

Synthesis and Atomic Resolution AC-TEM Characterisation of Graphene Edges

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Abstract

My primary goal was to perform an in depth characterisation of the atomic structure of graphene edges, which was fulfilled through the use of an aberration corrected transmission electron microscope (AC-TEM) – OJ2200 MCO that was enhanced with a double Wien slit monochromator to improve its spatial resolution to $\sim 80\text{pm}$. The chemical vapour deposition grown graphene was characterised by various techniques, including the use of Scanning Electron Microscopy (SEM) and Raman spectroscopy to respectively determine the homogeneity and number of layers, and selected area electron diffraction (SAED) to distinguish the size of single crystal region. With this set up, I obtained images of graphene edges at atomic resolution that allowed bond length determination. Based on the acquired information and the application of the density functional theory, it was possible to correlate structural information with the bonding nature of graphene edges; allowing me to further determine the hydrogenation states of graphene with a single AC-TEM frame. Imaging with electron beam monochromation also allowed me to discover the theoretically predicted extended Klein edge structure, which is included as the fourth inherent periodic structure of graphene edges.

With the aid of an *in situ* heating holder, the temperature dependence of graphene edges were investigated over 350 frames: zig-zag edges are found to dominate at $\leq 400^\circ\text{C}$; and at temperatures above 600°C , the proportion of armchair and reconstructed 5-7 edges increase dramatically. This is because low temperatures allow contamination, which result in edges becoming etched at a more rapid rate that favours the formation of intrinsic zig-zag edges. The predominance of armchair and reconstructed zig-zag

edges at high temperatures could be attributed to the evaporation of surface adsorbates, which resulted from higher thermodynamic stability.

Finally, the *in situ* growth of a second layer graphene was investigated. Extra layers of graphene was found to heterogeneously nucleate around gold nanoparticles and continuous to grow at 600°C. This study shed light on the growth mechanism of CVD. By bridging the dangling bonds from the edges of two layers of graphene, this structure was extended to form a closed edge graphene nanopore with diameter ranging from 1.4 – 7.4 nm, The closed edge nanopores in bilayer graphene are robust to back-filling even after exposure to atmospheric conditions for days - this opens new possibilities of nanopore fabrication routes for applications such as graphene sensors and DNA sequencing technology.

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Kuang He

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Publications

Presented below is a list of published works and papers developed during the course of this doctorate project that are currently under review or close to submission. Where applicable, the relevant section in the thesis that relates a particular publication is noted. Some of the co-authored works listed below are, however, not within the scope of the discussion of this thesis: readers are invited to consult the actual publication if they are deemed of interest.

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Ref.[1] – Chapter 4.

Ref.[2] – Chapter 5.

Ref.[3] – Chapter 6.

Ref.[4] – Chapter 7.

Ref.[5] – Chapter 8.

Ref.[7, 25] – The graphene synthesis and transfer method is described in Chapter 3.

Ref.[8,10,11,12,13,15,17, 20, 21, 22, 23, 24, 26, 27] – The AC-TEM study of graphene defect, dislocation and edge structures is discussed in Chapter 2, Literature Review.

Table of Abbreviations

Abbreviation	Descriptions
AC-STEM	Aberration Corrected Scanning Transmission Electron Microscopy
ADF	Angular Dark Field
AFM	Atomic Force Microscopy
BCD	Beam Current Density
CTF	Contrast Transfer Function
CVD	Chemical Vapour Deposition
DFT	Density Functional Theory
DFTB	Density Functional Tight Binding
DI	Distilled
EBL	Electron Beam Lithography
EDS	Energy-dispersive X-ray Spectroscopy
EDTB	Environment-dependent tight binding
EDX	Energy-dispersive X-ray
EELS	Electron Energy Loss Spectroscopy
EK	Extended Klein
ELNES	Energy-loss Near Edge Structure
FEG	Field-emission Gun
FFT	Fast Fourier Transform
FIB	Focused Ion Beam
GB	Grain Boundaries
GNR	Graphene Nanoribbons
GPA	Geometric Phase Analysis
HCL	Hydrochloric Acid
HOPG	High Ordered Pyrolytic Graphite
HRTEM	High Resolution Transmission Electron Microscopy
ISW	Inverse Stone-Wales Defect
LEED	Low Energy Electron Diffraction
LUT	Colour Look-up Table
MV	Mono-vacancy
MWCNT	Multi-Wall Carbon Nanotube
PEEM	Photoelectron Emission Microscope
PMMA	Poly(methyl methacrylate)
RT	Room Temperature
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
STM	Scanning Tunnelling Microscopy
TBMD	Tight-binding Molecular Dynamics
TEM	Transmission Electron Microscopy
VASP	Vienna <i>ab initio</i> simulation package

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Chapter 1

Introduction

1.1 Objective of this project

The main objective of this thesis is to study the behaviour of graphene edges at atomic resolution, with the use of AC-TEM and *in situ* heating holder. The graphene specimens were prepared with a novel chemical vapour deposition method developed in our laboratory that uses molten copper as a catalyst.

1.2 Outline of the thesis

This thesis summarises research that was carried out over the course of 3.5 years of DPhil work at the Department of Materials, and at Wolfson College, University of Oxford. The literature review provides a brief introduction to the attractive properties, various synthesis routes, characterisation method – and most importantly in relation to this thesis – the recent advances in AC-TEM of graphene atomic structure.

The majority of the graphene samples used to obtain results in this thesis are prepared in our laboratory in Oxford. A considerable amount of time (the first year and part of the second year) was devoted to developing synthesis routes and characterisation of the CVD graphene. Chapter 3 provides details of the experimental setup, synthesis parameters, characterisation techniques, image processing, simulation techniques, and aberration correction techniques that were used in my experiments.

Based on the work carried out in the first year, the research activity was later shifted to AC-TEM of graphene. The Majority of the AC-TEM data were obtained using the Oxford-JEOL 2200 monochromator equipped aberration corrected TEM operated at 80kV, with sub angstrom resolution. This enabled atomic resolution imaging of graphene. The raw TEM data used in in Chapter 4 were acquired by Professor Jamie Warner. The atomic resolution was only made possible by operating the monochromator, which allows precise bond length mapping. From this I was able to determine the hydrogenation states of graphene edges. The raw TEM data used in Chapter 5 were acquired by both Dr. Alex Robertson and by me: the extended Klein (EK) edges were identified for the first time. The dynamics of carbon atom movements and comparison with the density functional theory (DFT) relaxed model were made in order to analyse the out-of-plane distortion status of this new periodic edge type. The raw data used from Chapters 6-8 were taken by me: they all aim to enable the high temperature behaviour of graphene edges to be studied. Chapter 6 addresses discrepancies in graphene edge behaviour between room temperature and high temperature (600°C and above), with zig-zag edge being the predominant edge configuration at room temperature and this configuration being reconstructed as a periodic 5-7 configuration when the temperature is increased to beyond 600°C. My study provided the first systematic and statistical insights into the mechanism behind this behaviour. In Chapter 7, I investigate the *in situ* growth of second layer graphene at 600 °C, mediated with gold nanoparticles on the surface, which facilitates heterogeneous nucleation. The growth mechanism and the origin of multilayer formation are also studied. Chapter 8 reports a temperature dependent method for fabricating closed edge nanopores, with the aim of addressing the instability issues that arise when graphene nanopores are utilised in sensors and DNA sequencing.

The final chapter summarises and concludes the present work and provides an outlook of possible future experiments to explore more novel research areas within the field of AC-TEM of graphene.

