}^* \cdot \mathbf{a}_{j0}) \quad (2.24)$$

where $j = 1, 2, 3$ corresponds to three C-C bonds of a C atom with vector $\mathbf{a}_j = (\mathbf{I} + \boldsymbol{\epsilon})\mathbf{a}_{j0}$ and bond length a_j while t_j is the hopping parameter depending on the bond length such that $t_j = t_0(a_0/a_j)^2$. When no strain or a biaxial strain is imposed on the graphene, the hopping parameters are all equal and the Dirac points are located at the corners of the hexagonal Brillouin zone, i.e. the K and K' points. When an uniaxial or a shear strain is applied on the other hand, the Dirac points can be found by solving the equation $E(\mathbf{k}_F) = |H(\mathbf{k}_F)| = 0$. In that case the hopping parameters are no longer equivalent and the Fermi points will thus deviate from the K and K' points. If we denote $\Delta\mathbf{k}_F^*$ the deviation of the Fermi points and expand $|H(\mathbf{k}_F)| = 0$ to the first order terms of $\boldsymbol{\epsilon}$ then $\Delta\mathbf{k}_F^*$ can be calculated to be

$$\Delta k_{FX}^* = (1 + \nu)\sigma \cos(3\theta) + \gamma \sin(3\theta) \quad (2.25)$$

$$\Delta k_{FY}^* = (1 + \nu)\sigma \sin(3\theta) + \gamma \cos(3\theta) \quad (2.26)$$

where θ is the angle between the zigzag direction and the x-axis, σ is the uniaxial strain in the zigzag direction, γ is the shear strain and ν is the Poisson's ratio. By expanding $E(\mathbf{k}^*) = 0$ near the Fermi points, one can obtain the electron dispersion relation in strained graphene given by

$$E(\mathbf{k}^*) = \pm \frac{3}{2} a_0 t_0 |\mathbf{k}^* - \mathbf{k}_F^*| \quad (2.27)$$

This equation clearly shows the shifting of the Dirac cone in the $\mathbf{k}^*$ space just as illustrated in Figure 2.24b. Then if the strain is important enough, two inequivalent Dirac points moving away from K

and K^* points might encounter one another and eventually merge. This will result in the opening of a bandgap in the electronic structure of graphene as has been observed by several studies. [18]

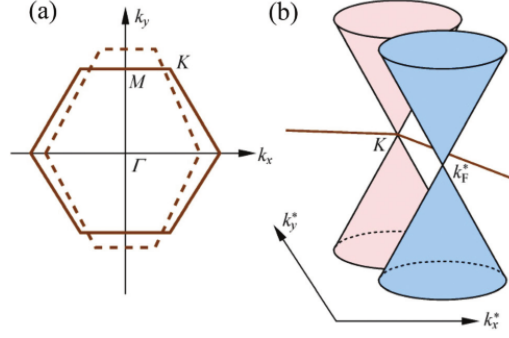


Figure 2.24: The effect of strain on the electronic properties of graphene. **a.** The deformation of the Brillouin zone. **b.** The shifting of the Dirac cone, in the k^* space, away from the k -point. [18]

2.5 Strain induced pseudomagnetic fields

There is an analogy to be made between strain and a magnetic field applied to a graphene sheet. If the mechanical strain varies smoothly it will not break the sublattice of the graphene but it will deform its Brillouin zone so that the Dirac cones situated at points K and K' will be shifted in opposite directions. [19] This is very similar to the effect one will get by applying a magnetic field perpendicularly to a graphene sheet. This leads to the question of whether it might be possible to create a strain induced pseudomagnetic field B_S leading to a pseudo-quantum Hall effect (QHE) observable without any real magnetic field. It has been shown in [19] that by applying a stress with a triangular symmetry it is indeed possible to create such a uniform pseudomagnetic field B_S equivalent to tens of Teslas observable at room temperature.

With a two-dimensional strain field $u_{ij}(x, y)$ one gets a gauge field

$$A = \frac{\beta}{a} \begin{pmatrix} u_{xx} - u_{yy} \\ -2u_{xy} \end{pmatrix} \quad (2.28)$$

where a is the lattice constant and $\beta = -\frac{\delta \ln t}{\delta \ln a}$ and t the nearest neighbour hopping parameter. Using polar coordinates (r, θ) this can be written as

$$A_r = \frac{\beta}{a} \left[\left(\frac{\delta u_r}{r} - \frac{u_r}{r} - \frac{1}{r} \frac{\delta u_\theta}{\delta \theta} \right) \cos 3\theta + \left(-\frac{1}{r} \frac{\delta u_r}{\delta \theta} + \frac{u_\theta}{r} - \frac{\delta u_\theta}{\delta r} \right) \sin 3\theta \right] \quad (2.29)$$

$$A_\theta = \frac{\beta}{a} \left[\left(-\frac{\delta u_\theta}{r} + \frac{u_\theta}{r} - \frac{1}{r} \frac{\delta u_r}{\delta \theta} \right) \cos 3\theta + \left(\frac{1}{r} \frac{\delta u_\theta}{\delta \theta} + \frac{u_r}{r} - \frac{\delta u_r}{\delta r} \right) \sin 3\theta \right]. \quad (2.30)$$

Applying $\underline{B} = \text{rot} A$ we then have

$$B_S = \frac{\delta A_y}{\delta x} - \frac{\delta A_x}{\delta y} = \frac{1}{r} \frac{\delta A_r}{\delta \theta} - \frac{\delta A_\theta}{\delta r} - \frac{A_\theta}{r}. \quad (2.31)$$

One can then show that a uniform B_S is obtained when

$$u_r = cr^2 \sin 3\theta \quad u_\theta = cr^2 \cos 3\theta \quad (2.32)$$

with c a constant.

The strain described by these equations on a graphene disc is shown in Figure 2.25a alongside its crystallographic alignment in Figure 2.25b. In Figure 2.25c we see the forces one would need to apply to a graphene disc to obtain the strain field in Figure 2.25a and Figure 2.25d shows the shape

that would allow the pseudomagnetic field B_S to be created by applying only normal forces to the perimeter of the graphene sheet.

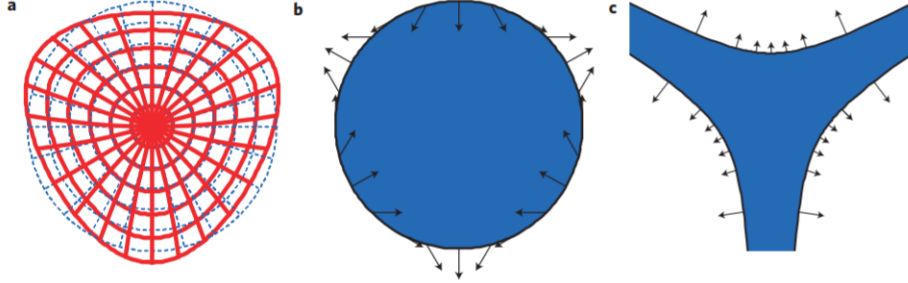


Figure 2.25: **a.** Deformation (red) of the graphene disc needed to create a uniform magnetic field. **b.** Distribution of the forces at the edge of the graphene disc needed to create the deformation in **a.** **c.** Alternative shape of a graphene sheet in which a uniform magnetic field by applying only normal forces to its edge. [19]

The strain field shown in Figure 2.25 creates a uniform pseudomagnetic field $B_S = 8 \frac{\beta c}{a}$. For a disc of diameter D under a maximum stress Δ_m at its perimeter we have $c = \Delta_m/D$. For a diameter $D = 100\text{nm}$ and a maximum strain $\Delta_m = 10\%$ we get a pseudomagnetic field $B_S \approx 40\text{T}$. [19] In the case of the disc the in plane forces applied to its perimeter to obtain a uniform B_S are given by

$$F_x(\theta) \propto \mu \sin(2\theta) \quad F_y(\theta) \propto \mu \cos(2\theta) \quad (2.33)$$

with μ the shear modulus. These forces can be seen in Figure 2.25c. Such a strain field is difficult to create experimentally as it involves both compression and stretching. One way to avoid this problem is to create samples with a shape so that all the forces are normal to its perimeter so that only stretching is involved. Such a sample is represented in Figure 2.25d.

Another easier geometry that allows to obtain is the one shown in Figure 2.26a where we see a graphete sheet shaped as a regular hexagon. Normal stresses are applied to the three non-adjacent sides of the hexagon along the $\langle 100 \rangle$ crystallographic directions. That way the symmetry of graphene is matched which prevents the pseudomagnetic field from changing sign. [19] The pseudomagnetic field created with this geometry is not perfectly uniform but it should still allow the observation of a pseudo-quantum Hall effect. If we assume that the side length of the hexagon is $L = 100\text{nm}$ and $\Delta_m = 10\%$, the numerical solution gives $B_S \approx 20\text{T}$ over the majority of the central part of the hexagon. A strong B_S should lead to Landau quantization which would also be proof of a pseudo QHE. One can thus calculate the density of state $D(E)$ resultnig from the non-uniform B_S in Figure 2.26a to see whether or not Landau quantization is observable. The results that where calculated by [19] are plotted in Figure 2.26b. The black curve is the case of graphene without either strain or magnetic field, the blue one represents the density of state in the case of a real magnetic field of 10T and finally the red curve is the $D(E)$ from a pseudomagnetic field $B_S \approx 7\text{T}$ induced by strain. At the absence of strain and magnetic field, the pic at $E = 0$ is due to states localized at the edges. It seems clear in this Figure that both B_S and B induce Landau levels and the qualities of these levels look pretty similar. This gives a fair proof that pseudo-Landau levels are in fact created by the strain induced B_S and that we are therefore observing a pseudo-quantum Hall effect.

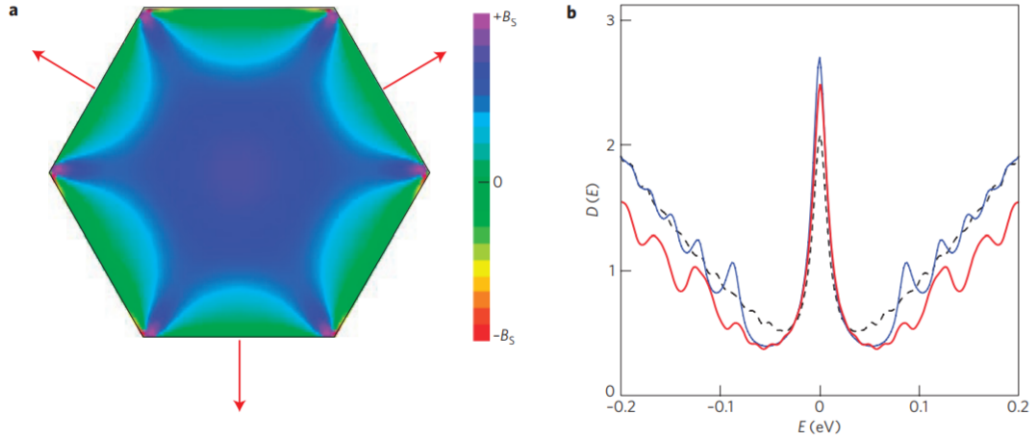


Figure 2.26: **a.** Distribution of a magnetic field of an hexagonal graphene sheet stretched in the three directions shown by red arrows. **b.** Normalized density of state of the hexagonal graphene sheet. The black curve is the case without magnetic field, the blue curve shows the Landau quantification induced by a magnetic field $B=10\text{T}$ and the red curve shows the quantification induced by the pseudo magnetic field $B_S \approx 7\text{T}$ at the center of the hexagonal flake. [19]

It is also interesting to see that this concept can lead to the opening of a gap in the electronic band structure of graphene. To illustrate this one can imagine a graphene sheet deposited on a corrugated surface as shown in Figure 2.27a. The sheet is considered as fixed to the sides of the surface. In Figure 2.27b we then see the pseudomagnetic superlattice resulting from the corrugated graphene sheet while Figure 2.27c shows the resulting energy spectrum. The important thing to notice in this last image is the fact that at high E there are multiple small gaps δE which would not exist without either strain or magnetic field. These gaps are quite small which is due the weak strain used for the calculation ($\Delta_m < 0,1\%$ in this geometry) but improving the design of the superlattice and increasing the strain would probably make it possible to achieve much larger gaps.

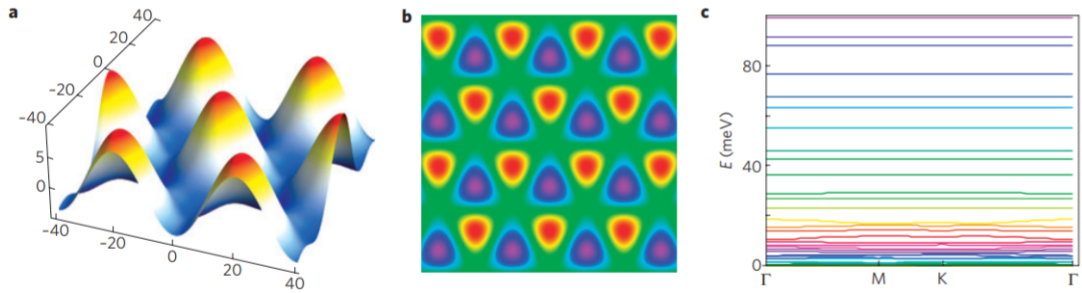


Figure 2.27: **a.** Graphene deposited on a profiled surface creating strain with triangular symmetry. **b.** Pseudomagnetic field resulting from the distribution in **a.** **c.** Low-energy bands induced by the periodic strain. The bands are symmetric with respect to zero E . [19]

Experimental methods

In this chapter we will first describe the different methods we have used to create our samples by exfoliation and transfer. Then we will explain the thermal treatment we applied to these samples and finally we will describe the characterization methods we used that were Atomic Force Microscopy and Raman spectroscopy.

3.1 Materials and exfoliation

Until now we have mainly discussed the properties of graphene and hBN but those are not the only materials we will be using in our experiments. Another 2D material on which we will try to evidence wrinkles is graphite which is basically stacked layers of graphene. Graphite has very similar properties to hBN since it also has an hexagonal crystal structure and its lattice parameters are very close to those of hBN (see Table 3.1).

As for the substrates we will use two very different materials: the first is a 300 nm silicon oxide (SiO_2) layer on bulk silicon (Si) and the other is barium fluoride (BaF_2). The first is a very common substrate for hBN while the second on the other hand is not so commonly used as substrate but is often used in optical devices where it is mostly used as transmission window for infrared spectroscopy. Here we chose to use it because of its much higher thermal expansion coefficient (TEC) of $18.1 \mu\text{m} \cdot (\text{m} \cdot ^\circ\text{C})^{-1}$ compared to the one of SiO_2 . BaF_2 is a crystal with a face centered cubic (FCC) structure and a lattice constant of $6.196 \text{ \AA}$. Its melting point at only 1354°C is also lower than all the other materials we use. Images of all four materials are shown in Figure 3.1.

Material	h-BN	Graphite	SiO_2	BaF_2
Crystal structure	hexagonal	hexagonal	-	FCC
Lattice constant ($\text{\AA}$)	2.5040 (a) 6.6612 (c)	2.461 (a) 6.708 (c)	-	6.196
Melting point ($^\circ\text{C}$)	2970	3652	1713	1354
Thermal expansion coefficient ($10^{-6}/^\circ\text{C}$)	-2.7	-3.75	3-5	18.1

Table 3.1: Properties overview for the different materials used in the experiments

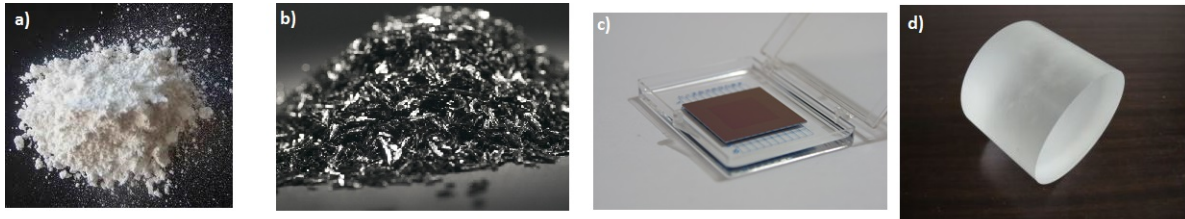


Figure 3.1: Pictures of the different materials used. **a.** hBN powder [20] **b.** Graphite flakes [21] **c.** A Si/SiO₂ substrate [22] **d.** A block of BaF₂ [23]

The exfoliation technique we used is called mechanical exfoliation and is the same as the one used by K. Novoselov and A. Geim when they first discovered graphene in 2004.[35] It is a top-to-bottom technique in which one proceeds to obtain graphene sheets by starting off with bulk graphite. The process is illustrated in Figure 3.2.