Chapter 2

Literature Review

2.1 Introduction

Graphene, with its unique quasi-two-dimensional (2D) single layer of carbon atoms packed into a honeycomb structure, has garnered tremendous attention from both scientific and engineering fields. Its extended honeycomb network structure and carbon atoms are sp²-hybridised bonded to each other. Graphene is considered to be the parent of crystalline carbon materials (Figure 2-1), including graphite, carbon nanotubes and fullerenes – despite exhibiting distinctively different properties. The term ‘graphene’ was introduced by Boehm in 1986, derived from the combination of the word ‘graphite’ and the suffix ‘-ene’ that refers to polycyclic aromatic hydrocarbons.¹ In keeping with its initial definition, ‘graphene’ should refer strictly to monolayer structures. Yet, in addition to ‘monolayer graphene’, terms such as ‘bi-layer graphene’ and ‘multi-layer graphene’ appear in the literary canon, and ‘graphene’ is generally used to describe graphite with a thickness of no more than ten layers. This is justified to some degree as the band structure only approximates the properties of bulk when the number of layers exceeds ten.

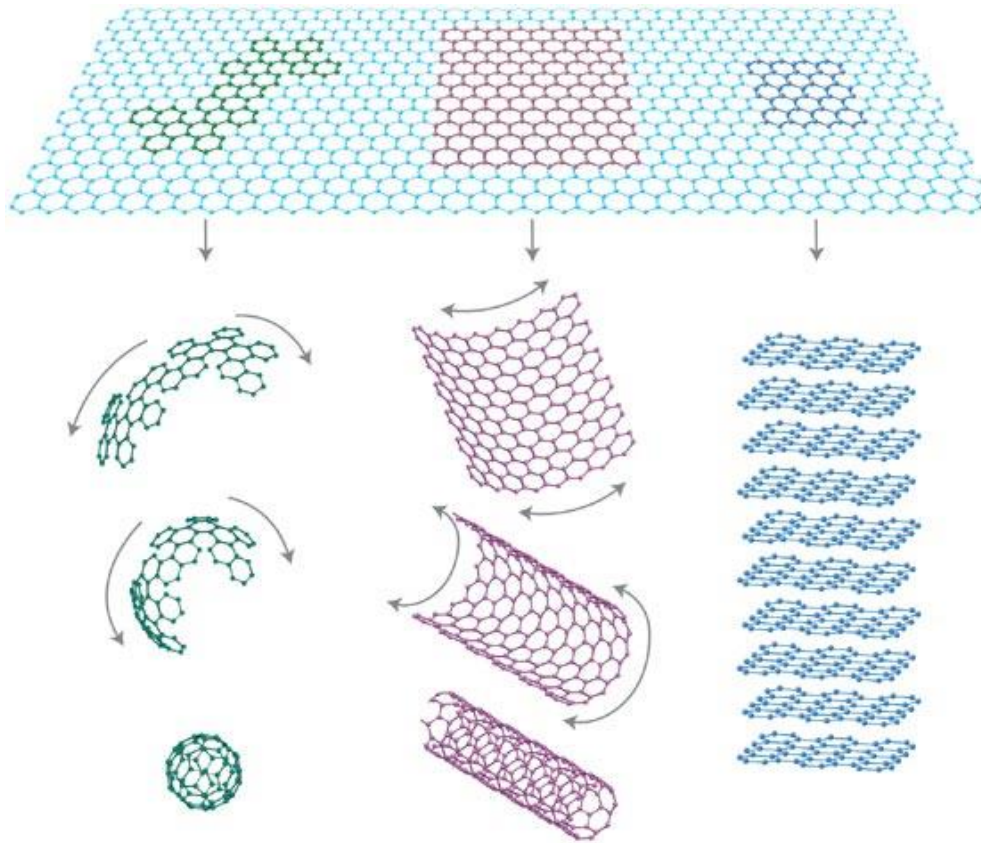


Figure 2-1. One atom thick planar sheet of sp^2 -bonded carbon atoms densely packed in a honeycomb crystal lattice, is considered to be the parent for carbon materials of all dimensionalities – Buck-balls, carbon nanotubes, graphite. (Adapted by permission from Macmillan Publishers Ltd: [Nature Materials] (2), copyright (2007))

Although the inception of graphene is more commonly associated with a process referred to as either micromechanical cleavage or the Scotch tape technique that was proposed by Andre Geim and Konstantin Novoselov in 2004,³ where a single layer of graphene was extracted and transferred onto SiO_2 for further characterisation, graphene has a far more extensive history that is unknown to many. The earliest attempt to exfoliate graphene can be traced back to 1840, where Schafhaeutil treated graphite flakes with both nitric and sulphuric acid.^{4,5} In 1859, Benjamin Brodie also believed he had discovered a new form of carbon material, which he called ‘graphon’, also by treating graphite with strong acids. This, in fact, resulted in the fabrication of small

crystals of graphene oxide,⁶ and it was not until 1948 that the first Transmission Electron Microscopy (TEM) images of graphene oxide revealed dimensions of only a few nanometres in thickness.⁷ In 1962, a fragment of thin reduced graphene oxide that was observed under TEM was considered to be a monolayer.⁸ However, limitations in TEM technology at that time resulted in measurements that were solely based on mass-thickness contrast, which was heavily dependent on the alignment of the microscope and made it difficult to unambiguously distinguish between mono- and multilayer graphene. Recent advances in high resolution TEM technology however, have allowed the more precise determination of graphene layers by enumerating the number of higher contrast lines that form at the edge of graphene.^{9–12} Notably, it was Geim and Novoselov that earned the 2010 Nobel Prize in Physics for their discovery of graphene.

2.2 Properties of graphene

Graphene adopts a distinctive band structure that accounts for the extraordinary electronic properties that have preoccupied physicists with the aim of employing graphene in next generation electronics. Graphene also possesses specific mechanical and chemical properties that could be manipulated to optimise the behaviour of graphene in its applications. A comprehensive review that includes the aforementioned properties – discussed in detail in ref. [13–15] – is however, not within the scope of this writing, as this thesis devotes attention to the structural characterisation of graphene edges. This D.Phil project focuses on studying the edge effect of graphene, particularly on nanostructures such as graphene nanoribbons (GNR) and nanopores.

2.2.1 Electronic properties

As shown in Figure 2-2 (a), graphene is made of carbon atoms arranged in hexagonal structure. The primitive unit cell illustrated is composed of two inequivalent sublattices A and B corresponds to two carbon atoms within the unit cell. The lattice vectors are

$$a_{1,2} = \frac{a}{2} (3, \pm\sqrt{3}) \quad (2-1)$$

Where $a \approx 1.42\text{\AA}$ is the nearest carbon-carbon distance. The reciprocal lattice vectors are

$$b_{1,2} = \frac{2\pi}{a} (1, \pm\sqrt{3}) \quad (2-2)$$

The three nearest-neighbour vectors which links the one sublattice to the other sublattices are given as

$$\delta_1 = \frac{a}{2} (1, \sqrt{3}), \delta_2 = \frac{a}{2} (1, -\sqrt{3}), \delta_3 = a(-1, 0) \quad (2-3)$$

The six second nearest neighbours are located at

$$\delta'_1 = \pm a_1, \delta'_2 = \pm a_2, \delta'_3 = \pm(a_2 - a_1) \quad (2-4)$$

The high symmetry K and K' points at the corners of the graphene Brillouin zone shown in Figure 2-2 (b) are of particular importance for the physics of graphene. They are the Dirac points which will be discussed in more detail later, and their positions in reciprocal space are given by

$$K = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right), K' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right) \quad (2-5)$$

The large scientific interest in graphene is predominantly focused on its distinctive band structure. In pristine graphene, each carbon atom is linked to its three closed neighbours *via* covalent bonds, i.e. the σ bond; they occupy the 2s, 2p_x, and 2p_y valence orbitals.