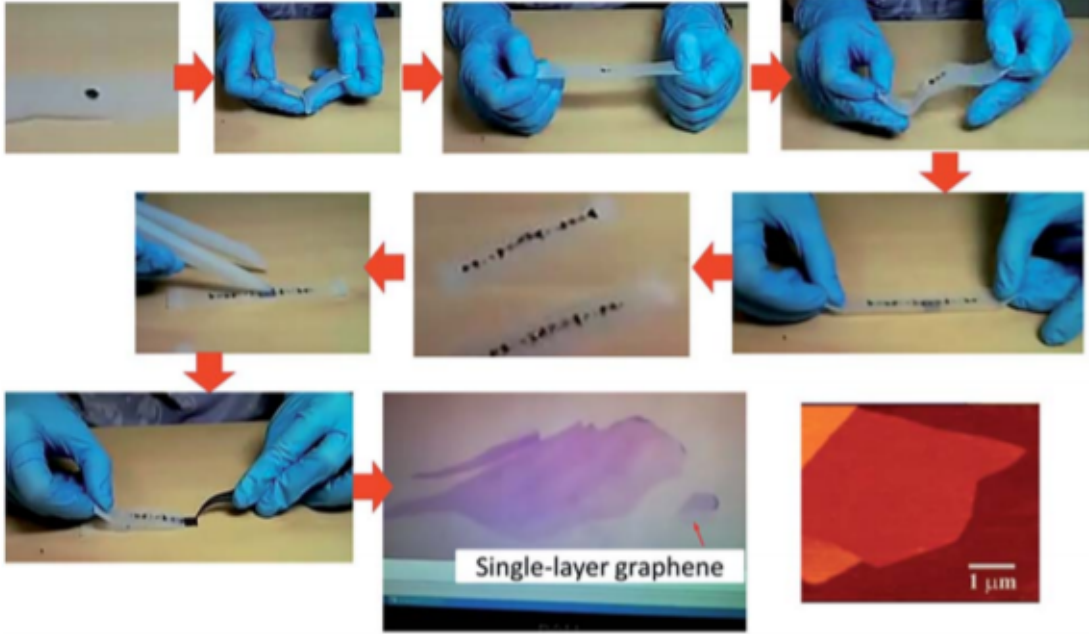


Figure 3.2: Illustration of the mechanical exfoliation of graphene [24]

The idea is to separate the layers of the bulk graphite as seen in Figure 3.1b to obtain thin graphene layers. These layers are held together by Van der Waals forces that have to be overcome by applying a normal force to the surface. In mechanical exfoliation, one uses Scotch tape applied to the surface of the graphite to exert this external normal force as shown in Figure 3.2. By applying this force numerous times the graphite will become thinner and thinner until we finally end up with a single-layer graphene sheet. Once graphene has been obtained, the tape will be applied onto a Si/SiO₂ substrate. The latter then has to be cleaned by thermal treatment at 300°C in ultra high vacuum (around 10⁻⁶mbar) for a couple of hours. This treatment should remove the remaining glue from the surface of the sample in order to have a final graphene sheet as clean as possible. The exfoliation process for hBN follows the exact same steps as the one for graphene.

3.2 Transfert of graphene onto hBN

Transfer Blade Manufacture

First of all, in order to transfer graphene onto an hBN flake, we need to create a transfer blade. To do so we need a microscope glass, a piece of polymer called polydimethylsiloxane (PDMS), a thermoplastic material called polypropylene carbonate (PPC) diluted in anisole and transparent tape (Crystal Tape). The transparency of the device is of high importance for the process of stacking graphene on hBN since we will need to be able to see both the graphene and the hBN flakes through the blade. Therefore all the materials used need to be transparent. The different materials are shown in Figure 3.3.



Figure 3.3: Necessary materials for the fabrication of a transfer blade. PDMS, PPC, and PPC diluted in anisole in **a.** and **b.** and **c.** respectively.[25]

To create the transfer blade as depicted in Figure 3.4, we first need to cut a piece of PDMS, generally a cube, and place it on the microscope glass where it is fixed with crystal tape. Then we have to create a thin layer of diluted PPC on a Si/SiO₂ substrate using the spin coating technique and evaporate the anisole by warming up the substrate. The next step is to make a hole in a piece of crystal tape and place it over the substrate so that the hole is centered on the latter. When removing the tape slowly from the substrate the thin PPC film should then remain attached to the tape and thus create a thin membrane covering the hole previously made. Finally we fix the piece of tape with the PPC on the microscope glass such that the PPC is covering the PDMS cube. A finished transfer blade can be seen in the pictures of Figure 3.4.

The PPC will be the material that comes in contact with the different samples to pickup and deposit the flakes. The PDMS on the other hand simply allows the PPC to be in contact with the samples without the rest of transfer blade touching it in order to minimize the contact zone and thus maximize the precision of the process.

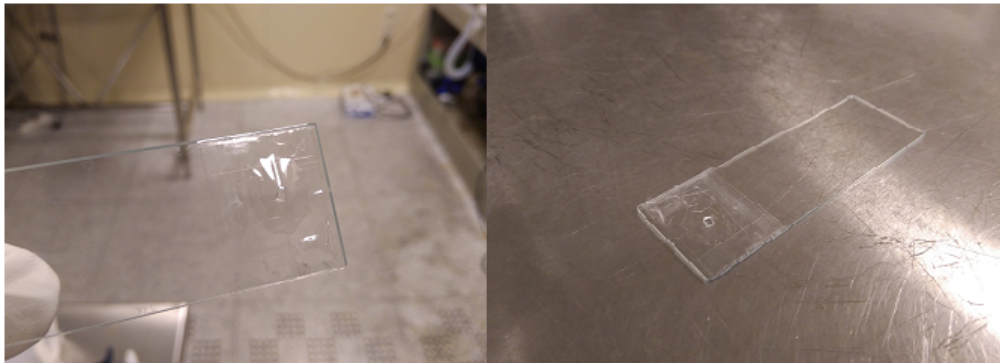


Figure 3.4: Pictures of a finished transfer blade made with a microscope glass, PDMS and PPC

Transfer process

Once the transfer blade has been manufactured we can proceed to the transfer itself. For this process we need two tools other than the blade itself, which are an optical microscope and what we call a transfer station. Both are shown in Figure 3.5.

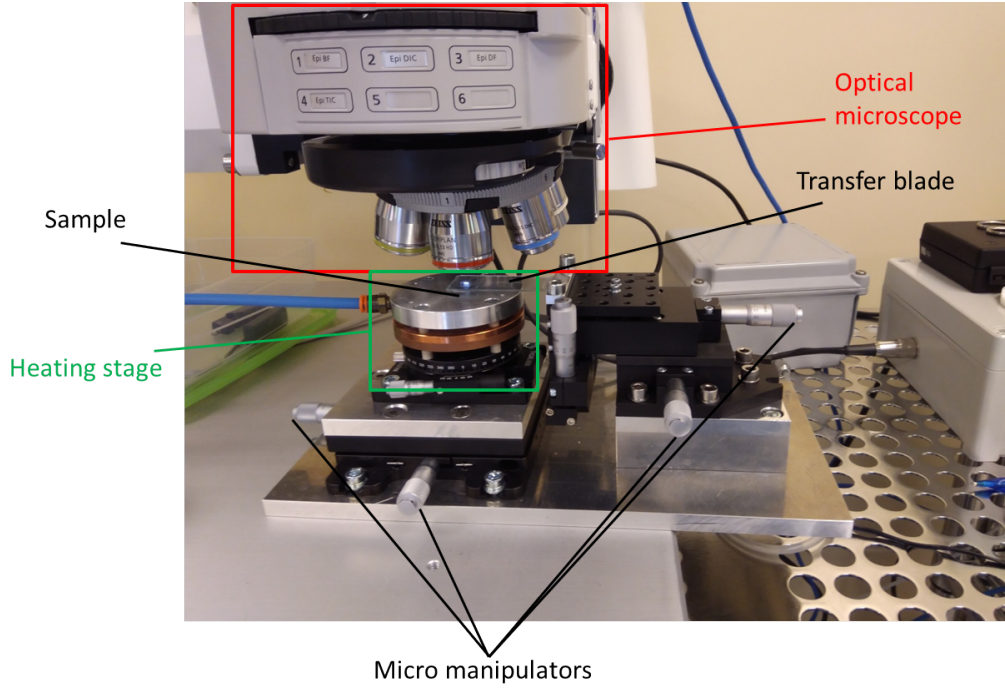


Figure 3.5: Picture of the transfer station under the optical microscope.

The transfer station consists of a heating stage on which the sample is fixed by suction through a small hole in the stage leading to a small pump. This is to avoid that the sample remains attached to the transfer blade during the pick-up process. There are micro-manipulators allowing to move the heating station in both lateral directions. The transfer blade is fixed onto the device so that the PPC can come in contact with the sample but micro-manipulators allow it to move both in the lateral directions but also in the vertical direction. This way the blade and the sample can be moved independantly wich is very important for us to be able to align the targeted graphene sheet with the hBN flake on which we want to transfer it.

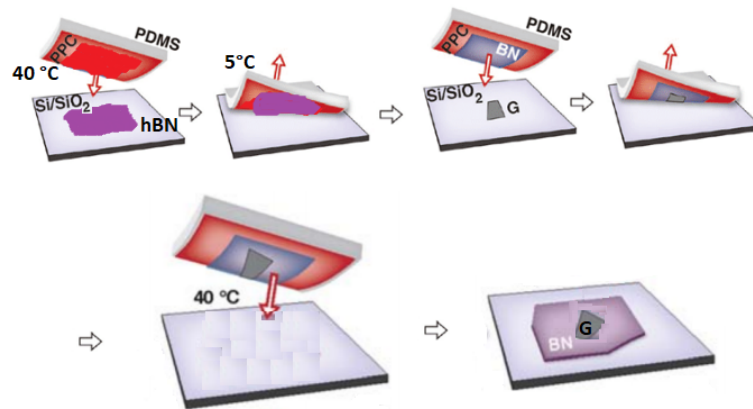


Figure 3.6: Cartoon of the different steps of the transfer of graphene on hBN process. Modified from [26]

The transfer process is divided into different steps that are all shown in Figure 3.6. First we need to pick-up the targeted hBN flake from the substrate onto the PPC on the transfer blade. As the blade is slowly brought into contact with the sample a "contact front" will begin to appear. It is shown in Figure 3.8 a where the contact front is the blue and purple curve crossing the targeted sample

highlighted by the red dots. The grey area is the one in which the blade and the substrate are already in contact while the contact is not yet complete in the purple area. We continue the approach of the blade until we find ourselves in the situation shown in Figure 3.8 a which corresponds to the one in Figure 3.7 a. We see that at that moment the PPC has begun coming into contact with the targeted hBN. At that point we heat up the transfer stage to 40°C . This leads to the thermal expansion of the PPC that will mold the flake as much as possible and by doing so establish an optimal contact with the desired flake. The stage has to be kept hot for a few minutes in order to optimize this step which is illustrated in Figure 3.7b. A corresponding optical image of the step can be seen in Figure 3.8b where we can see that the contact front has moved with the temperature rising. After a few minutes we can begin cooling down the heating stage to around 5°C before letting it slowly come back to ambient temperature. The purpose of the down cooling is to solidify the PPC around the flake in order to get a better grip on it. The lift-up can then be started as the blade is slowly removed from the sample and if everything went as expected the flake should remain attached to the PPC as in Figure 3.7c. We believe it is worth noting that the success rate of this step is not maximal and it might take a few tries before managing to pick-up a flake.

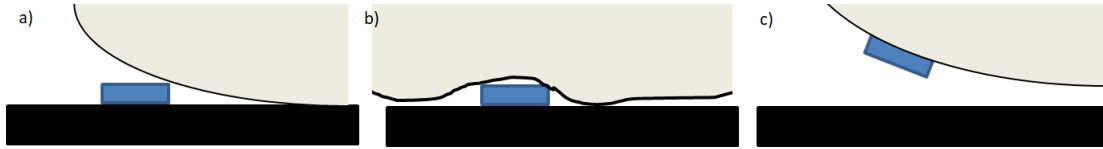


Figure 3.7: Cartoon of the different steps of the pick-up process

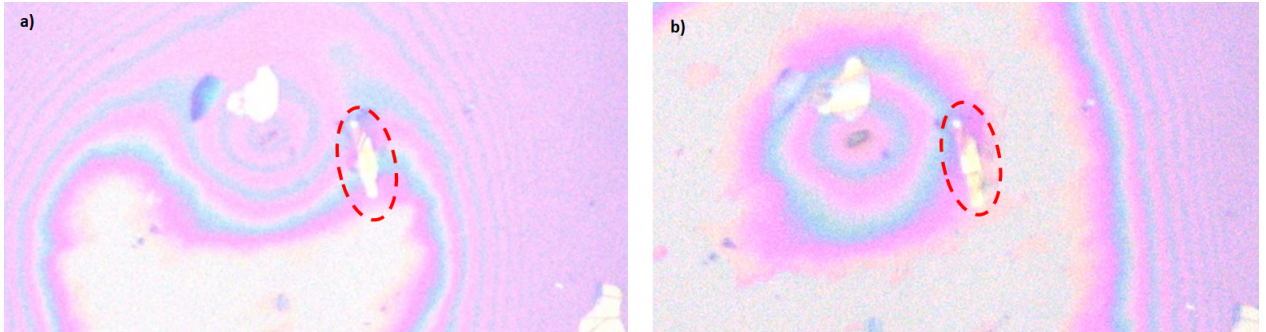


Figure 3.8: Optical images of the thermal expansion of the PPC during the pick-up process.

Once the hBN flake has been picked-up, the stacking process can begin. Here the first step is obviously to select the graphene flake we would like to stack on our hBN. When this is done the two flakes have to be aligned under the microscope. This is where the independent movements of the heating stage and the transfer blade via micro-manipulators becomes very useful. One will have to switch the focus of the microscope between the blade and substrate surface in order to see both flakes as the blade is slowly approaching the substrate. In Figure 3.9a an example is shown of an hBN flake aligned with a graphene flake seen through the transfer blade. The same process is then repeated as for the pick-up of the hBN to establish the best contact between the flakes during the heating and get as good a grip as possible on the flake with the cooling. As the blade is lifted up the graphene should follow as it will be attached to the hBN flake. If the graphene flake is bigger than the hBN only parts of the flake will be removed from the substrate, an example of which is shown in Figure 3.9b. Once again the process might take several tries before succeeding.

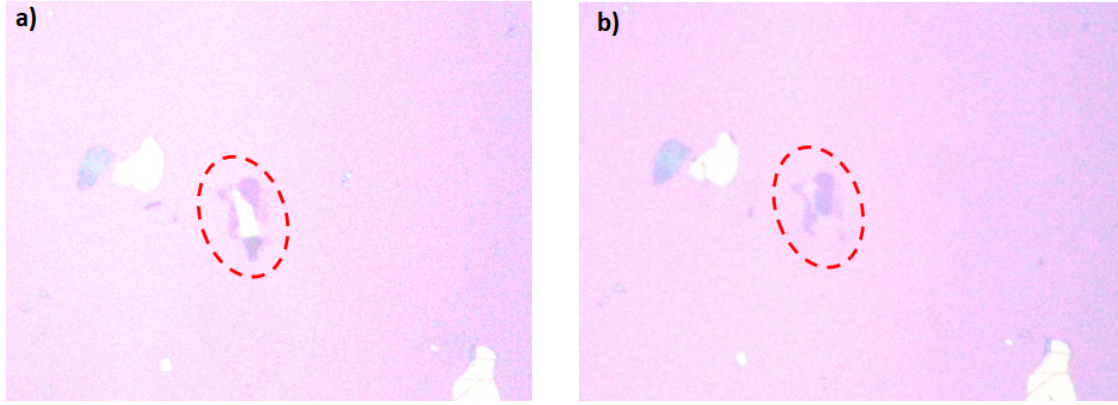


Figure 3.9: Optical images of the an hBN flake aligned with a graphene flake (**a.**) and of what remains of the graphene flake after the stacking step.

Finally the third step of the transfer process is the stack flip which is illustrated in Figure 3.10. First the tape layer with the PPC membrane is cut off the blade and placed on a new substrate so that the PPC comes in contact with it. The side of the PPC that comes into contact has to be the one without the stack which will therefore be flipped compared to how we saw it with the microscope through the blade. When the process is done the top layer will therefore be the graphene and no longer the hBN.

Once the tape has been placed on the substrate we heat it up to 90°C so that the PPC begins melting on the substrate. After a few minutes of heating it is then possible to remove the tape while leaving the PPC on the substrate. The PPC then has to be removed in order for the stack to be "dropped" on the surface of the substrate. To do so the sample is annealed at 320°C under ultra high vacuum (of the order of 10^{-7} mbar) during a few hours. After this annealing the PPC should have disappeared and the flake be deposited on the substrate so that the transfer process is completed.



Figure 3.10: Optical images of the thermal expansion of the PPC during the pick-up process.

3.3 Annealing

Now that the samples are ready, they have to be subject to thermal treatment. To do so we used a Rapid Thermal Annealing (RTA) oven shown in Figure 3.11a. The annealing was divided into four steps, all depicted in Figure 3.11b. In the first phase, the oven remains at 20°C but a argon-helium gas (Ar/He_2) is injected into it. The idea is to do the annealing in the atmosphere of a noble gas instead of air is to avoid undesired interactions with the sample. After 10 minutes, the heating begins at a rate of 32,33°/min so that the maximum temperature of 990° will be achieved after 30 min. That's the second step. Once that temperature is reached, the third phase begins. The oven simply remains at the maximum temperature for 25 min which forms a heating plateau. After that, the cooling begins at a much slower rate of 8°/min until oven is back at the ambient temperature of 20°C, ending the fourth and last phase of the process. The values of maximum temperature, plateau length and cooling rate were all taken directly from article [15] in which they showed the existence of wrinkled hBN flakes after thermal treatment. This particular annealing process is the one all the other annealing processes are based on and will thus be referred to as the "standard annealing".

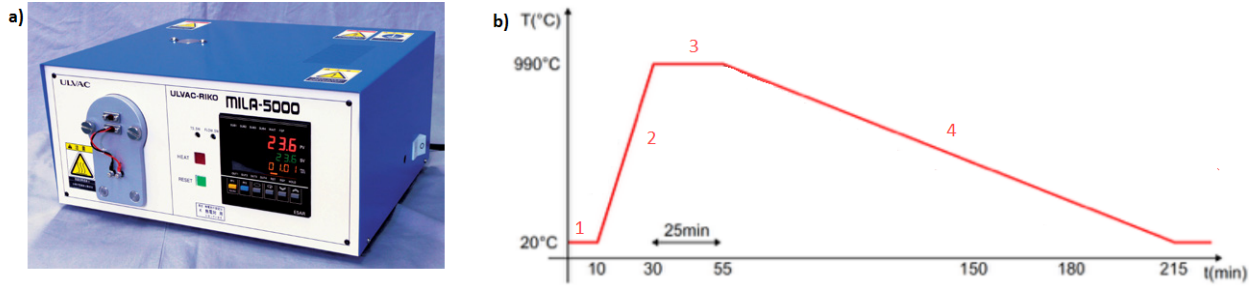


Figure 3.11: **a.** Picture of the Rapid Thermal Annealing oven [27] **b.** Heating profile of the standard annealing process. The different steps are explained in the text.

As the heating profile might have an impact on the wrinkle formation in hBN we will also try to modify the annealing process. Two examples of modified profiles are given in Figure 3.12 a and b in which in the first case the maximum temperature has been lowered to 800°C and in the second case the cooling rate has been changed to either 6°C/min or 10°C/min. We also tried annealing the samples under other atmospheres to see if this would impact the wrinkling. The atmospheres we tried, other than Ar/He₂ are high vacuum (around 10⁻⁶ mbar) and nitrogen (N₂).

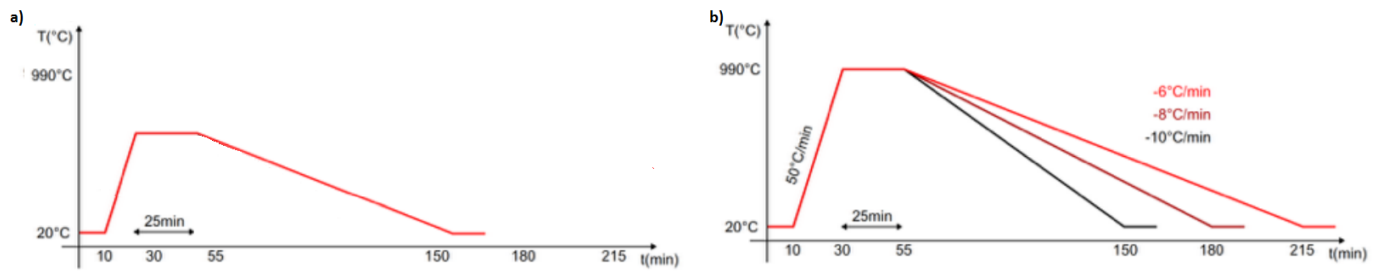


Figure 3.12: Variation of the main characteristics of the annealing process. The variations of maximum temperature and cooling rate are shown in **a.** and **b.** respectively.

3.4 Atomic force microscopy

The first characterization technique we will describe is the Atomic Force Microscopy (AFM) which can be classified as an SPM (Scanning Probe Microscope) due to the fact that the topographic image will be obtained by scanning the sample with a probe. In the case of AFM, this probe is a microscopic tip at the end of a cantilever (see Figure 3.13a.). A laser beam is reflected on this cantilever and detected by a 4 quadrant photo detector. The tip is brought into contact with the sample then the scanning begins. As the tip encounters an obstacle (difference in the topography of the sample) it will be deflected which will lead to a deflection of the position of the laser on the photo detector. The vertical position of the probe is then adjusted so that the position of the laser comes back to its original point. That way, by recording the tip adjustments we obtain a topographic image of the sample.

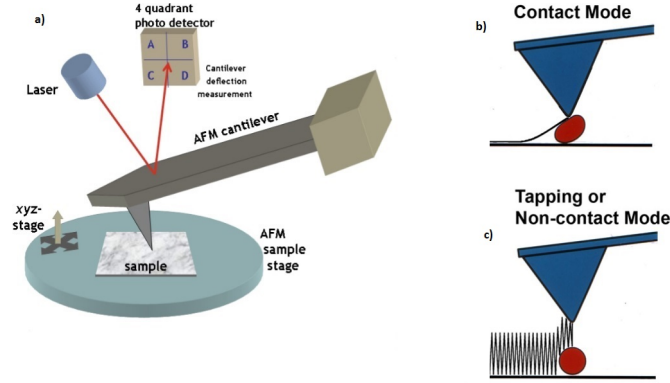


Figure 3.13: Atomic Force Microscopy principle. **a.** Cartoon of the AFM cantilever and tip in contact with a sample surface. [1] A laser is reflected on the cantilever and detected with a 4 quadrant photo detector. **b.**, **c.** Different working modes of the AFM. In our case, the tapping mode will be used. [28]

The process described here above is known as the "Contact Mode" of an AFM which is the most basic mode. The main other two modes are the "Tapping mode" where the tip and the cantilever are oscillating and are therefore brought into contact with the sample periodically and very briefly, and the "Non-Contact Mode" where the tip and cantilever are also oscillating but the never touch the sample. The three different modes are illustrated in Figures 3.13b. and c.

The main mode we used in our characterization was the Tapping Mode simply because this mode is less invasive than the Contact Mode. As already said, in this mode the tip and cantilever are oscillating at predefined frequency, often close to their resonance frequency. As the tip approaches the sample surface it will be submitted to different forces. First the attractive Van der Waals forces and then as it gets even closer the repulsive Coulomb forces. Both of these forces will create a shift in the oscillation frequency of the cantilever which also leads to an amplitude shift at the given original frequency. By measuring this oscillation amplitude shift it is then possible to adjust the vertical position of the cantilever and that way obtain the wanted topographical image. An other advantage of this mode is that it also records the phase modifications (due for example to the presence of different materials) and the error signal, both of which can give extra information that can prove to be very useful.

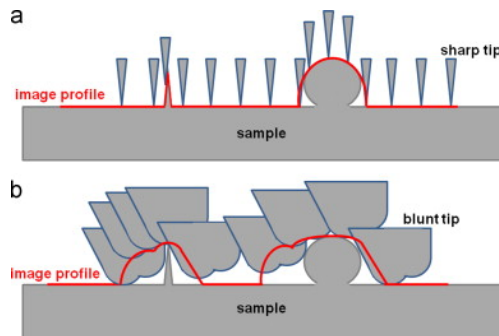


Figure 3.14: Difference in AFM profile depending on the tip geometry. A thin and sharp tip will give a very accurate profile (**a.**) while a bigger blunt tip will give a very different result as we can see in **b.** [1]

Finally, it is extremely important to take into account the fact that the images obtained with an AFM completely depend on the tip geometry. As it is shown in Figures 3.14a. and b., one will obtain completely different profiles with a same sample depending on how thin and how sharp the tip is. Therefore it is crucial to be sure that the tips we use are well shaped and to always remember that the profiles we observe are never entirely accurate.

3.5 Raman spectroscopy

The next characterization method is called Raman spectroscopy. This time, the sample will be scanned, not by a tip nor an electron beam, but by a laser beam. This beam passes through a monochromator and the photons are given a specific energy E_0 and frequency ν_0 . As the laser light comes in contact with the sample, it will interact with the vibrational modes, the phonons, of the latter. This interaction is called inelastic scattering. It results in an energy shift, and thus a frequency shift, of the laser photons which gives information on the vibrational modes in the system. A cartoon of a Raman spectrometer is given in Figure 3.15a.

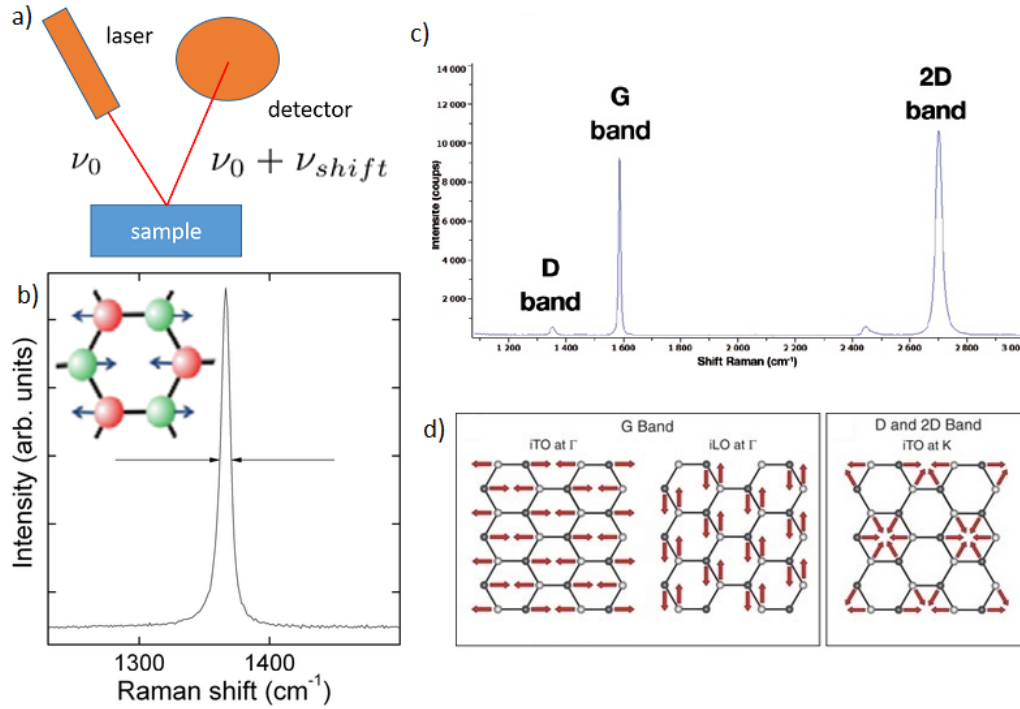


Figure 3.15: **a.** Cartoon of a Raman spectrometer. **b.** Typical Raman spectrum of an hBN crystal. The peak is located at a Raman shift of 1366 cm^{-1} . The inset shows the activated phonon vibrational mode at this particular Raman shift. [29][30] **c.** Typical Raman spectrum of a graphene sheet. The three bands are located at 1360 cm^{-1} , 1580 cm^{-1} and 2750 cm^{-1} . [31] **d.** Activated phonon vibrational modes corresponding to the Raman spectrum of graphene. We see that two different modes are responsible for the G band while one single mode generates both the D and the 2D band. [32]

All materials have a specific Raman spectroscopy spectrum that simply depends on the number and type of phonon modes that can be activated in that material. For example, the hBN spectrum only presents one peak at a Raman shift of 1366 cm^{-1} because only one phonon mode is activated by the laser beam. A typical hBN spectrum and the activated phonon mode are illustrated in Figure 3.15b. On the other hand, the graphene spectrum shows three peaks called bands: the D band at 1360 cm^{-1} , the G band at 1580 cm^{-1} and the 2D band around 2750 cm^{-1} . An example of graphene spectrum is to be found in Figure 3.15c. The phonon vibrational modes responsible for the different bands are depicted in Figure 3.15d.

Each peak has three main characteristics which are their exact position, their intensity and their full width half maximum (FWHM). These three values depend strongly of the properties of the targeted sample. This means that the comparison of Raman spectra taken at different points of the sample will give on different properties like the number of layers and the effects of doping, disorder or strain. It has for example been shown [40] that the broadening of the 2D band of a graphene Raman spectrum contains information on local strain variations at the nanometer-scale. In other words, Raman spectroscopy is a great non-invasive characterization tool which can provide useful

structural information. The only disadvantage is its resolution of the order of $1\text{ }\mu\text{m}$ which relatively low compared to those of other techniques as the AFM.

Results and discussion

This chapter will be dedicated to the different experiments we made and the results we obtained. Our main goals were to get a better understanding of the wrinkling process, to identify the parameters that play a predominant role in the process and to figure out how the wrinkles are structured within the layers of a flake. Ultimately we also wanted to create stacks of graphene that would be wrinkled following the wrinkle pattern of their hBN substrate. To do so we first studied the effect of changing certain parameters of the heating profile such as the maximum temperature, the cooling rate and the length of the plateau. We also tried changing both the flake and the substrate material. We then transferred graphene onto hBN flakes to see both how the graphene sheets would react to the transfer and how the stacks would react to the thermal treatment afterwards. We then finally tried creating a stack of encapsulated graphene to avoid wrinkling issues in the stacks that we thought might come from the transfer process.

After presenting the results of these experiments we will discuss them and suggest a scenario for the wrinkling process based on our observations and on the previous work in [41].

4.1 Exfoliation

The first step of our experimental process was of course to obtain both hBN flakes and graphene sheets through exfoliation process. Figures 4.1 a and b show examples of hBN flakes while c and d display optical images of graphene flakes.

The obtained hBN flakes were of all sizes and shapes as well as of different colours. The colour gives an indication on the thickness of a flake. We assume that the thicker a flake is the less the chances are that it will present wrinkles after annealing. This assumption is based on previous work done by Alice Nsengimana in her master thesis [41] in which she shows a direct correlation between flake thickness and wrinkle density after annealing. In our case it is therefore interesting to select the thinnest possible flakes which are those of blue colour as in Figure 4.1a. They have a thickness of around 30 nm as will be shown further on. Of course the size and shape also come into consideration when selecting a flake for stacking. Concerning the shape we try to find flakes that are as convex as possible since this will provide a more uniform contact zone with the graphene and thus facilitate the pick up of the latter during the stacking process. Sizewise it is important that the flakes are not too small as that would make them more difficult to study afterwards especially if they have to be contacted electrically. On the other hand we don't want them to be too big either as they then become difficult to characterize with our AFM that can only cover a maximum area of $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ at the time. We found that flakes with a lateral size in the range of 20 to $50\text{ }\mu\text{m}$ was the ideal sizing for our further experiments. Finally one last thing we try to avoid is the presence of irregularities at the surface of the flake as those that can be seen in Figure 4.1b. Again this is to optimize the contact with the graphene sheet during the pick-up but also to get the best possible quality of graphene in the final stack and to do so the substrate under the graphene has to be as flat as possible.