The fourth valence electron occupies the $2p_z$ orbital, whose axis is perpendicular to the in-plane axis. The delocalised electrons from the $2p_z$ orbitals overlap with each other, forming a π bond. The electronic properties of graphene are principally determined by the presence of this hybridisation orbital.¹⁵

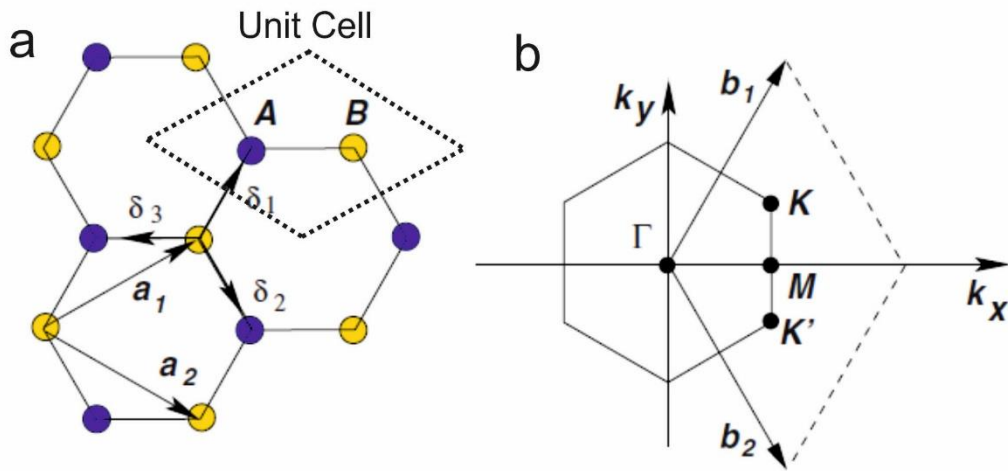


Figure 2-2. (a) Graphene honeycomb lattice made out of two interpenetrating triangular lattices, a_1 and a_2 are the lattice unit vectors. The unit cell is outlined with dashed line rhombus shape. δ_1 , δ_2 , δ_3 are the nearest-neighbour vectors. (b) is the first Brillouin zone of graphene, the Dirac cones are located at the K and K' points. (Reprinted figure with permission from ref.[15], Copyright (2009) by the American Physical Society.)

If we consider the electrons can hop to both the nearest- and next-nearest-neighbour atoms, the tight-binding Hamiltonian would have the form

$$\begin{aligned}
 H = & -t \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + H.c.) \\
 & -t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + b_{\sigma,i}^\dagger b_{\sigma,j} + H.c.)
 \end{aligned}
 \tag{2-6}$$

Where $a_{i,\sigma}$ and $a_{\sigma,i}^\dagger$ annihilates and create an electron with spin σ on site R_i of sublattice A; the same analogues apply to sublattice B. The nearest-neighbour hopping

energy $t \approx 2.8eV$ considers hopping between different sublattices; the next-nearest-neighbour hopping energy t' considers hopping between the same sublattice. There is no universal agreement on the value of t' , but *ab initio* finds $0.02t \lesssim t' \lesssim 0.2t$ depending on the tight binding parametrization.¹⁶ The energy bands derived from this Hamiltonian have the form¹⁷

$$E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k}) \quad (2-7)$$

Where the auxiliary function

$$f(\mathbf{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right) \quad (2-8)$$

The plus and minus signs in Equation (2-7) correspond to the π^* and π band respectively. If we only consider electron hopping between the nearest neighbours, that is $t' = 0$, then electron spectrum is symmetric in respect to zero energy. If there is a finite value of intercell hopping, that is $t' \neq 0$, then the electron-hole symmetry breaks, as it causes π and π^* bands to be asymmetric. The full band structure where both t and t' have finite values are shown in Figure 2-3, the zoom in of the band structure close to one of the Dirac points is also shown in the same figure. The dispersion relationship can be obtained by expanding the full band structure, and is first shown by Wallace in 1947.¹⁷ At close to K and K' points in reciprocal space, if $\mathbf{k} = \mathbf{K} + \mathbf{q}$, where $|\mathbf{q}| \ll |\mathbf{K}|$

$$E_{\pm}(\mathbf{q}) \approx \pm v_F |\mathbf{q}| + O\left[\left(\frac{q}{K}\right)^2\right] \quad (2-9)$$

Where $\mathbf{q}$ is the moment measured relative to the Dirac points and v_F is the Fermi velocity, given by $v_F = 3ta/2$, with a value of $V_F \cong 1 \times 10^6 m/s$, this is remarkably different from conventional conductors.¹⁸

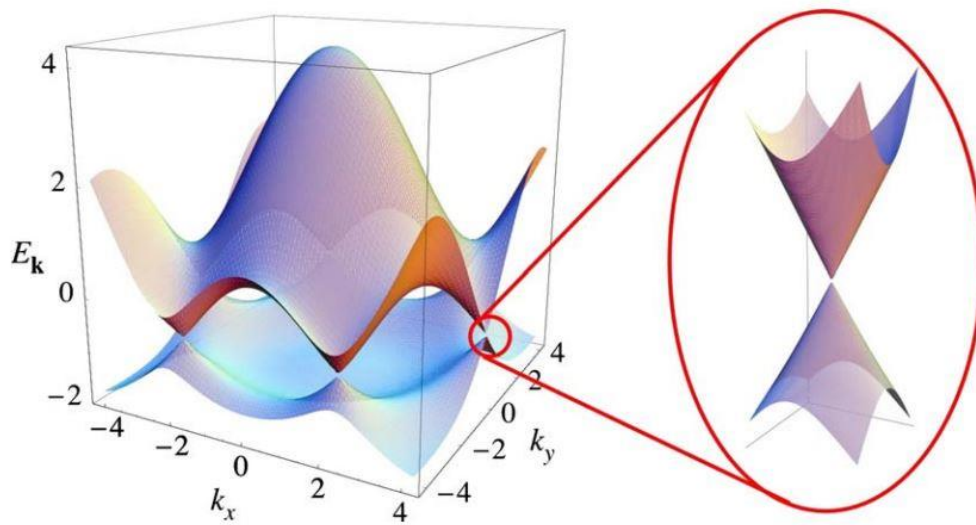


Figure 2-3. Band structure of graphene. The conduction and valence band touches at six discrete points, namely K and K' points. The zoomed in image in the inset shows the dispersion relation close to the K points, electrons close to this point behave as massless Dirac particles. (Reprinted figure with permission from (15), Copyright (2009) by the American Physical Society.)

While theoretically, the density of carriers should approach zero at the Dirac point, the conductivity remains at a finite value of $4e^2/h$.^{19,20} This is due to the combined effect of thermal excitation, charge impurities, and graphene out of plane rippling.^{21–23} A field effect mobility μ_{FE} of $100,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ has been measured for graphene on boron nitride.²⁴ By performing a Hall effect measurement, a value in excess of $200,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ has been further reported for suspended graphene devices with carrier densities as low as $5 \times 10^9\text{cm}^{-2}$.^{25,26}

2.2.2 Chemical properties

The chemical functionalization of graphene can be achieved by either disrupting the pristine lattice or introducing covalent bonds into it, or by non-covalently attaching molecules to the surface *via* van der Waals interactions. For example, graphene has

been subjected to cold hydrogen plasma for 2 hours, which results in the formation of graphane.²⁷ This transformation has been evidenced by the technique of selected area electron diffraction (SAED), where a shift in position in the diffraction pattern reflects a lattice structure that is characteristic of graphane. The modified structure reveal an insulating behaviour and reduced carrier mobility. This process can be reversed by annealing graphane in inert gas environment (Ar) at 450°C for 24 hours.²⁸

Fluorine can also be incorporated into graphene, to form fluorographene, an insulating material with a band gap of 3eV and that remains stable at temperatures to up to 400°C. In addition, surface reaction sites can be introduced into graphene by oxidation and this further allows molecular attachment. Electrochemical oxidation, for example, allows the controlled introduction of the new reactive sites.²⁹ When the density of surface charges becomes sufficiently large, oxygen atoms form covalent bonds with the graphene surface as the conjugated carbon atoms are allowed to transition from sp^2 to sp^3 hybridization. Nitric acid provides a medium for the electrochemical oxidation of graphene that is grown on a SiC substrate.

Diazonium, which is often used to functionalise graphite systems, is equally effective for graphene. These exist in the form of $R - N_2^+ X^-$ where R refers to an organic molecule, and X is either an organic or inorganic anion. Diazonium performs its function by attaching aryl groups to carbon nanotubes,³⁰ diamond,³¹ (High ordered pyrolytic graphite)HOPG,³² and glassy carbon.³³ A patterned mask can be used to selectively functionalise a specific area on graphene, thus allowing more control over the area of functionalisation.³⁴

In summary, graphene, like silicon, has limited functionality on its own, but when modified by various chemical functionalization techniques, n- or p- type doping can be

achieved, with the widening of the band gap to a reasonable size. Whether future generations of graphene-based electronics can revolutionise current technologies will largely depend on the continuous discovery of novel manipulations to the chemical structure of graphene.

2.2.3 Edge Predominant Structures

In order to harness the potential that stemmed from the exceptional properties of graphene, its application in nanoelectronics have heavily promoted. The semiconductor industry, for example, could hugely benefit from the outstanding physical properties of graphene. For example, its extraordinary electron mobility could improve device on-off ratios dramatically and at a rate that is unsurpassed by any other material - even silicon which is most widely used today. However, the lack of band gap has so far discouraged its use in this industry.

When continuous graphene film is patterned down to nanostructure such as GNR, edge became the most important role to affect its property, and are known to introduce bandgap. A GNR of width below 10 nm, has therefore been proposed to restrict the size of band gap.³⁵ The properties of a GNR, particularly its band gap, are inseparably related to its atomic edge structure.^{36–38} Armchair terminated GNRs can be adjusted to either behave as metallic or semiconducting by controlling the width of the ribbon.³⁹ The hydrogenation and oxidation states of the edge also affects the electronic properties of GNR.⁴⁰ The ability to exercise full control over edge roughness and the crystallographic direction of the ribbons is therefore, highly desirable in reducing the electron scattering effect at the edge as this would contribute significantly to better performance.^{36,41,42}

As graphene sheets shrink in size, their edge states also become important in determining its properties and there are several theoretical predictions that describe its unique spin and magnetic states.⁴³⁻⁴⁸ A tight-binding model predicts the occurrence of smooth zig-zag termination in GNRs could alter its magnetic state from diamagnetic to paramagnetic with decreasing temperature.⁴⁷ Stable magnetic states could also be achieved by polarising the electron spins in the system.⁴⁵ The ability to achieve atomically precise edges remains a challenge that could be experimentally addressed: while graphene edges appear regular at the micron scale, closer examinations at the atomic level reveals complex edge terminations that are not fully periodic.^{49,50} In this section, I will attempt to review the current experimental progress and difficulties associated with the capturing of graphene edges *via* both top down and bottom up approaches.

2.2.3.1 The top-down approach

Electron beam lithography (EBL) is widely used to pattern nanostructured materials, and has reportedly allowed the fabrication of GNRs that do not exceed 10nm in width.^{37,51} As shown in Figure 2-4, EBL can be used to pattern graphene into ribbons with width ranging from 10 - 100 nm and with different relative orientations. The energy band gap scales inversely with the ribbon width - GNRs with a width of 15nm exhibit an energy band gap of up to ~0.2eV. A study describing the relative angle of GNR band gaps exhibits randomly scattered results, indicating the occurrence of a crystallographic orientation dependent effect that albeit theoretically predicted, has not been experimentally observed. The signal noise caused by high edge roughness are thought to have blocked the detection of this crystallographic orientation dependent effect.^{35,38} GNRs produced by state-of-the-art EBL technology have reportedly exhibited an edge roughness of ~ 1-3 nm, which is significant when considering a width

of only 15 nm.^{51,52} Nevertheless, its width can be further reduced to 8 nm by high temperature gas phase oxidation – i.e. exposure to a mixed atmosphere of oxygen and ammonia at high temperatures. The resulting higher reactivity at the edge allows the slow and isotropic etching of carbon atoms, resulting in uniformly thin and smooth GNRs.⁵³ The most successful EBL-derived GNRs exhibit an on-off ratio of $\sim 1 \times 10^4$, a band gap of 0.4 eV and a width of 0.4 nm.

Nanowire lithography provides another method for the fabrication of GNRs of sub-10 nm width.^{52,54} Chemically synthesised silicon nanowires are deposited onto graphene and they act as a protective mask during oxygen plasma etching. With a cross shaped nanowire, one can synthesize graphene devices that do not exceed 10 nm in width. Moreover, GNRs that are synthesized with this method display a more uniform edge roughness than those that are synthesized by EBL.⁵⁵ As the deposition of nanowires occurs through a random process, a metal mask that is fabricated by EBL confers greater control over the area of functionalization.⁵⁵

Direct writing provides a further approach to pattern graphene, and an obvious advantage is its independence from the use of photo-resist, which can lead to contamination; this method therefore potentially offers a route for the production of clean graphene nano-structures.^{56–58} In one example, graphene was patterned with sub-nanometre precision using a focused electron beam from a TEM.^{56,59} Nevertheless, this method requires graphene to be transferred on to a TEM grid prior to the patterning process, and this hinders the scalability of this method. A focused laser beam can also be applied to pattern graphene oxide that has settled on a quartz substrate – this process locally heats the sample up to 500°C and results in localised oxidative burning.⁵⁸ Finally, the small ion probe size, low atomic mass and high accelerating voltage of helium ions

position it as a prime candidate for sculpturing graphene; its probe diameter of $< 0.5\text{nm}$ has allowed the manipulation of graphene with sub 5 nm precision.^{57,60}

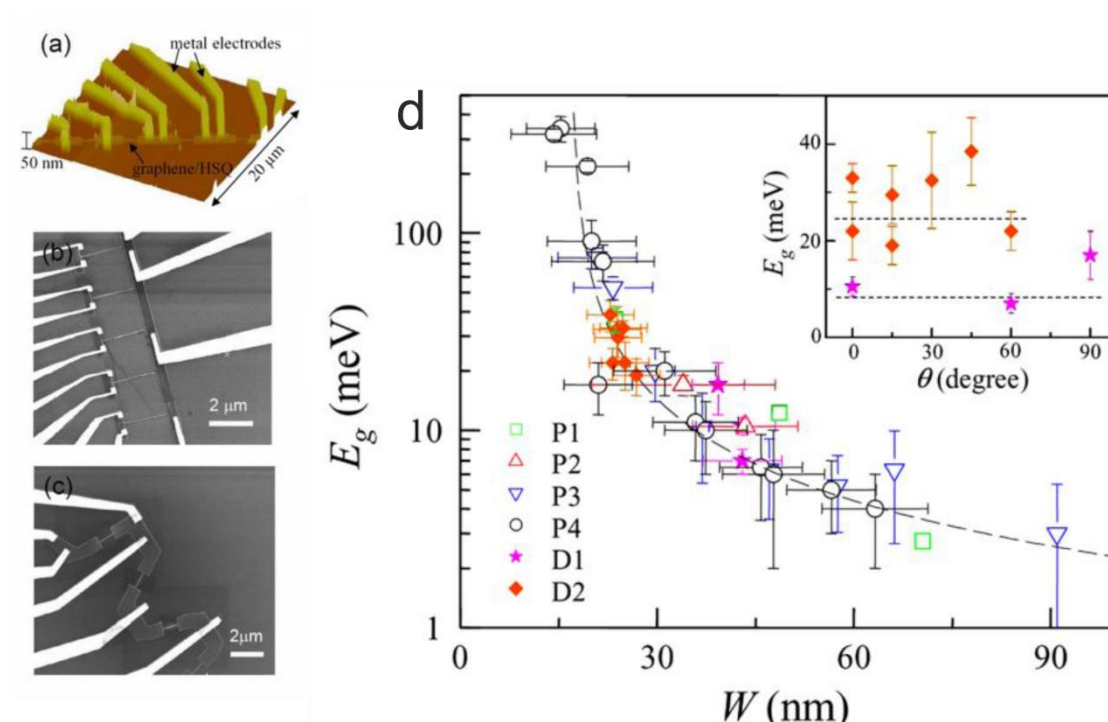


Figure 2-4. (a) Atomic force microscope image of GNRs covered by hydrogen silsesquioxane etch mask. (b) Scanning electron microscopy (SEM) image of graphene nanoribbons with different width arranged in the same orientation, (b) same width arranged in different directions. (d) Energy band gap plotted as a function of GNR width, inset shows the band gap variation with the relative orientation of the nanoribbons. (Reprinted figure with permission from ref.[37], Copyright (2007) by the American Physical Society)