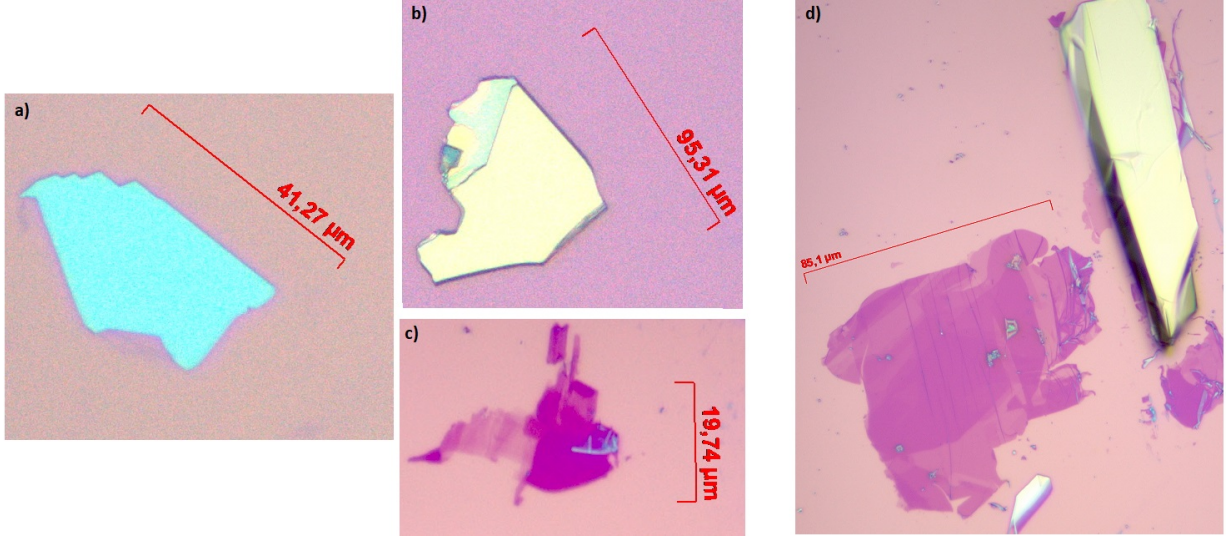


Figure 4.1: Optical images of exfoliated hBN flakes (a. and b.) and graphene sheets (c. and d.)

As for the graphene sheets, we also obtain all sorts of different sizes and shapes and even more so different thicknesses. In fact, the flakes we obtain can go from one single layer of graphene to graphite flakes that are hundreds of nanometers thick. One of these can be seen in the upper right corner of Figure 4.1d. To get a single layer graphene sheet one has to find a flake as light purple as possible that can actually be quite difficult to detect with an optical microscope as the colour is very similar to the one of the substrate. In our case we could also use double and triple layer graphene which are more frequent and of a darker purple colour that makes them easier to find. Concerning shape and size we tried to find some that would match the selected hBN flake as well as possible while being a little smaller so that it would be entirely covered by the hBN during the pick-up. There are two reasons for this. The first is that it is much easier to pick-up an entire graphene flake rather than tear one a part and only pick-up only parts of it. The second is that if the graphene is torn during the pick-up it might create additional corrugations and ripples in the sheet in the final stack which we of course want to avoid as much as possible. For the same reason we try to avoid graphene sheets that present too many irregularities at their surface.

4.2 Transfer

Once the flakes for stacking were exfoliated and selected we could proceed to the transfer process as described in Section 3.2. An example of a completed stack is shown in Figure 4.2a.

The hBN flake is completely covered by a graphene sheet as has been confirmed by Raman spectroscopy. The Raman spectrum taken on the flake is given in Figure 4.2b. We see the typical peak of hBN around a Raman shift of 1350 cm^{-1} . [29] As the peak of the D band of graphene is also located around that Raman shift it is absorbed into the hBN peak and thus it is not observable. We then see the G band and the 2D band peaks of graphene at Raman shifts of 1600 cm^{-1} and 2750 cm^{-1} respectively. [31] As can be observed the 2D peak is not as sharp as the other two and it presents two elbows. This is due to the fact that the peak we can see is actually the results of multiple peaks merging into one. This shows that the graphene is not a single layer sheet but more probably a bilayer or a trilayer sheet. Figures 4.2 c and d show AFM images of the flake and Figure 4.2e is the topography of the flake following the red line in Figure 4.2d. As expected the blue colour corresponds to a thickness of $\pm 30 \text{ μm}$.

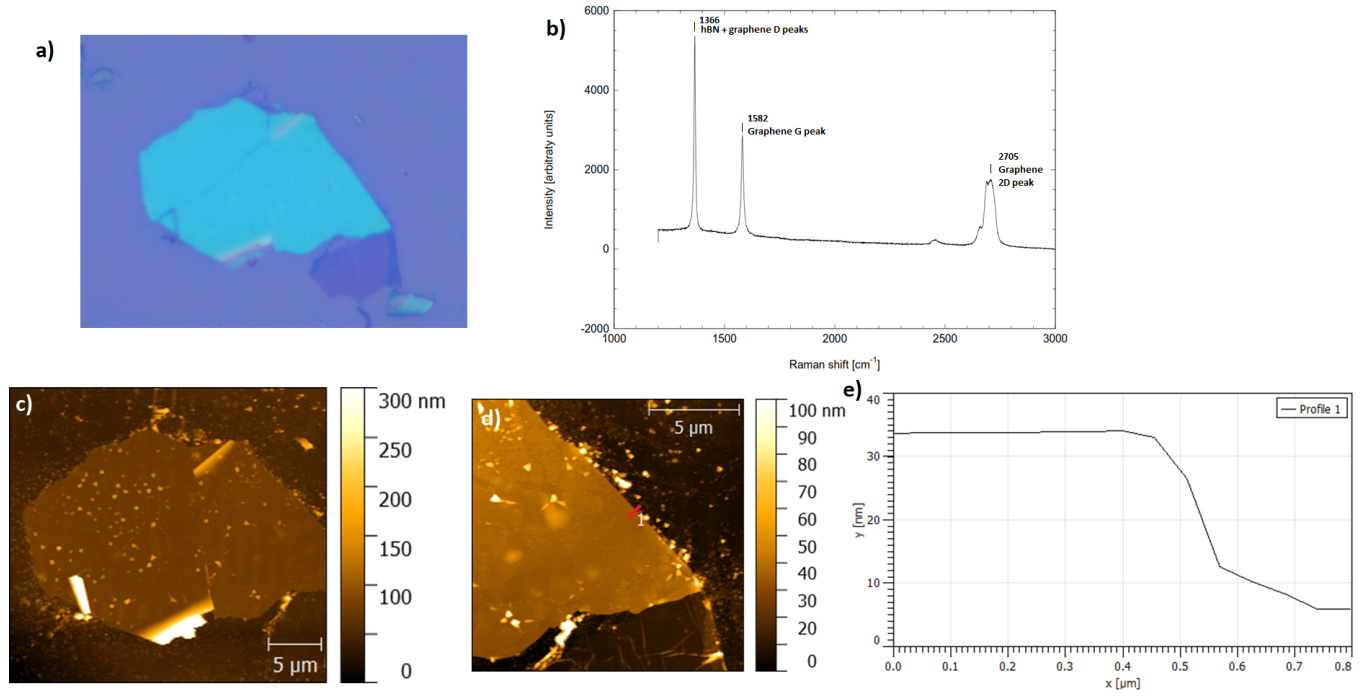


Figure 4.2: **a.** Optical image of a stack consisting of a graphene sheet on an hBN flake. **b.** Raman spectrum taken at the surface of the flake in **a**. **c.** and **d.** Atomic force microscope images of the same flake. **e.** Height profile of the flake following the red line in **d**.

Sadly it was actually quite rare to obtain final stacks with a uniform graphene sheet covering the hBN flake. Most of the time only parts of the graphene flakes got ripped of the substrate and stayed on the hBN flake. An example of this is the stack shown in Figure 4.3a. Figures 4.3 b and c show and AFM image of this stack and its height profile respectively. The black profile corresponds to the blue line in Figure 4.3b while the red profile follows the red line. Even though it is very difficult to observe in the image, the graphene flake only appears in the red rectangle in Figure 4.3b. This will appear much more clearly in the AFM images of Figure 4.4. We also see that this flake is a little bigger and a lot thicker than the previous one but that should not impact the pick-up of the graphene.

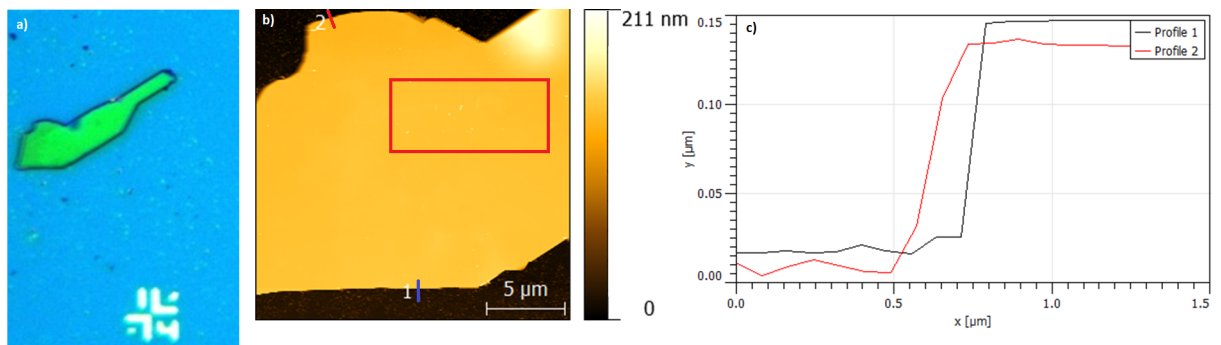


Figure 4.3: **a.** Optical image of an hBN flake on which a small graphene sheet has been stacked. **b.** AFM image of the flake. The red rectangle shows the region where the graphene sheet is to be found. **c.** Height profiles of the flake following the blue line (profil 1) and the red line (profil 2) in **b**.

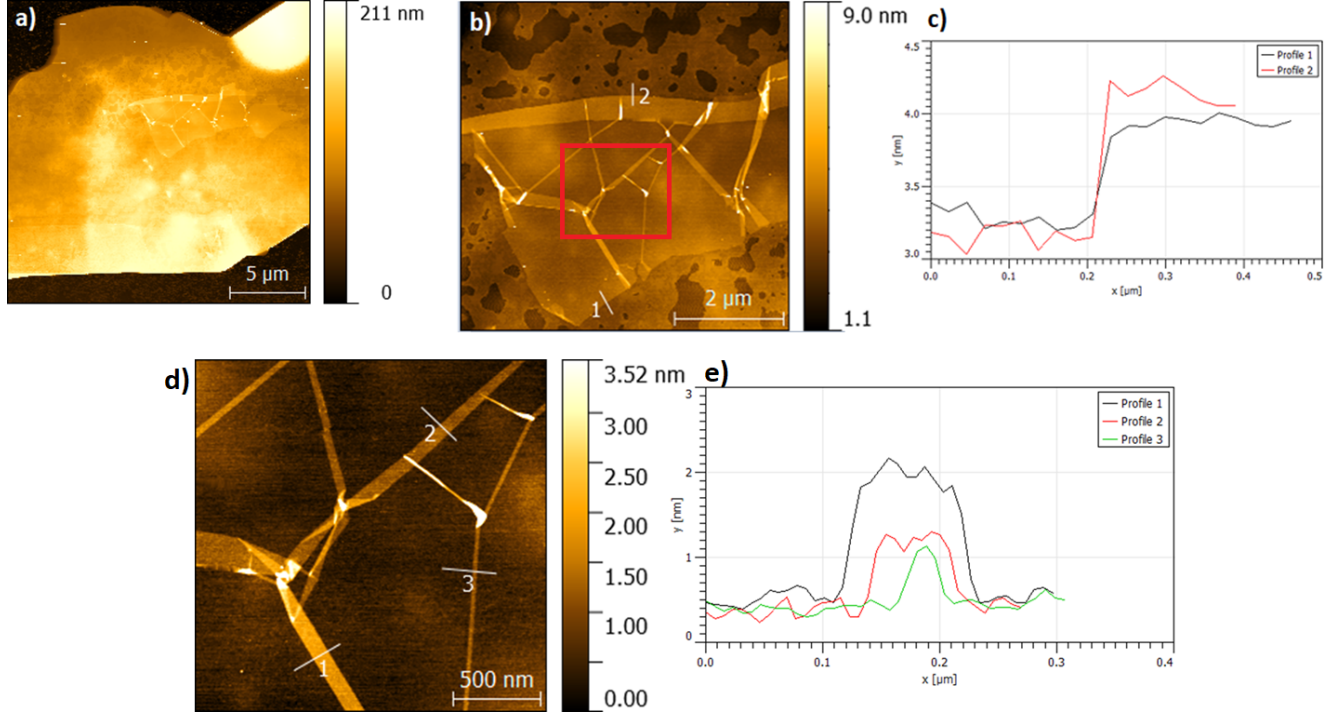


Figure 4.4: **a.** AFM image of the flake in Figure 4.3 with modified colour scale to evidence the graphene sheet. **b.** Zoom in on the graphene sheet. **c.** Height profiles following the two white lines in **b**. **d.** Zoom in on the red rectangle in **b**. **e.** Height profiles following the three white lines in **d**.

By modifying the colour scale it was possible to highlight the graphene sheet on the flake as can be seen in Figure 4.4a. We could then zoom in on this flake to obtain the AFM image in Figure 4.4b. By analysing the height profiles in Figure 4.4c corresponding to the white lines in Figure 4.4b we see that the graphene sheet is less than 1 nm thick (profil 1) which indicates that it is probably a monolayer graphene sheet. [42] Profil 2 shows that in its upper region the sheet seems to have folded back on itself which gives a slightly thicker sheet. We suspect that this fold was created when the graphene flake was ripped off during the stacking process. We also see some strange black areas on the hBN around the flake. We do not know exactly what causes this but it could be remains from the tape used for exfoliation. In that case it would be rather problematic as the epitaxial contact between the graphene sheet and the flake would be lost. In Figure 4.4d we see a zoom in on the irregularities of the graphene sheet in the red rectangle of Figure 4.4b and the height profiles corresponding to the three white lines are shown in Figure 4.4e. We see that the graphene sheet presents wrinkles of various width and heights but it is worth noting that some of them are more than double as high as the sheet is thick which therefore seems quite huge. If we calculate the aspect ratio of these wrinkles, i.e. their height over their width, we obtain ratios between 0.02 and 0.05 which is quite small compared to the aspect ratios of thermally activated wrinkles extracted in previous works that were between 0.4 and 0.7. [41] Furthermore the patterns of these wrinkles seem completely random and not at all like those that have been found for thermal wrinkles in [15] with very specific angles and only three different direction for the wrinkle propagation. It can also be seen by comparing these wrinkles to those of Figure 4.5 in which the wrinkles have appeared after thermal treatment. It is possible that some of these wrinkles appeared during the exfoliation process but we suspect that most of them happened during the pick-up of the graphene sheet as it was ripped from the flake on the substrate. More AFM images of flakes with similar graphene sheets can be found in Appendix A.

4.3 Annealing

As said in Section 3.3 we tried to modify the standard annealing process used in [15] to see how this would impact the wrinkling of flakes. This was done on simple hBN flakes on SiO_2/Si substrate. We first tried to do the annealing in a different atmosphere and we found that it did not seem to

matter to use nitrogen instead of argon but when we made the annealing under ultra high vacuum ($\approx 10^{-6}$ mbar) there were never any wrinkles to be found. This was also the case when we lowered the maximum temperature of the annealing. The cooling rate also had an impact on the wrinkling as the flakes annealed with a cooling rate of $10^\circ/\text{min}$ seemed to present wrinkles most frequently. Also these wrinkles seemed bigger than the ones we found after annealing with a cooling rate of $6^\circ/\text{min}$ and $8^\circ/\text{min}$. Therefore we decided to use this cooling rate for the annealings after transfer as it seemed to be the most efficient. Two examples of flakes annealed at maximum temperature of 990° under nitrogen atmosphere and with a cooling rate of $10^\circ/\text{min}$ are shown in Figure 4.5.

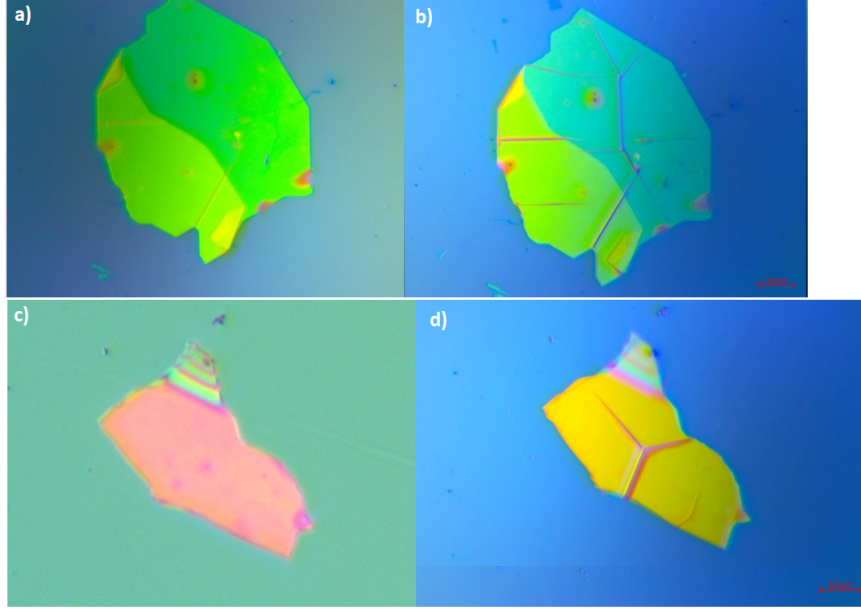


Figure 4.5: Optical images of two flakes before (**a.** and **c.**) after (**b.** and **d.**) annealing. The red scale bars in the lower right corner of **b** and **d** indicate $10\ \mu$.