Numerous approaches have been developed to etch graphene along a selective crystallographic direction – catalytic hydrogenation,^{61,62} catalytic oxidation,⁶³ and the carbothermal reduction of SiO_2 have all been employed.⁶⁴ The hydrogenation and oxidation approach involves dispersing nanoparticles, such as Fe, Ni, Co and SiO_2 , onto graphene sheets and subsequently exposing the latter to hydrogen or oxygen gas at elevated temperatures. The nanoparticles then penetrate the graphene sample along a specified direction by reacting with the carbon atoms to form methane gas, this process

leaves behind a trench whose dimensions mirror the width of the nanoparticles. It was observed that channels whose width exceeded 10 nm preferentially adopted a zig-zag orientation, while those below 10 nm predominantly settled in an armchair configuration.^{61–63,65–67} With this method, the edge roughness as observed by High resolution transmission electron microscopy (HRTEM) oscillates, between 1-2 nm, which is sizable in proportion to the width of the nanoribbon.

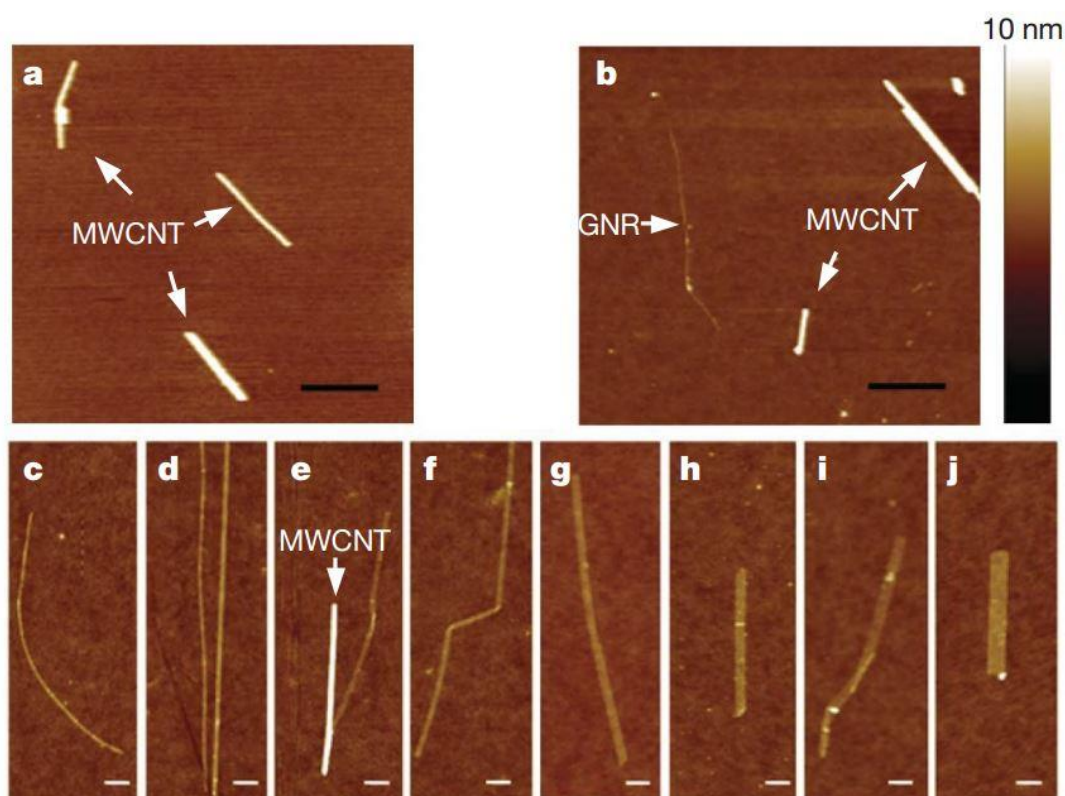


Figure 2-5. GNRs converted from Multi-wall carbon nanotube (MWCNTs). (a) An Atomic force micrograph (AFM) image of MWCNT deposited onto Si substrate. (b) An AFM image taken after the MWCNT to GNR conversion process, both GNR and MWCNT exist in this case. Scale bars, 1 μm . (c-j) are monolayer and few layer GNRS of various sizes, with width ranging from 8 to 51 nm and height ranging from 0.8 to 2.0 nm. Scale bars, 100 nm. (Reprinted by permission from Macmillan Publishers Ltd: [Nature] (68), copyright (2009))

GNRs can also be obtained *via* the unzipping of carbon nanotubes (CNTs), in which there are three possible routes: plasma etching of partly embedded CNTs,⁶⁸ solution-phase oxidative processes,⁶⁹ and catalytic cutting of CNTs.⁷⁰ For plasma etching, multi-wall CNTs (MW)CNTs are dispersed onto the Si substrate and spin coated with poly(methyl methacrylate) (PMMA). Both MWCNT and PMMA could be peeled off after curing, which leaves a narrow strip of MWCNT that is unprotected by PMMA. The process continues with subsequent plasma treatment, which allows the exposed area to be etched while the rest of the MWCNT expand to form GNRs. As shown in Figure 2-5, GNRs with smooth edges and whose dimensions vary from 8 to 50nm in width were obtained. Nevertheless, Raman spectroscopy reveals minor D peak signals, indicating that its edges do not purely adopt zig-zag or armchair configurations.

2.2.3.2 The bottom-up approach

As an alternative to the top-down approach, the bottom up approach promises precisely controlled smooth edge structures.^{71,72} By the surface-assisted coupling of molecular precursors into linear polyphenylenes and their subsequent cyclodehydrogenation, a fabricated GNR with width of ~ 1 nm, and length of ~ 30 nm was synthesised.⁷² The 10,10'-dibromo-9,9'-bianthryl monomeric precursors were thermally evaporated and adsorbed onto an Au(111) face at 200°C to facilitate dehalogenation and monomer diffusion on the surface; further heating at 400°C then induced the intramolecular cyclodehydrogenation of the polymer chains to allow the formation of GNRs that orientate in an armchair direction. If the precursors were substituted by 6,11-dibromo-1,2,3,4-tetraphenyltriphenylene or precursors whose phenyl rings have been substituted by heterocycles, chevron-type and chemically doped GNRs could be obtained.

2.3 Synthesis routes

Since the discovery of graphene in 2004,³ four synthesis methods have been principally used to obtain graphene for either academic research or industrial scale production – these are mechanical exfoliation,³ Chemical Vapour Deposition,^{73–75} solution processing, and thermal decomposition of SiC.⁷⁶ Synthesis *via* mechanical exfoliation and Chemical vapour deposition (CVD) will be discussed in detail in this section as these are the routes that are predominantly adopted in graphene applications, and this is particularly true for HRTEM imaging; because these methods result in a clean graphene lattice that can be transferred onto TEM grids. Moreover, solution processing often results in contamination of the graphene surface by amorphous carbon material, and this prohibits further lattice imaging in a HRTEM; it is also difficult to transfer SiC grown graphene onto TEM grids. Nevertheless, the latter two methods are reviewed in detail in refs.[13,77,78]. The synthesis routes for graphene are still constantly evolving, with the aim to achieve continuous graphene sheet with minimum grain boundaries, to suit all aspects of graphene applications.