We have seen that wrinkling of hBN flakes by thermal treatment was possible but as we tried the same annealing process on different stacks of graphene/hBN we never succeeded to obtain anything that looked like thermally activated wrinkles. The closest we came is with the flake from Figure 4.2 that is shown after annealing in Figure 4.6. If we compared to the images before annealing we see that a new wrinkle has appeared in the red rectangle of Figure 4.6a on which we have zoomed in in Figure 4.6b. The height profile in Figure 4.6c follows the white line in Figure 4.6b. We see that the wrinkle has a width around $200\ \text{nm}$ and a height of approximately $15\ \text{nm}$. Also when observing the darker areas left to the wrinkle in Figure 4.6b it could be looking as if the graphene was ripped after wrinkling so that we would actually be looking at the hBN beneath. According to our measurements the difference in height between the darker area and the lighter area we suppose is graphene is approximately $1.5\ \text{nm}$ which could very well be the thickness of the graphene sheet.

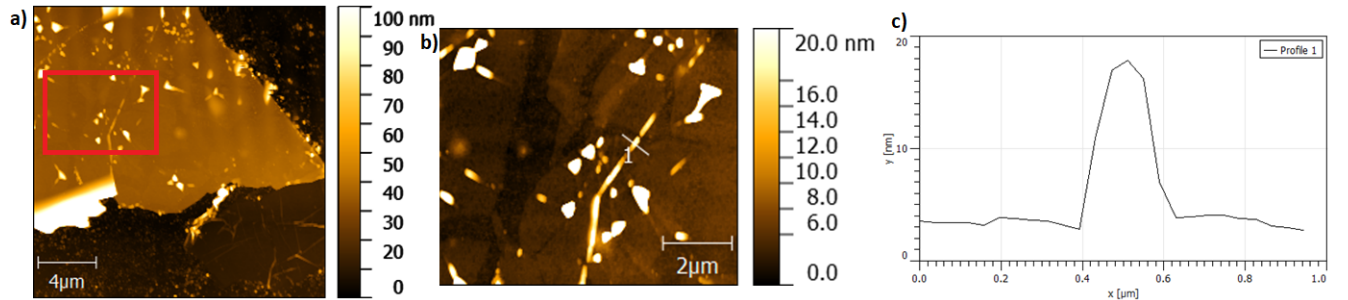


Figure 4.6: Optical images of two flakes before (**a.** and **c.**) after (**b.** and **d.**) annealing. The red scale bars in the lower right corner of **b** and **d** indicate $10\ \mu$.

Although this result is approaching what we were hoping for it is, as mentionned earlier, the only one of our stacks that showed any form of wrinkling. Even the hBN not covered by graphene in the other stacks did not wrinkle as can be seen in the AFM images of Appendix A.

4.4 Change of substrate

The lack of wrinkles in our stacks is what lead us to change the substrate material. As our hypothesis is that the wrinkling is due to a difference in thermal expansion coefficient (TEC) between the positive one of the substrate and the negative one of the hBN we thought that by increasing the TEC of the substrate the wrinkling effect might be stronger. We therefore used barium fluoride (BaF_2) as substrate instead of the conventionnal SiO_2/Si going from a TEC of $3 \times 10^{-6}/^\circ\text{C}$ to one of $18.1 \times 10^{-6}/^\circ\text{C}$. The result was pretty spectacular as can be seen in Figure 4.7 where we observe a flake on BaF_2 before and after annealing. The wrinkle density is extremely high compared to samples on SiO_2 and that was the case on all the flakes we observed.

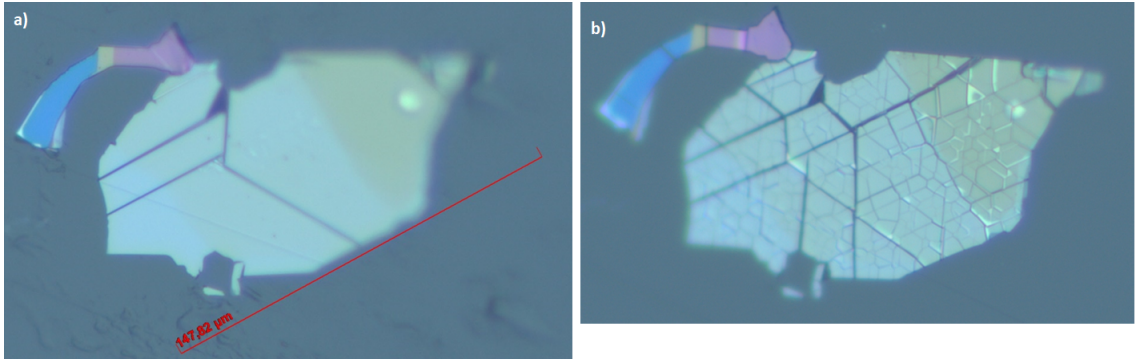


Figure 4.7: Optical images of an hBN flake on BaF_2 substrate before (a.) and after (b.) annealing.

With such a high wrinkle density we decided to test the influence of a plateau at the maximum temperature during the annealing process. We therefore annealed a sample at 990°C under Ar/H_2 atmosphere with a cooling rate of $10^\circ/\text{min}$ but without plateau then we annealed the same sample with the same annealing parameters but adding a 25 min plateau at the maximum temperature. The two heating profiles can be seen in Figure 4.8.

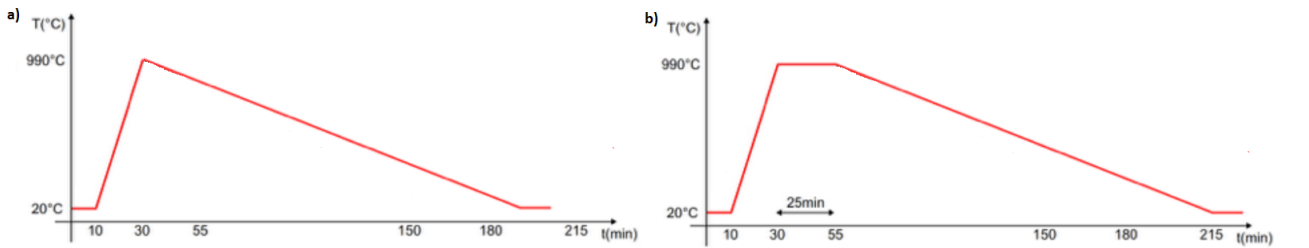


Figure 4.8: Heating profiles of an annealing at 990°C with a cooling rate of $10^\circ/\text{min}$ and no plateau (a.) or a 25 min plateau (b.).

The results on two hBN flakes can be seen in Figure 4.9. We see that wrinkles already appear after the annealing without plateau. After the second thermal treatment some of these wrinkles seem to have disappeared while new one have been created, completely modifying the wrinkle structure on both flakes. It therefore seems like the wrinkle structure can not be considered as in a stable thermodynamical equilibrium as the wrinkles evolve when thermal energy is added to the system.

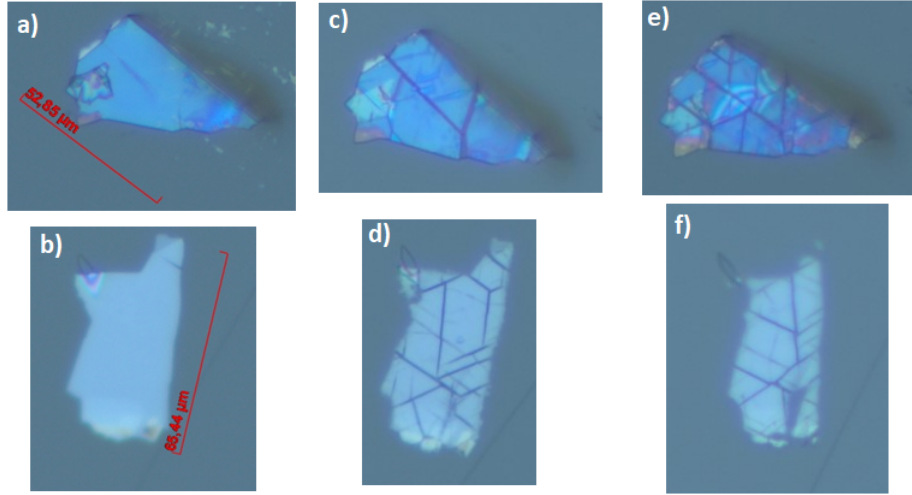


Figure 4.9: Optical images of hBN flakes on BaF₂ substrate before (**a.** and **b.**), after annealing without plateau (**c.** and **d.**) and after annealing with a 25 min plateau (**e.** and **f.**).

As it seemed that the wrinkling was way more effective on BaF₂ we tried to fabricate a stack on SiO₂ and transfer it onto a BaF₂ substrate. In Figures 4.10 a and b we see optical images of the hBN flake and the graphene sheet that were used for the stacking while the final stack on BaF₂ can be seen in Figure 4.10c. The area highlighted by the red line is where the graphene sheet has been picked up.

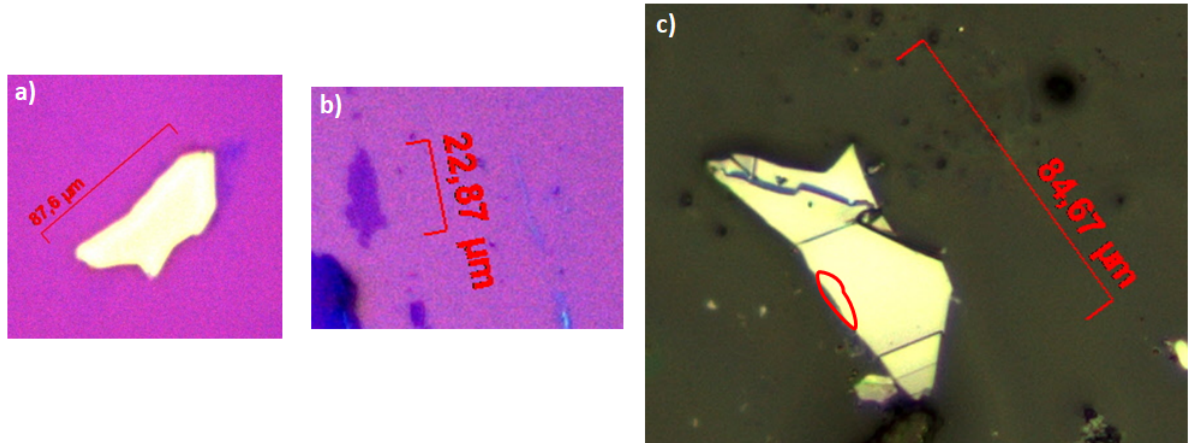


Figure 4.10: Optical images of an hBN flake (**a.**) and a graphene sheet (**b.**) used to make the stack in **c.** that was transferred onto a BaF₂ substrate. The region highlighted by the red line is where the graphene is to be found.

This sample was then annealed at 990° with a cooling rate of 10°/min. AFM images of the area with the graphene before and after annealing are shown in Figures 4.11 a and c while Figures 4.11 b and d show the height profile of a wrinkle before and after annealing, following the white lines in a and c respectively. We see that the annealing does not seem to have affected either the graphene sheet or the wrinkle in any major way. The wrinkle is a little bit higher and a little less wide but the difference is barely noticeable. What is even more strange is that the rest of the flake does not present any wrinkles at all which is very different from the behaviour we observed with hBN flakes simply exfoliated onto BaF₂. Even more so as other flakes also were transferred during the process and none of them presented any wrinkles either. This made us think that there might be an issue with the contact between the flakes and the substrate after the transfer process. The most obvious reason would be that after the cleaning part of the stack flip some PPC remains between the flakes and the substrate and thus prevents the wrinkling from happening. We also see that the surface of

both the hBN and the graphene seem to be more granular after annealing. We believe that this is not a physical phenomenon but rather an artefact of the AFM as there were days where all the AFM images we made had similar features.

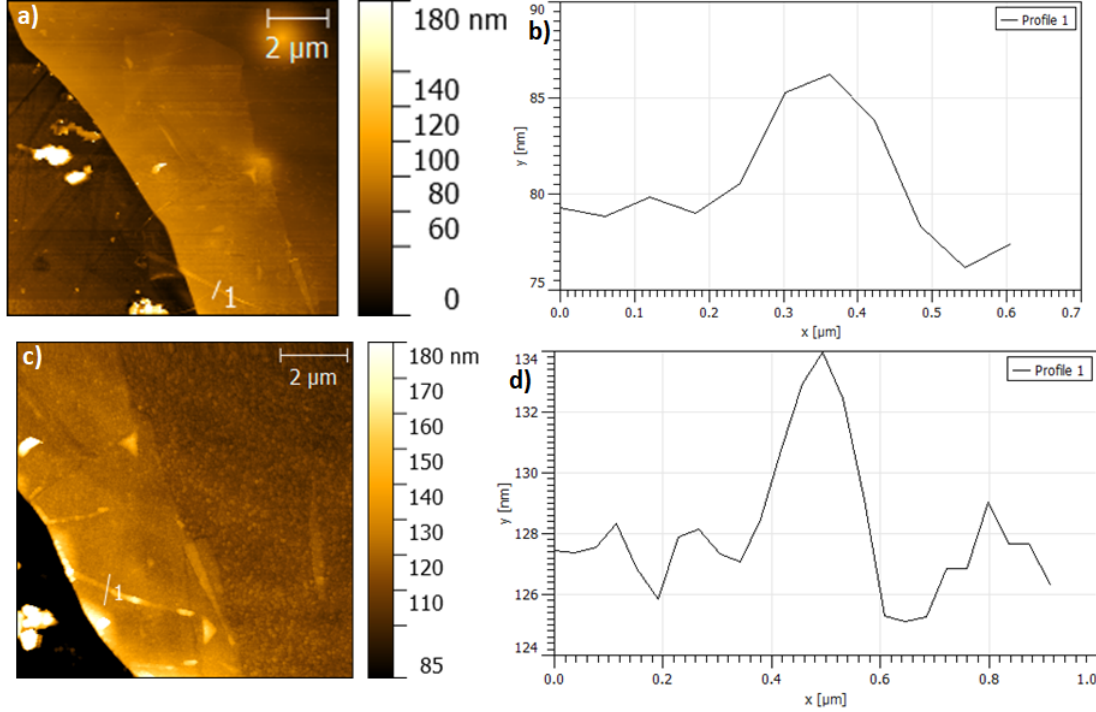


Figure 4.11: **a.** and **c.** AFM images of the stack in Figure 4.10 before and after annealing respectively. **b.** and **d.** show the height profiles following the white lines in **a** and **c**.

4.5 Encapsulated graphene

To avoid a possible contact issue between flake and substrate we decided to try to make consisting of hBN on graphene on hBN and thus creating an encapsulated graphene sample. To do so we could follow the normal transfer process described in Section 3.2 until the point where a stack of graphene on hBN has been picked up and is trapped in the PPC on the transfer blade. Then instead of doing a stack flip to transfer the stack onto a substrate we simply deposit it on another hBN flake that has been exfoliated directly onto the substrate. This way we avoid any risk of PPC remaining between the stack and the substrate. To deposit the graphene/hBN stack we follow the same steps as to pick up the graphene sheet. The flakes are alligned under the microscope and then contact is established thermally by heating up the transfer stage. But this time instead of cooling down the sample to do a pick-up we simply lift the transfer blade while the PPC is still warm. As the PPC has expanded the grip on the stack should be pretty loose and the stack should remain on the targeted hBN flake.

Figures 4.12 a and c show the hBN flakes we used for our encapsulated graphene stack while Figure 4.12c is an optical image of the graphene sheet. As the hBN flakes had to be stacked on each other it was even more important to use as thin flakes as possible to increase the chances of them wrinkling after annealing. We used the flake in Figure 4.12a to pick-up the graphene and then we deposited the stack on the flake in Figure 4.12c. An optical image of the final stack is shown in Figure 4.12d while Figure 4.12e displays an AFM image of it. As the flake was too big to be imaged in one AFM picture we had to use two images to get the full stack. It is worth noting that we can actually see the graphene sheet between the two hBN flakes even in the optical image which is a good indication that the chosen hBN is very thin just as we wanted it to be.

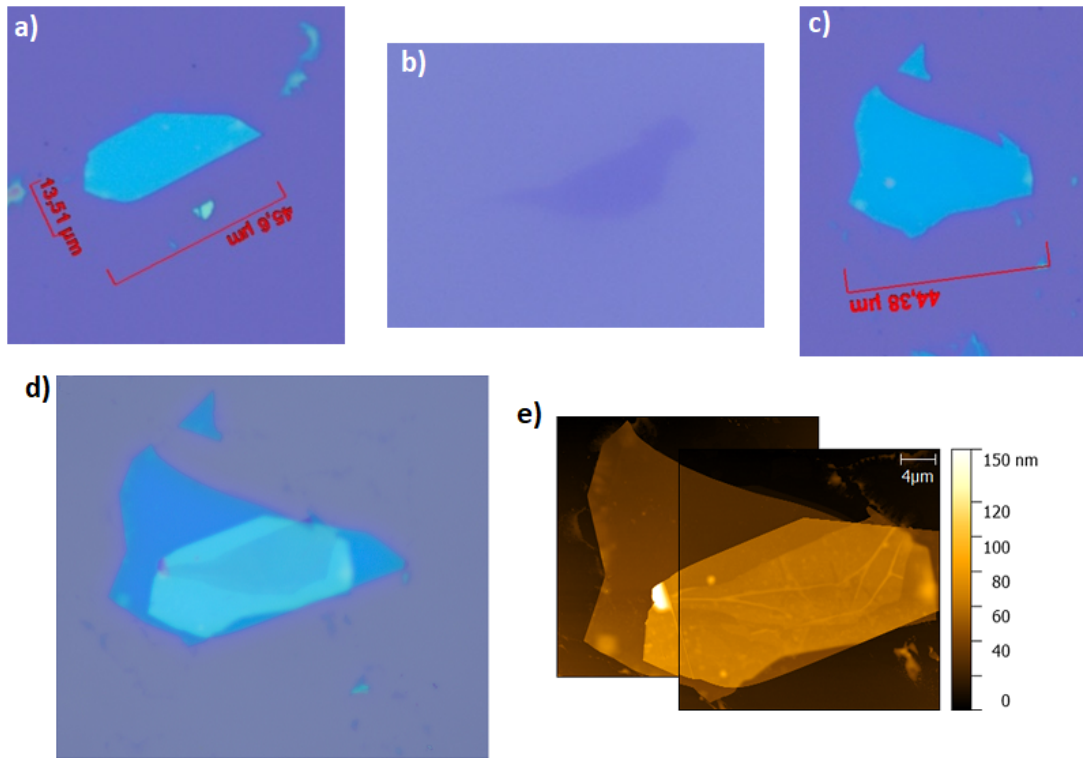


Figure 4.12: Optical images of the top hBN flake (**a.**) the graphene sheet (**b.**) and the lower hBN layer (**c.**) used to fabricate the encapsulated graphene stack in **d.** In **e.** is an AFM image of the stack.

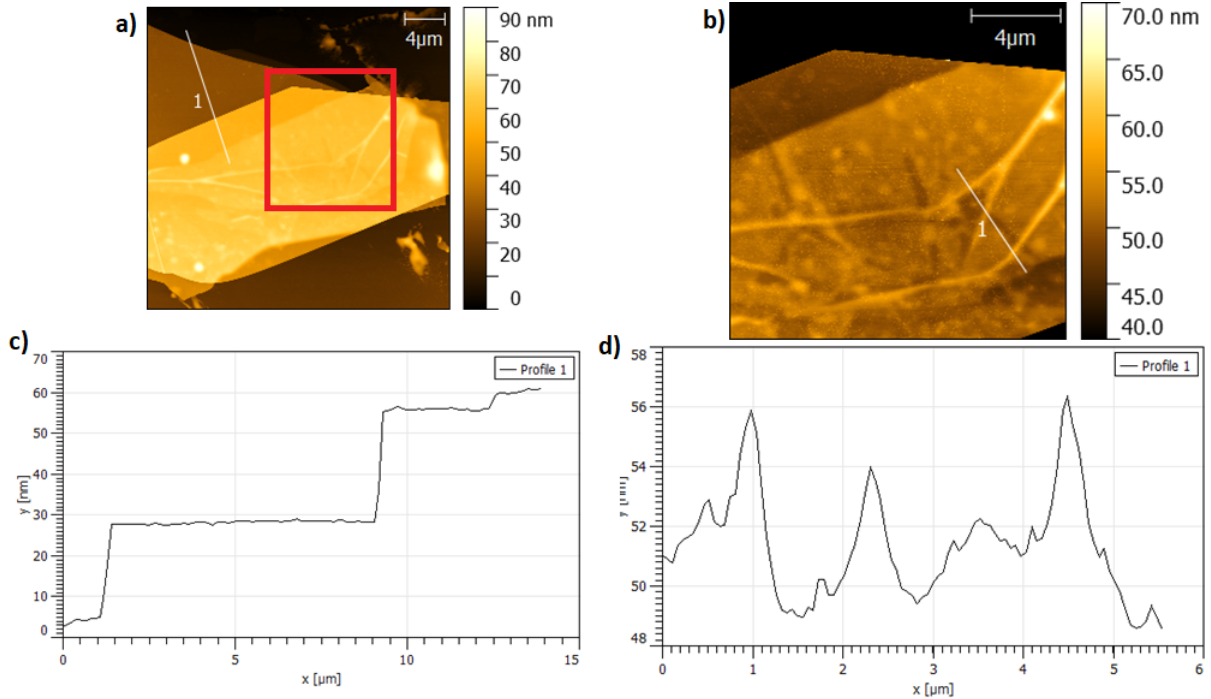


Figure 4.13: **a.** AFM image of the encapsulated graphene. **b.** Close up AFM image on the red rectangle in **a.** **c,d.** Topographic profiles of the stack following the white lines in **a** and **b** respectively.

In Figure 4.13a we get a closer look at the encapsulated graphene and following the white line we get at topographic profile of the stack in Figure 4.13c. We see that both hBN flakes are around 20-30 nm thick while the graphene is around 4 nm in thickness which probably makes it a triple layer graphene sheet. It is interesting to see that even though the graphene lies under the top hBN flake it still deforms that top layer enough to be detected by our AFM. In Figure 4.13b we find an AFM image of the area in the red rectangle in Figure 4.13a while Figure 4.13d gives us the height profile following the white line in Figure 4.13b. We see that the graphene sheet seems to have multiple wrinkles and since this time the whole graphene sheet was picked up the wrinkles probably did not happen during the stacking process but rather during the exfoliation.

The stack was annealed at 990°C under Ar/H₂ with a cooling rate of 8°/min as we wanted to go back to the standard annealing process. The stack is shown after annealing in Figure 4.14a with the topographic profile following the white line given in Figure 4.14c. Figure 4.14b displays a close up look at the area with graphene and in Figure 4.14d is the corresponding height profile. We see that there is a new wrinkle with a height around 500 nm according to Figure 4.14c but it does not really look like the typical thermally activated wrinkles of [15]. On the other hand it is interesting to observe that the wrinkles that existed in the graphene seem to have almost completely disappeared after annealing except for the one we see in Figure 4.14d. The profile of this wrinkle is pretty similar to those of the wrinkles we found before annealing.

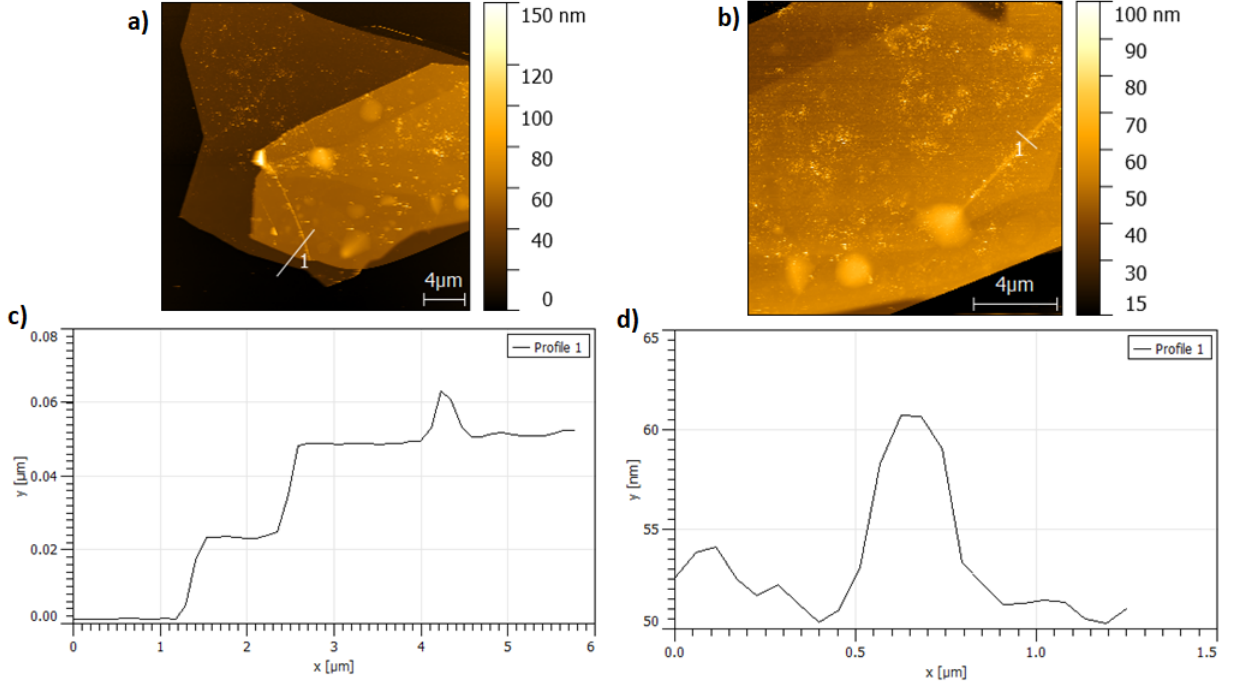


Figure 4.14: **a.** AFM image of the encapsulated graphene after thermal treatment. **b.** Close up AFM image on the area containing graphene. **c,d.** Topographic profiles of the stack following the white lines in **a** and **b** respectively.

4.6 Backside of a wrinkled flake

As we were not able to obtain wrinkles in our stacks we wanted to try to understand the wrinkling effect in more detail. One of the things we wanted to find out is whether the wrinkles we see at the surface of a flake are also present on the backside of this flake. We therefore used a flake that had been annealed at 990°C under N₂ atmosphere with a cooling rate of 10°/min and that showed a very typical thermally activated wrinkle. The flake is shown in Figure 4.15a. We proceeded to pick-up the flake with a transfer blade in order to take pictures of the backside of the flake. The result can be seen in Figure 4.15b. We observe that one of the three wrinkles, the one that seem biggest, can actually

be seen on the backside of the flake and is indicated by the red arrow. It is possible that the other wrinkles also exist on the backside of the flake but that they are too small to be seen with the optical microscope. To find out we wanted to get an AFM image of the flake which would also have given us more information on the depth of the wrinkle we can see. Sadly the transfer blade was too big for the AFM and we were not able to get the image we wanted. What is very interesting though is that when we look at the frontside of the flake on the blade we see that the wrinkle has disappeared as shown in Figure 4.15c. This means that the PPC has probably pressed down on the wrinkle causing its vanishing. The fact that we are still able to see the wrinkle on the backside of the flake even after the wrinkle has been flattened could signify that the wrinkle might actually have been way deeper on the backside than what we are able to see here.

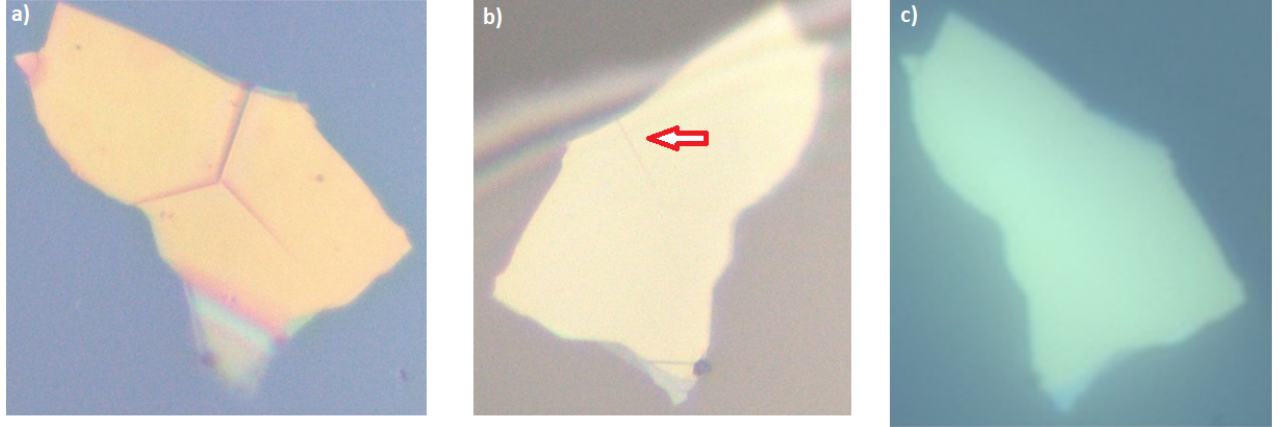


Figure 4.15: Optical images of a wrinkled hBN flake after annealing (a.) and the backside of the same flake after pick-up on a transfer blade (b.)

4.7 Change of flake material

Another experiment we wanted to conduct was to find out whether the wrinkling effect was characteristic of hBN or if it could be expanded to other materials. We therefore exfoliated graphite onto BaF_2 as we have seen that the wrinkling is easier to observe on that substrate compared to SiO_2 . We obtained multiple flakes of all types of size and shape as can be seen in Figure 4.16.

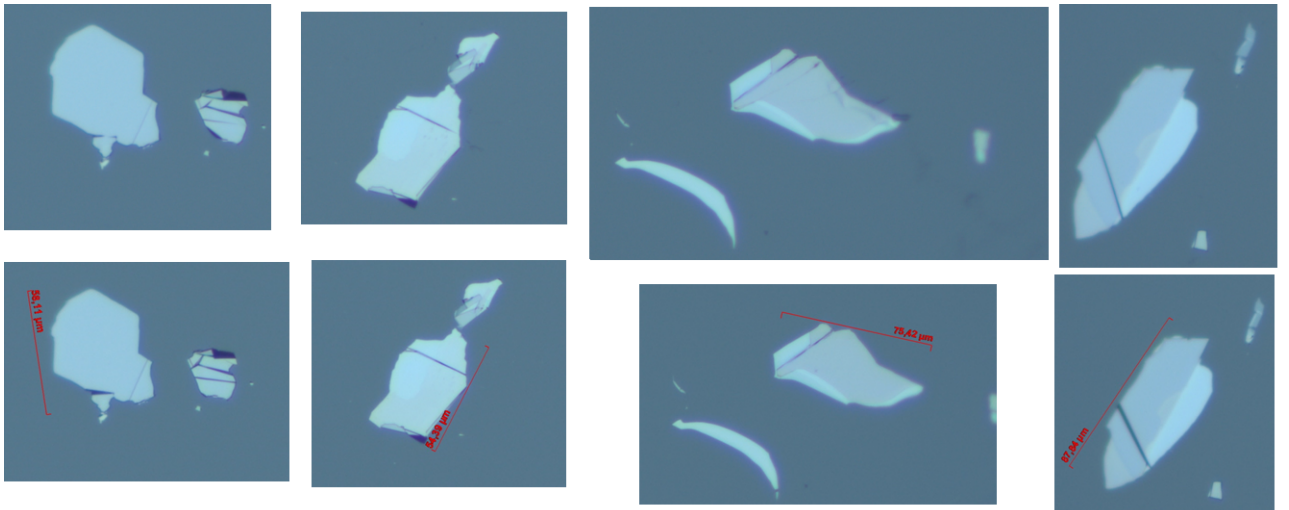


Figure 4.16: Optical images of graphite flakes on BaF_2 substrate before annealing.