2.3.1 Mechanical exfoliation

The success of mechanical exfoliation was reported by Geim et al. in 2004³ – a landmark event that is believed to mark the first instance where single layer of graphene was isolated. Commercially available 1 mm thick platelets (www.2spi.com) HOPG were used as the raw materials. Scotch tape were also repeatedly used to peel off thin layers of graphite, which were then transferred onto a SiO₂/Si substrate. These layers exist either as monolayers or bilayers, and these were differentiated by the combined use of light microscope and AFM – the former to exam the contrast and the latter to investigate changes in height.^{3,13,78}

This technique is advantageous in allowing the synthesis of graphene of the highest quality without an investment in bulk quantities of sophisticated synthesis instruments – graphene originating from this method have exhibited carrier mobility in excess of $10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.² Nevertheless, this method suffers from an inability to produce continuous sheets of graphene that amount to wafer size, and is therefore not suitable for use in the semiconductor industry.

2.3.2 CVD

CVD is an established method that is employed in thin film deposition,^{79,80} synthetic diamond⁸¹ and carbon nanotube fabrication.^{82,83} Initially, a gas precursor that contains the desired element is heated to high temperatures within the reaction chamber. The gas decomposes at high temperatures to form thin layers of the desired material – this reaction is usually catalysed by transition metals that are applied as a substrate. The parameters of gas flow rate, pressure, reaction temperature can all be adjusted within the chamber to obtain the desired product.

The production of very thin graphite films by CVD was first reported by John May as a product of his low energy electron diffraction (LEED) study in 1969,⁸⁴ where he referred to the former as “monolayer graphite”. In 2006, this study was followed up by Somani and co-workers in greater detail where camphor and Ni foils were used as the precursor and catalyst respectively.⁸⁵ The latter study paved the way for a novel graphene synthesis route and heralded a great research interest that funnelled towards the advancement of CVD-derived graphene, vastly accelerating the pace at which the latter improved in quality. Since then graphene has been suitably grown on various transition metal substrates such as Ni,^{86,87} Cu,⁸⁸ Co,⁸⁹ Ru,⁹⁰ Ir,⁹¹ Pt.⁹² Amongst the popular catalysts, Ni and Cu have garnered the most interest because of their cost, grain

size, chemical reactivity, and thickness. The growth mechanism associated with each of the two metal substrates is however, distinctively different, and the understanding of both is essential to controlling the grain size and thickness of the product.

2.3.2.1 Graphene growth on Ni

As depicted in Figure 2-6 (a), it has been proposed that nickel facilitates the activation of graphene growth by carbon segregation,⁹³ and this allows further growth by precipitation.⁹⁴ Here, segregation refers to compositional inhomogeneity in thermal equilibrium while precipitation refers to inhomogeneity that arises from ‘phase separation’.^{73,95–97} With control of Ni film thickness to limit the number of C atoms dissolved into the metal substrate, one could produce few layer graphene. But, to date, graphene produced on Ni have not yielded single layer uniform layers consistently. In a $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ isotope dosing experiment, where methane precursors containing ^{12}C and ^{13}C carbon isotopes are sequentially introduced, Raman characterisation yields a uniform distribution of the two isotopes.⁹⁸ Figure 2-7 (j-L) demonstrates the Raman results for graphene grown on deposited Ni film. As could be seen in Figure 2-7 (k), no distinguishable separation of isotopes can be found, therefore no correlation between the sequential placement of different isotopes and the resultant growth pattern can be found. The variations in colour in the optical micrograph shown in Figure 2-7 (j) is an indication of the unevenness of the graphene grown on Ni film. A typical Raman spectrum shown in Figure 2-7 (L) has its G band located at $\sim 1553\text{cm}^{-1}$ corresponds to 45% of ^{13}C and 55% of ^{12}C according to the calculations performed in ref.[88]. All of the above experimental evidence demonstrate the growth mechanism performed on Ni is by segregation and precipitation; carbon dissolves into Ni at high temperature and different isotopes diffuse into each other to create a random mix of isotopes and upon

cooling, the segregated and precipitated graphene will have isotopes randomly distributed.

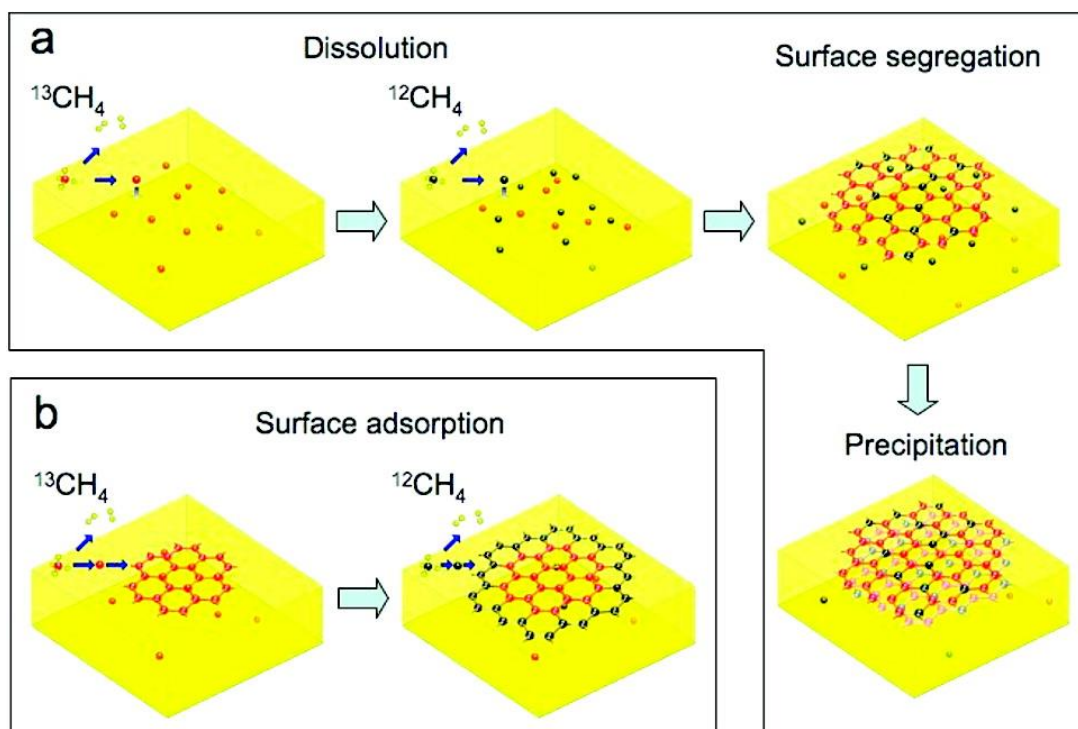


Figure 2-6 Carbon isotopes distribution for graphene growth on nickel and copper. (a) Schematic illustration of graphene grown on nickel by the segregation and precipitation pathway. (b) Schematic illustration of graphene grown on copper via surface adsorption. (Reprinted with permission from (98), Copyright (2009) American Chemical Society.)

2.3.2.2 Graphene growth on Cu

In contrast, the use of a copper catalyst facilitates surface adsorption. The experimental results of CVD performed with Cu as a catalyst are shown in Figure 2-7 (a-i), the optical micrograph image in Figure 2-7 (a) showed a smooth surface except occasional appearance of wrinkles which is believed to have caused by the difference in coefficient of expansion between graphene and its underneath metal substrate.^{99,100} As could be seen in Figure 2-6 (b), for Cu catalyst, carbon atoms does not diffuse into the metal, instead, it is the surface adsorption that dominates nucleation process. Figure 2-7 (b)