Each flake is shown before annealing in the first row then after annealing in the second. As BaF_2 is transparent there is way less colour contrast between the flakes which makes it more difficult

to estimate their thickness but we assume that it varies just as much as for hBN. The sample was annealed at 990°C under N₂ atmosphere with a cooling rate of 10°/min. After annealing we found that absolutely none of the graphite flakes presented any wrinkles. To be sure there were no problem with the RTA we thus annealed the sample again alongside a sample with hBN exfoliated on BaF₂. The flakes on the second sample had plenty of wrinkles just as expected but again there were none to be found on the graphite flakes. This was a highly unexpected result as graphite and hBN are very similar as we saw in Table 3.1. As graphite has a negative thermal expansion coefficient that is higher than the one of hBN in absolute value we actually expected the wrinkling to be more accentuated.

4.8 Discussion

Wrinkle formation

As we have seen the wrinkling phenomenon of hexagonal boron nitride and graphene is still far from well understood and raises a lot of questions. Even so it does seem to be confirmed that it is closely linked to thermal strain given by $\epsilon = \alpha\Delta T$ with α the thermal expansion coefficient (TEC) and T the temperature.

Indeed we have seen that the maximum annealing temperature plays an important role in the wrinkling since there were no wrinkles to be found when this temperature was lowered. This suggests that there is a minimum temperature that has to be exceeded in order for the wrinkling to happen. This makes a lot of sense with the hypothesis of thermal strain since that would mean there is a minimum strain required for the flakes to induce the formation of wrinkles. Furthermore we saw that the change of substrate and thus of thermal expansion coefficient had a huge impact on the wrinkling. Again a higher TEC means a higher strain which could perfectly well increase the wrinkle density on each flake as we observed. It is of course important to mention that by changing the substrate we also change other parameters that concern the contact between flake and substrate such as friction and adhesion. These parameters almost certainly play an important role in the wrinkling phenomenon and can not be neglected but they are extremely difficult to characterize as they concern the interface between micrometer sized objects.

We have also seen that the atmosphere has an influence on the wrinkling process. In fact, when annealed under ultra high vacuum there were no evidence of any wrinkles on the annealed flakes. We believe that this is due to the fact that the atmosphere will affect the heating of the sample inside the RTA. By using vacuum we take away the heating by convection thus the heating of the samples will be less effective and they might not reach the targeted temperature. This could make an important difference in our case since we have seen that there is a threshold temperature that has to be exceeded for the wrinkling to happen. The choice of atmosphere is even more crucial when using BaF₂ as substrate. This material is indeed completely transparent to infrared heating meaning that if there is no heating by convection via a gaseous atmosphere the samples will not be heated at all.

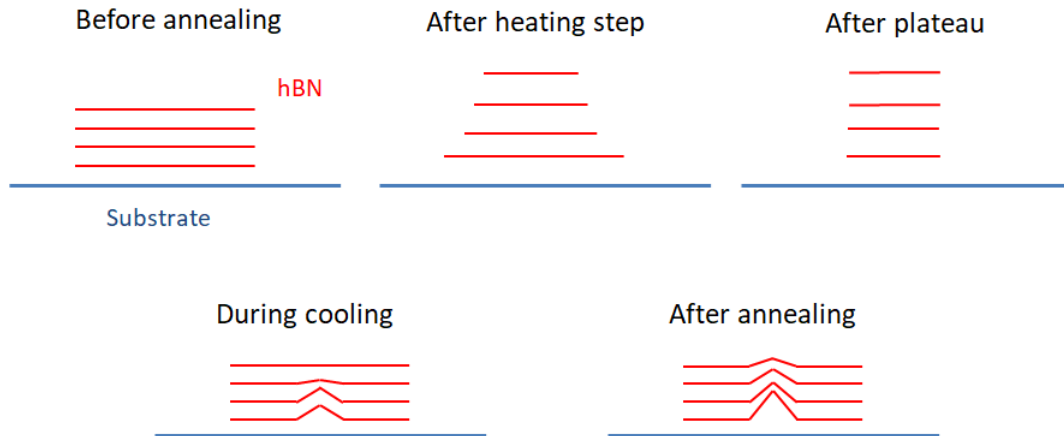


Figure 4.17: Cartoon of the proposed scenario of the wrinkling process during thermal treatment

With these observations it seems fair to assume that the wrinkling effect is closely linked to thermal strain. But one obvious question then comes to mind. Why is thermal reaction of the flakes not elastic? Since the samples are heated up and then brought back to their original temperature it would seem logical to think that they would come back to the exact same state as they were before thermal treatment as the strain created during heating would be canceled out during cooling resulting in a final unexisting strain. Instead the surfaces of the flakes are deformed by wrinkles. The scenario we propose based on our observations and on the previous work in [41] is depicted in Figure 4.17. We believe that at high temperatures, somehow, the flakes, whose size tends to shrink while the substrate is expanding, have to slide and contract with respect to the substrate as soon as their elastic deformation becomes insufficient to accomodate the expansion of the substrate. This relative dissipative sliding or slipping motion may take some time to occur (which would explain that the plateau length has an effect on the wrinkling). Then upon cooling the sliding motion becomes less favourable than at high temperature. Therefore, as the substrate is contracting and the flake is anchored on the substrate, the only way to accomodate the constraint is to deform in the out-of-plane direction and form wrinkles. This is what we see in Figure 4.17. Before annealing there is a multilayer hBN flake on a substrate. Then at the end of the heating we see that the layers are further apart due to the thermal expansion coefficient in the out-of-plane direction of hBN which is quite high. Also the top layers have contracted but as the bottom layer was anchored to the substrate the expansion of the latter has made it impossible for this layer to shrink as much as the others. This is the moment where we believe that over a certain threshold temperature the bottom layer will begin to slide on the substrate and thus be able to shrink as the other layers. If the plateau at maximum temperature is long enough the bottom layer will then have time to shrink as much as the others and we would end up with a situation as the one we can see after the plateau. Then during the cooling at some point the sliding motion will become less favourable and the bottom layer will again be anchored to the substrate. To accomodate the constraint created by the shrinking of the substrate it will then have to deform and create wrinkles just as in the case of an isotropic compression showed in the model of Section 2.3. As the height of the wrinkles increase, the wrinkling will propagate to the top layers and if the flake is not too high they will be observable and the surface at the end of the annealing process.

This theory can explain the results of Figure 4.9 that shows flakes with wrinkles after a thermal treatment without plateau. In fact, even if there is no plateau the flakes will still be able to slide on the substrate and contract once the temperature is high enough which might be enough for the wrinkling to happen. Still, the results also suggest that the plateau has some kind of influence on the wrinkles since the wrinkle patterns change after a second annealing with a 25 min plateau. Again this makes sense as the bottom layer of the flake will have more time to shrink during the plateau and thus the final wrinkles will be affected.

The key element, in addition to the temperature of course, to the wrinkling process is then the contact between substrate and flakes and more precisely the adhesion between the two surfaces. We do not have any certainties on why the flake would be able to slide on the substrate at high temperatures but we believe it could be linked to the thermal expansion coefficient in the c-direction. As mentioned the one of hBN is quite high with a value of $38 \times 10^{-6}/^{\circ}\text{C}$ which supposedly means that at high temperature the distance between the bottom layer of hBN and the substrate will be strongly increased. This might be enough to reduce the adhesion between the two surfaces enough for the bottom layer to be able to shrink.

A flake/substrate contact issue could very well explain the lack of wrinkles in our transferred stacks which is particularly strange in the case where we used BaF_2 as substrate since we have seen that this highly increases the wrinkling but none of the transferred flakes presented any form of wrinkles. In fact, the contact between the stack and the substrate after a transfer process might very well be completely different from the contact after exfoliation. It is possible that there are some remains of PPC that does not completely disappear after the transfer and thus modify or entirely removes the direct contact between the flakes and the substrate. Still, the interface adhesion is not able to explain all our results since we did not manage to create wrinkles in our encapsulated graphene in which the bottom layer was exfoliated onto the substrate.

To figure out which other parameters could have an impact we tried changing the flake material by using graphite instead of hBN. The two materials having very similar hexagonal structures with almost identical lattice parameters and in plane thermal expansion coefficients, we believed that the results after thermal treatment would be almost identical and we then wanted to extend the tests to other two dimensional materials to see wheter the wrinkling could actually apply to a multitude of materials. We were therefore quite astonished when we had to admit after multiple tries that there were no wrinkles to be found at the surface of the graphite flakes. Once again the adhesion between substrate and flake could be to blame for the lack of wrinkles but it seems unlikely. Indeed, it has been shown that the adhesion forces at the surface of an hBN flake and a graphite flake are very similar. [43] This study was conducted on the adhesion between these flakes and an epoxy resin so the result might not be relevant to our case with an hBN crystal but still it seems to suggest that the surfaces of the two materials have similar adhesion properties. It could still be that some interaction with the BaF₂ substrate makes the adhesion with graphite completely different from the one with hBN but it seems likely that another parameter comes into play. This could for example be some kind of interlayer interactions within the layers of the flake material. Even though the interlayer distances are almost identical in both materials and even though it has been shown [44] that the interlayer van des Waals forces are very close, there is one property that varies between the two materials which is the thermal expansion coefficient in the direction of the c-axis. While the one of hBN is constant and worth $38 \times 10^{-6}/^{\circ}\text{C}$, the TEC in the c-direction varies with temperature as shown in Figure 4.18 where the different curves show the results of different theoretical and experimental models used to calculate the TEC. More detail can be found in [33].

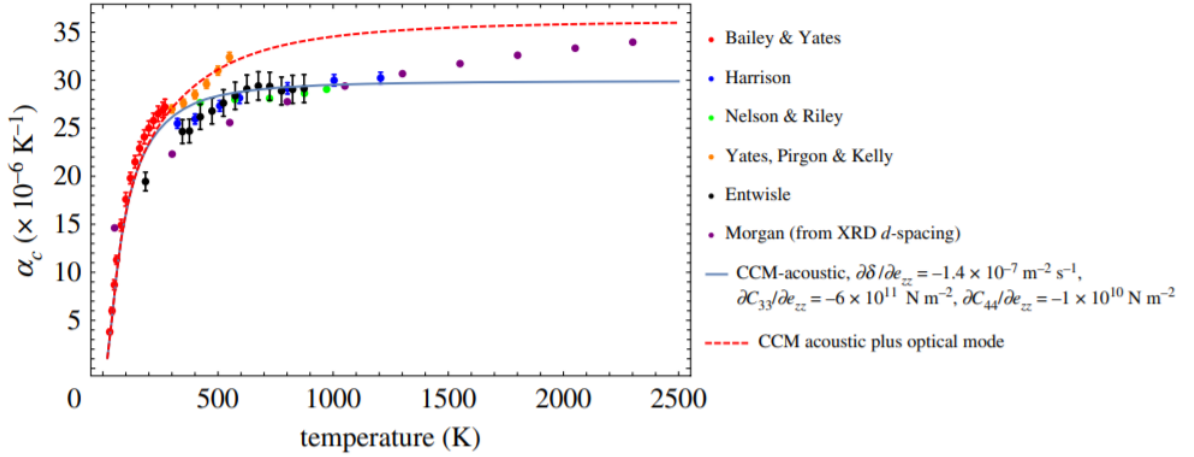


Figure 4.18: Layout of the evolution of the thermal expansion coefficient of graphite with temperature according to different models and experiential studies. [33]

This means that even though the interlayer spacing of the two materials are very similar at ambient temperature, it will grow way faster during heating in the case of hBN since the TEC of graphite is quite low at lower temperatures. We believe that this could very well have an effect on the interlayer interactions which would then affect the wrinkling process.

Interlayer wrinkle structure

Another question we have tried to answer is the how wrinkles are structured within the flakes. The three main possibilities we had in mind are shown in Figure 4.19.

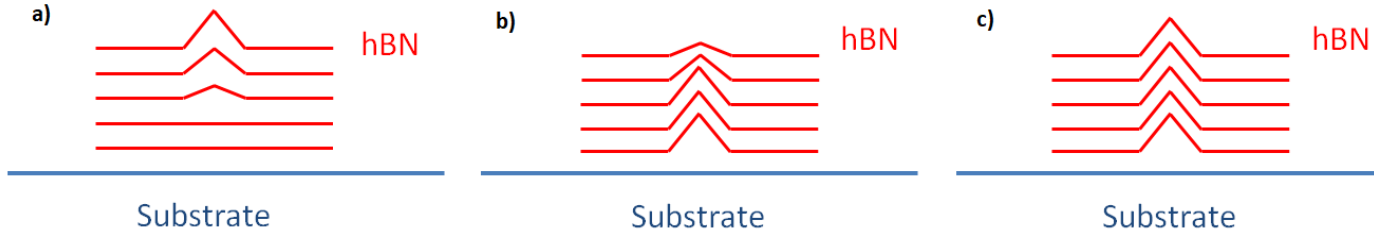


Figure 4.19: Cartoons of the structure of a wrinkle within the layers of hBN flake **a.** if only the top layers are wrinkles, **b.** if the wrinkling starts at the bottom layer of the flake and decreases through the layer and **c.** if the wrinkles are constant in all the layers.

In the first case shown in Figure 4.19a the wrinkling starts in the top layer of the flake and only a few layers on the top of the flake have any wrinkles. In the second case of Figure 4.19b the wrinkling has its origin in the bottom layer and the layers above present smaller and smaller wrinkles the further away they are from the substrate. The third case presented in Figure 4.19c also shows a wrinkling that starts in the bottom layer but this time all the layers above are wrinkled the same way as the bottom one so that the width and height of the wrinkle does not change from layer to layer. Based on the fact that the backside of a wrinkled flake showed a similar pattern as the wrinkled side (Figure 4.15) it seems safe to say that the wrinkles appear in all the layers of the flake. Furthermore, in previous work [41] it was shown that the height of the flakes plays an important role in the wrinkling and that over a certain thickness it is very rare to observe thermally activated wrinkles. This leads us to believe that the size of the wrinkles has to decrease from layer to layer going upwards from the bottom and thus the wrinkles would have an internal structure as the one shown in Figure 4.19b. That way it makes sense that if the layers in a flake exceeds a certain number and thus a certain height of the flake the wrinkles will no longer appear at its surface. This would also be coherent with the wrinkling scenario we presented in Figure 4.17.

Wrinkles in graphene

One of the objectives of this master thesis was to create wrinkled graphene sheets by wrinkling the hBN substrate on which we had transferred them with a thermal treatment. As we have seen this was not achieved due to problems with the wrinkling of hBN flakes after transfer. That being said we still managed to create graphene/hBN stacks and we observed that in all the stacks we made it was extremely rare to find a graphene sheet that did not have some sort of corrugations, wrinkles or folds. As the whole idea of using hBN as a substrate for graphene is to get as plane a graphene sheet as possible to optimize its properties, the presence of all these completely uncontrolled irregularities is rather problematic. The irregularities could already be present after the exfoliation but it seems more likely that they appear during the pick-up as most of the time only parts of the targeted graphene flake are ripped off and stay attached to the hBN flake. The pick-up might therefore not be improved to try to avoid this problem for example by systematically selecting graphene sheets so that they are smaller than the hBN flakes and thus increasing the chances of picking up the whole sheet without ripping it. Even though when we succeed to do such a pick-up we have seen that the graphene still sometimes present different irregularities.

Another thing we observed was that the annealing process did not seem to affect the graphene sheets in any way. One could have expected that the graphene would create wrinkles of its own during the thermal treatment since it also has a negative thermal expansion coefficient. But if we assume as said above that the adhesion with the substrate is crucial for any wrinkling to happen it makes sense that the graphene sheet did not show any new wrinkles since it has been shown that the graphene-hBN adhesion is very low. [45]

There is one exception though where we saw wrinkles disappear from a graphene sheet which is the case of encapsulated graphene. Here we saw wrinkles with a height of 5 nm (which was comparable to the thickness of the graphene sheet itself) completely vanish after the thermal treatment, resulting in

a graphene sheet that looks almost perfectly flat. We believe that this must be due to the presence of the second hBN layer on top of the graphene sheet. We imagine that during the heating of the sample, as an already wrinkled graphene sheet is being compressed due to its negative TEC, the compression will tend to increase the height of the pre-existing wrinkles. This could be made impossible by the top hBN layer that would be blocking the increase of the wrinkling and thus keeping the wrinkles at their original size. Then during cooling, as the graphene sheet expands these wrinkles that have not increased in size will not go back to the size they had before annealing as in an elastic reaction but instead would be flattened out by the expansion of the graphene sheet resulting in a final flat sheet. Of course since we can not image the graphene sheet directly buth only through the top hBN layer it might also be that the graphene underneath is still wrinkled but the hBN layer does not show these wrinkles anymore after the annealing process.