are Raman spectra correlated to the coloured areas in Figure 2-7 (a). The most obvious information these have given out is the single layer nature of the graphene sheet produced since the intensity ratios of $2D/G > 1$ for all three spectra, which is conventionally considered to be a good indication for monolayer graphene. Regions of pure ^{12}C , ^{13}C and regions where both existed have been observed. The co-existence was believed to be caused when laser beam was focused at the coupling area of different isotope regions. Figure 2-7 (d-f) are the integrated G band mapping results, Figure 2-7 (d) is for the co-existence bands, the results show a smooth and uniform surface except where wrinkles existed. Figure 2-7 (e,f) shown G-band mapping results of ^{13}C and ^{12}C respectively, this has given information about the evolution of graphene growth on copper. $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ have been introduced in a sequential fashion repeatedly, that is 1 minute of $^{13}\text{CH}_4$ flush followed by $^{12}\text{CH}_4$ flush and repeat this process for 4 times. The middle bright area in Figure 2-7 (e) represent the first 1 minute growth of ^{13}C and the dark lines around it represent the first 1 minute growth of ^{12}C , the smaller strips of bright area in between the dark lines are second 1 minute growth of ^{13}C . Figure 2-7 (f) is just a simple inverse of Figure 2-7 (e) since there are only two isotopes exist in this particular system. The graphene growth mechanism on Cu is of fundamental difference to Ni. There is no mixing and diffusing process for different isotopes, and growth is by surface-adsorption only. It also shows after the second minute of ^{13}C evaporation, the film has reached a fully covered stage where further evaporation will not result in the thickening of graphene. The growth on copper is said to be self-limiting since there is no catalyst to promote decomposition of gases after full graphene coverage; the self-limiting nature of the surface reaction results mostly mono- and bi-layered graphene when copper is used.^{75,93,94} Occasionally multilayer graphene can be produced if the reaction parameters are not chosen appropriately. Figure 2-7 (g-i) are

results of D band mapping. D band is the characteristic frequency for the existence of structure disorder, such as wrinkles, defects and dislocations. Figure 2-7 (g) therefore shows a higher intensity area at the location where wrinkles sit. Some spots and short lines have appeared at random locations also indicates defects might have been created during the transfer process and the boundaries between graphene grains respectively. The mapping of D band has proved to be a useful tool for estimating grain sizes of graphene sheet and the diameter of grain produced using this method is $\sim 10\mu m$. Graphene growth rate for the first minute was noticeably faster than the second minute, this is due to the decrease in the number of available catalytic sites as growth progresses.

2.3.2.3 Growth conditions on copper

As explained in previous text, graphene growth on Cu mainly happens on the surface. This process involves catalytic decomposition of methane on Cu to form C_xH_y upon the exposure of Cu to methane and hydrogen. When there is a local supersaturation of C_xH_y , nuclei will form. Those nuclei grow to form graphene sheet if Cu surface has kept at saturation, or supersaturated with C_xH_y species. Full Cu surface coverage by single-layer graphene can be reached by optimising experimental parameters such as growth temperature, various gas flow rate and partial pressure. If the amount of available carbon source on the exposed Cu surface is insufficient to expand the carbon atoms to the island edge, Cu surface will be partially covered with graphene. Otherwise, if there is always sufficient carbon, graphene island should bond to each other and a continuous film will form. Li and coworkers⁹⁸ have demonstrated with the same growth recipe, growing with 60 minutes yielded a similar structure to growing for 10 minutes. Whereas any growth time under 10 minutes will yield an unfulfilled surface. With the understanding of the fundamental difference between Cu and Ni, several approaches have been reported to grow full coverage of monolayer graphene.^{88,101–103}

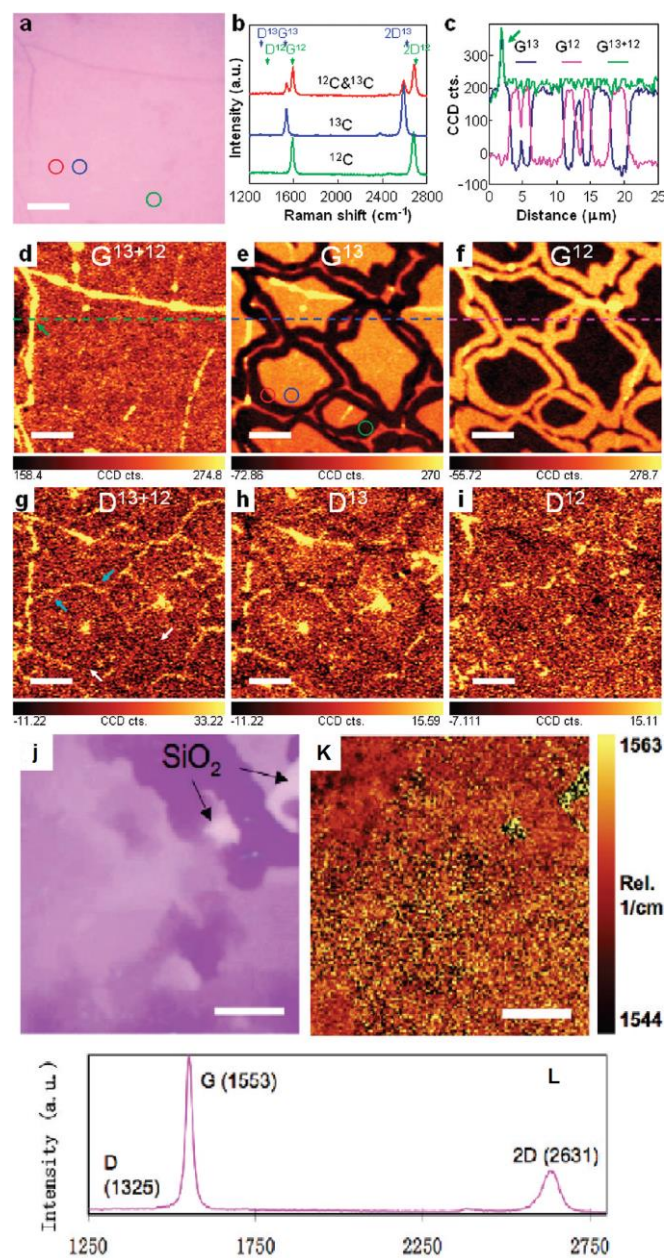


Figure 2-7. (a) An optical microscope image of graphene grown on copper and transferred onto SiO₂/Si wafer, the red, blue and green areas are the local area where typical Raman spectroscopy were taken. (b) Raman spectroscopy of 12C labelled graphene (green), 13C labelled graphene (blue) and a mixture of 12C and 13C labelled graphene (red), these colours are correlated to colours labelled in (a) and (e). (c) Line scan of dashed lines in (d)-(f). (d)-(f) are integrations of Raman G peak G¹³⁺¹² (1500-1620 cm⁻¹), G¹³ (1500-1560 cm⁻¹), G¹² (1560-1620 cm⁻¹), (g)-(i) are integrations of Raman D peak D¹³⁺¹² (1275-1375 cm⁻¹), D¹³ (1275-1325 cm⁻¹), D¹² (1325-1375 cm⁻¹), (j) Optical microscope image of graphene on

SiO₂/Si. (k) correspond to Raman mapping of the location of G band. (L) is a typical Raman spectrum. (Reprinted with permission from ref.[88], Copyright (2012) American Chemical Society)

References	Pre-treatment	Growth Parameters and Cooling rate	Temperature (°C)	Graphene layers
[98]	1000°C H ₂ (2sccm, 0.04Torr) for 30 minutes	35sccm of CH ₄ at a total pressure of 500m Torr, H ₂ /CH ₄ ratio at 0.06	1000	> 95% single layer
[104]	Acetic acid treatment and heating up to 1000°C in 50-200sccm hydrogen atmosphere	875sccm of CH ₄ at a total pressure of 11Torr for 10 to 20 minutes, H ₂ /CH ₄ ratio at 0.23, cooling rate at 20°C/min	1000	>93% single to bi-layer
[105]	10Torr H ₂ held at 900°C for 30 minutes	10Torr and 40Torr respectively for 10 minutes with CH ₄ at 99.999%	850-900	Few layer
[106]	Heating up to 1000°C in ambient pressure then grow at 1000sccm He and 50sccm H ₂ for 30 minutes	15sccm H ₂ 40sccm CH ₄ and 1000sccm He for 5 minutes, cooling in He atmosphere at 10°C/s	1000	Single and bilayer
[107]	20sccm Ar, 0.41Torr for 12 minutes, then 20sccm H ₂ 0.3Torr for 1.25 minute up to 766°C	4sccm C ₂ H ₂ and 20sccm H ₂ at 0.386Torr for 10 minutes, cooling under 80sccm Ar at 1.05Torr to room temperature.	800	Single, Bi- and few layer
[108]	Heating in hydrogen atmosphere under vacuum to 1000°C	H ₂ /CH ₄ ratio of 0.06 at a total pressure of 0.5Torr, CH ₄ (99%), growth time vary from 15 minutes to 420 minutes	1000	Mostly single layer with bilayer nucleation points
[109]	Pumped down to 0.01Torr before annealing, flowing Ar/H ₂ with flow rate of 400sccm at a pressure of ~8-9Torr with temperature heated up to 950°C	Stop Ar/H ₂ flow and passing hexane vapour to maintain the tube pressure of 0.5Torr at a flow rate of ~ 4mL/h for 4 minute	950	Single and bilayer
[101]	8sccm, 0.09Torr of H ₂ at 1000°C for 30 minutes	Mixture of 24sccm CH ₄ and 9sccm H ₂ is flowed at 0.46Torr for 30 minutes. Cooled to room temperature ~10°C/s with flowing H ₂ under a pressure of 0.09Torr	1000	Single layer
[103]	1000°C H ₂ (2sccm, 0.04Torr) for 30 minutes	0.5sccm methane, 2sccm hydrogen at 0.035Torr, fast cooled to room temperature	1035	Single layer and single grain graphene