Conclusion and perspectives

In this work we have studied stacks of graphene on hexagonal boron nitride and more precisely the wrinkling of such stacks due to thermal treatment. Our purpose was to try to understand the thermally activated wrinkling process of hexagonal boron nitride then study the effect on a stack of graphene transferred onto an hBN flake. The long term goal was to obtain graphene sheets with wrinkles that could be controlled by modifying the annealing process and to study how these local defects would affect the electronic properties of the graphene sheet.

To study the wrinkling process we exfoliated hBN onto two different substrates and applied different thermal treatments to observe how the wrinkle density and their aspect ratio would be affected. We also transferred graphene onto hBN flakes and then deposited these stacks on the two same substrates by stack flip method before annealing them to try to obtain wrinkled graphene. We then created a stack of encapsulated graphene between two hBN stacks on a SiO_2/Si substrate, once again to see how the thermal treatment would affect the stack. Finally we tried to use another two dimensional material in the form of graphite instead of hBN to see if the wrinkling phenomenon could be expanded to other materials. The different flakes and stacks were characterized by optical microscope and atomic force microscope in standard tapping mode.

The explanation of the wrinkling process in the literature was based on thermal strain $\epsilon = \alpha\Delta T$. This seems to have been confirmed by our experimental results as both the maximum annealing temperature and the thermal expansion coefficient of the substrate have shown to greatly affect the wrinkling of the hBN flakes. Based on our results we have found that the contact between flakes and substrate and more specifically the adhesion is of crucial importance for the wrinkling to happen. Furthermore the interlayer interactions in the flakes themselves also seem to play a dominant role in the appearance of wrinkles as our experience with graphite pointed to. Other parameters have shown to affect the wrinkling but not so much the existence of wrinkles after annealing as their pattern and aspect ratio. These parameters are the length of the plateau at maximum temperature and the cooling rate of the heating profil. We have also been able to show that the wrinkles originate in the bottom layer of the flake then decrease in the layers above making the thickness of the flakes another important parameter for the wrinkles to be observable at the surface of the flakes. Finally we have seen that it might be possible to straighten out wrinkled graphene by encapsulating it between hBN flakes and apply a thermal treatment.

It goes without saying that the results we have presented here still need more testing to be confirmed and for the wrinkling phenomenon to be fully understood. We have merely identified some properties and parameters that we believe are important without trying to establish a real model of the process. To further study the wrinkling process an important step would be to find a way of studying the adhesion between the different materials used as flakes and those used as substrate. It would also be interesting to try using other two dimensional materials as flakes to see how they react to the thermal treatment.

Concerning the study of wrinkled graphene as was the long term goal of the project there are different possibilities. The first would be to create an encapsulated stack as the one we made here

but on a BaF_2 substrate instead of the SiO_2/Si . There are better chances to obtain wrinkles on that substrate and if none appear it might help identify other properties that are essential for the wrinkling to happen. Another idea would be to start by annealing exfoliated hBN to get wrinkles then transfer graphene onto the wrinkled flake. That transfer would also have to be done by creating a stack of encapsulated graphene. That way it might be possible to obtain a graphene sheet following the wrinkled hBN surface that could then be contacted and studied in terms of electronic properties.

AFM images

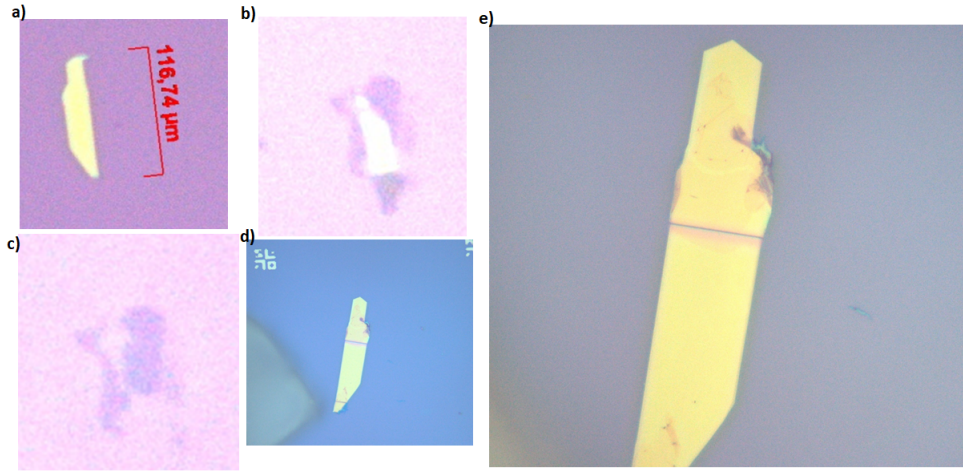


Figure A.1: Optical images of **a.** the hBN flake used for the stack **b.** the hBN flake aligned with the targeted graphene flake during pick-up **c.** the graphene remaining after the pick-up **d.** the final stack on a SiO_2 substrate and **e.** a zoom in on the final stack.

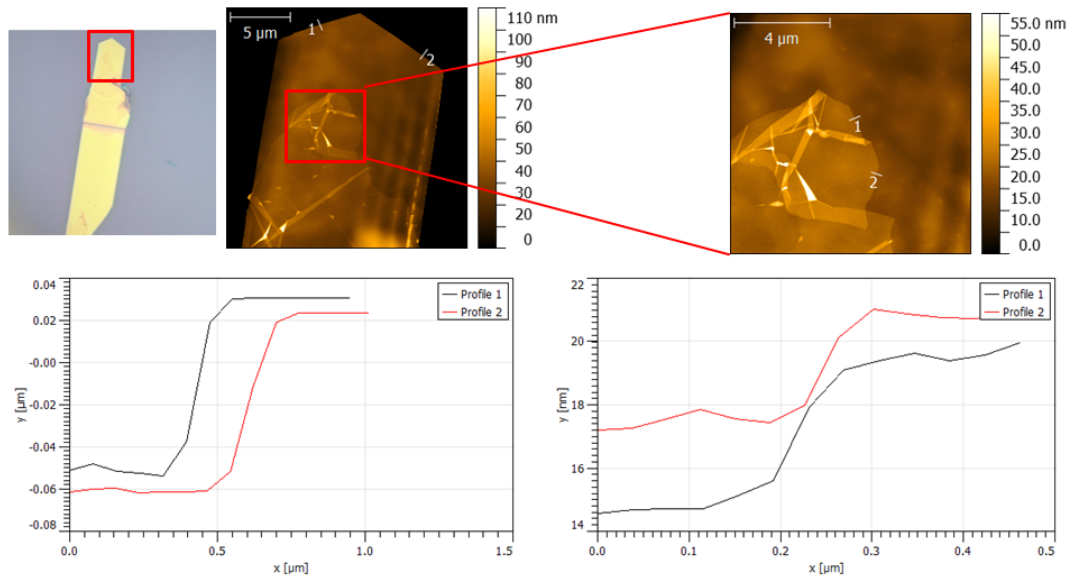


Figure A.2: AFM images and corresponding height profiles of the area in the red rectangle in the optical image.

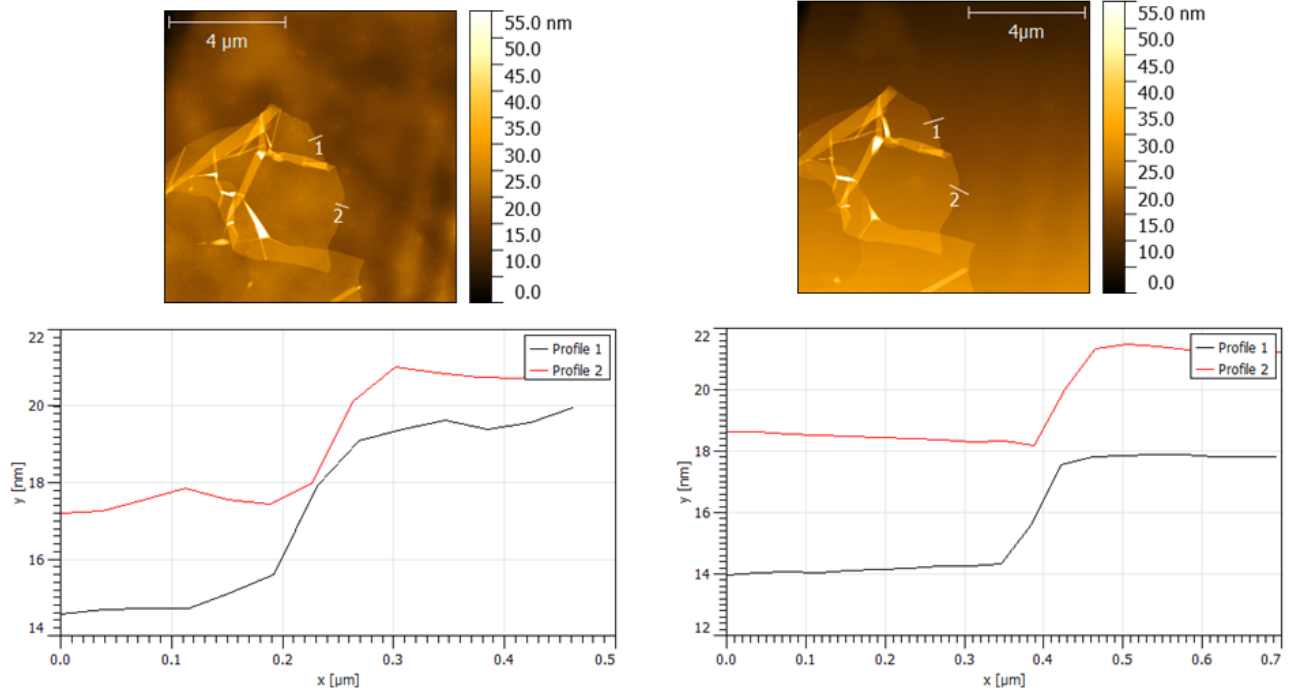


Figure A.3: Comparison of AFM images of a graphene flake before (left) and after (right) annealing and the corresponding height profiles.

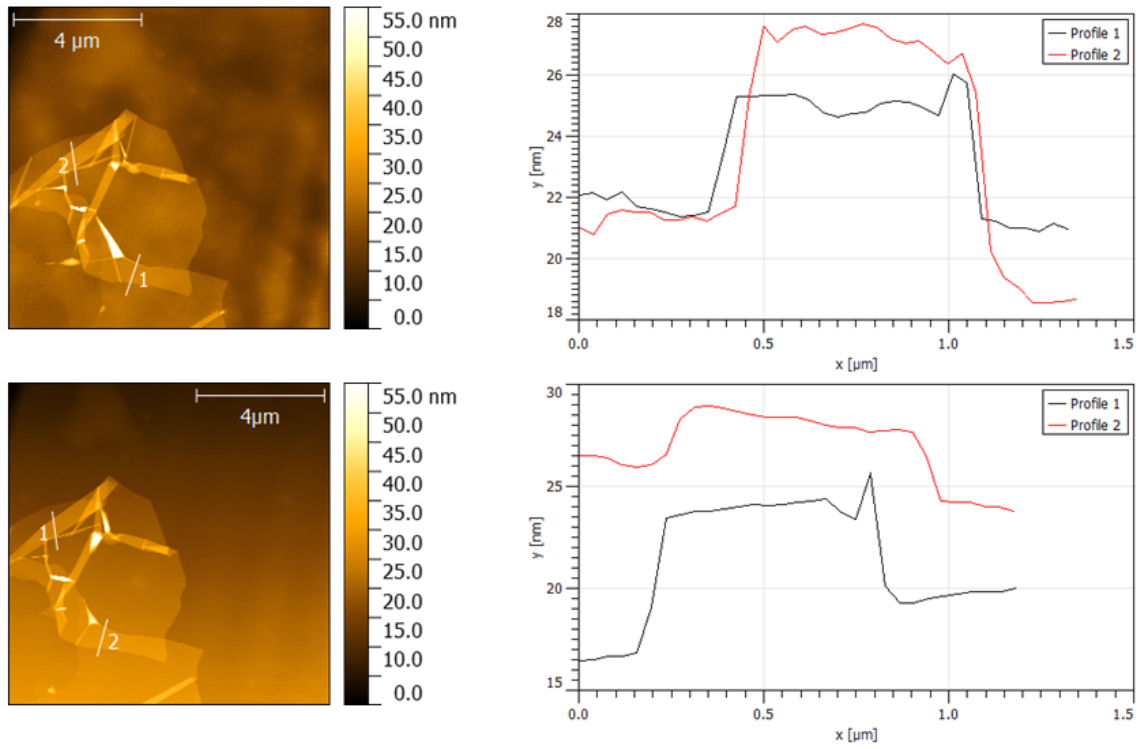


Figure A.4: Comparison of AFM images of a graphene flake before (first row) and after (second row) annealing and the corresponding height profiles.

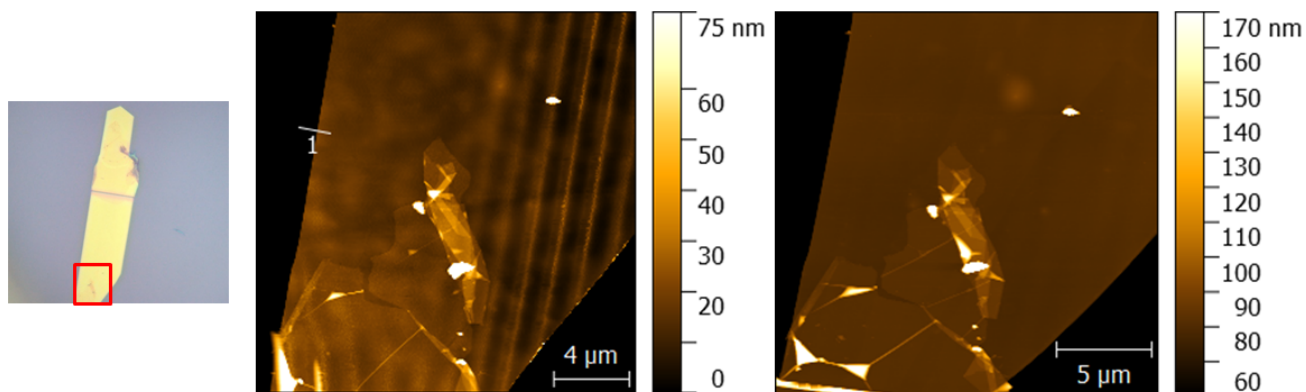


Figure A.5: Comparison of AFM images of a graphene flake before (left) and after (right) annealing in the red rectangle of the optical image on the far left.

Process sheets

This Appendix presents the process sheets of the different experimental steps that were used.

Exfoliation and Rapid Thermal Annealing

The Young's moduli of graphite and hBN are the moduli of a single layer sheet. By dividing the 2D Young's modulus by the thickness of a flake one can then obtain the Young's modulus of that particular flake.

Flakes		
Material	Boron nitride (BN)	Graphite
Crystal structure	Hexagonal	Hexagonal
Lattice parameter (Å)	2.5040 (a)	2.461 (a)
	6.6612 (c)	6.708 (c)
2D Young's modulus (GPa)	271	345 (graphene)
Melting point (°C)	2970	3652
Thermal expansion coefficient (10 ⁻⁶ /°C)	-2,7	-3.75
Substrate		
Material	Barium fluoride (BaF ₂)	Silicon oxide (SiO ₂)
Crystal structure	FCC	-
Lattice parameter (Å)	6.196	-
Young's modulus (GPa)	53.01	75
Melting point (°C)	1354	1713
Thermal expansion coefficient (10 ⁻⁶ /°C)	18.1	3-5
Exfoliation		
Expected flake lateral size	10-20 μm	
Expected flake thickness	5 nm to 1 μm	
Standard Rapid Thermal Annealing		
RTA Furnace	MILA-5000 series	
Gas	Argon-Helium (Ar/He)	
Gas flux	400 sccm	
Starting temperature	20°C	
Heating rate	32.33°/min	
Maximum temperature	990°C	
Plateau time	25 min	
Cooling rate	8°/min	

Table B.1: Process sheet of the exfoliation and the annealing process's

Atomic Force Microscopy

Tip and cantilever	
Probe type	PPP-NCHR-50 (NanoSensors)
Probe material	n-silicon
Probe resistivity (Ωcm)	0.01-0.02
Cantilever thickness (μm)	4 ± 1
Cantilever length (μm)	125 ± 10
Cantilever width (μm)	30 ± 7.5
Resonance Frequency (kHz)	204-497
Force constant (N/m)	10-130
Tip height (μm)	10-15
Cantilever stiffness (N/m)	43,9992
Mode specificities	
Mode	Standard Tapping
Microscope	Bruker Multimode Nanoscope VIII
Environment	Air
Probe resonance frequency (kHz)	381.7

Table B.2: Process sheet of the atomic force microscopy

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