Table 2-1. A summary of CVD conditions reported in recent literatures to grow graphene on copper.

Cu is chosen as the catalyst for CVD experiment reported in this thesis. As received Cu films is generally covered with native oxide (CuO, Cu₂O) which reduces its catalytic

activity. Therefore it is important to remove those oxides before growth. Hydrogen annealing process is an effective method as it not only removes oxide, but also enlarges Cu grain size and rearranging the surface morphology to improve the quality of as grown graphene sheet. Table 2-1 summarised specific growth parameters that have been reported in recent literatures in achieving the best quality graphene film. The table includes majority of important parameters such as surface treatment, growth gas flow, growth temperature, cooling rates and resultant quality of graphene. But some growing method uses very special techniques such as wrapping copper foil to achieve single crystal graphene and pre-vacuuming to eliminating environment contamination, those cannot be summarised in the table. Therefore readers are suggested to refer to specific literature using the reference provided to have a thorough understanding of the method.

2.3.2.4 Improving single crystal area

The existence of structural defects – such as grain boundaries, holes and dislocations – on CVD grown graphene is believed to damage its transport properties, resulting in depreciated electronic properties that fail to compare to mechanical exfoliated graphene.^{110–112} The defective areas provide popular resting sites for surface adsorbates, which subsequently impact on their transport properties. This has made it important to perform research on how large grain sizes form during continuous film growth. Using a copper-foil enclosure, where a 25 μm film was bent to keep the structure intact under gas flow in a CVD system, a graphene single crystal with dimensions of up to 0.5mm was formed at room temperature and under low pressure, the carrier mobility of $4000\text{cm}^2\text{V}^{-1}\text{S}^{-1}$ is measured.¹⁰³ Apart from a change in substrate preparation, which requires a lower methane flow rate and partial pressure (less than 1 sccm and 50mTorr), this process mirrors a basic CVD process. This process results in the synthesis of graphene on both sides of the enclosure, the graphene sheet on the outside exhibits

similar behaviour to those reported earlier while on the inside nuclei are much lower densities, allow the growth of large domains over a prolonged time period.⁷⁴ While these grains tend to reveal an extensive edge roughness, photoelectron emission microscope (PEEM) identifies them as single crystals.

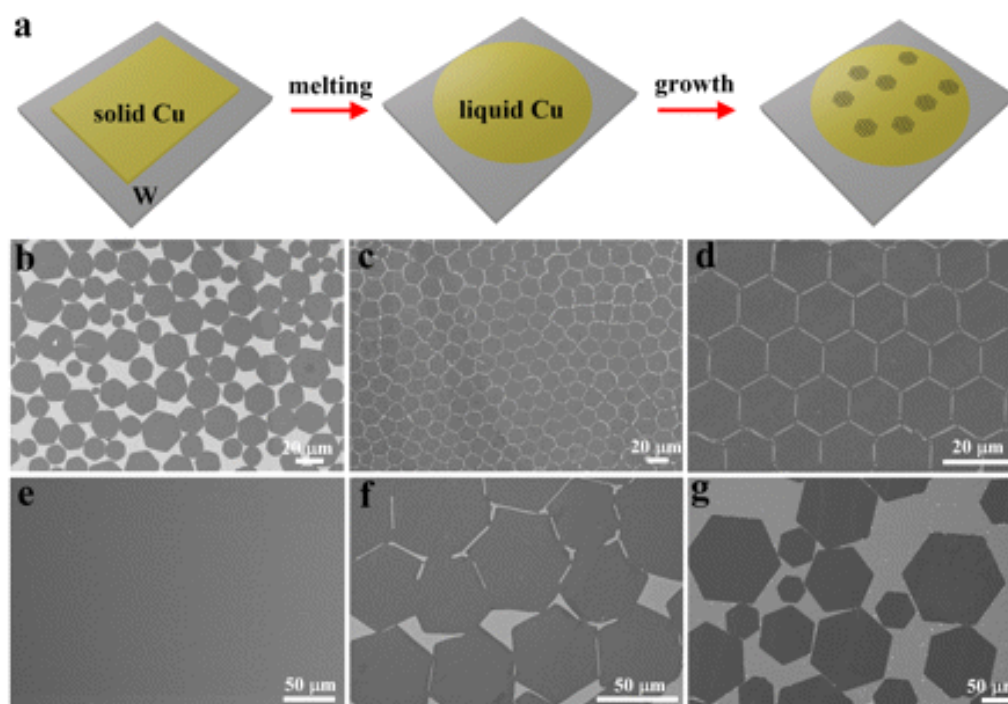


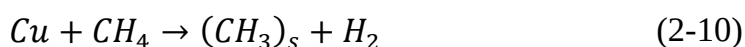
Figure 2-8 CVD on molten copper (a) Schematic illustration of CVD graphene growth on molten copper. (b-e) SEM images showing the evolution of grain growth, alignment and forming a continuous film. (f,g) shows zoomed in images of different grain size and orientation before alignment. (Reproduced with permission from ref. [113], Copyright (2012) National Academy of Sciences, USA)

It has been recently reported that the quality of graphene can be improved by raising the reaction temperature beyond the melting point of copper ($>1086^{\circ}\text{C}$) during CVD reaction.^{113,114} While molybdenum were initially used to support and wet the molten copper and to provide a flat surface to minimise the formation of wrinkles after the transfer process, tungsten emerged as the preferred element as molybdenum was found to interact with copper to form an alloy phase when subjected to high temperatures.¹¹⁵

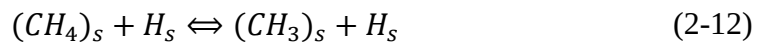
As shown in Figure 2-8, the growth of graphene on molten copper follows a slightly different mechanism. The process begins with the formation of nucleation points across the film and clear hexagonal-shaped graphene domains progressively emerge from these points. Then, the liquid nature of molten copper allows the graphene domains to move freely – these domains rotate and deviate from their original nucleation positions to minimise the total surface/edge energy before perfectly settling in an ordered alignment (Figure 2-8 (c,d)). The latter behaviour is believed to contribute to the minimisation and elimination of defects at the grain boundary and to facilitate the formation of a continuous film with large single crystal area. The combination of TEM-SAED and Raman spectroscopy has revealed a grain size growth that exceeds 200 µm with this method.¹¹³

2.3.2.5 Role of hydrogen

Both methane and hydrogen gas have been passed through the CVD tube during growth process in Ar buffer gas. The growth of graphene on copper is greatly affected by the amount and partial pressure of hydrogen gas. Hydrogen plays a dual role in this process, it firstly acts as a co-catalyst in the formation of active surface bound carbon species $(C_xH_y)_s$ which is required for graphene growth. Secondly, it controls the grain shape and dimension by etching away unstable carbon species.¹¹⁶ Without hydrogen flowing in the system, methane has to chemisorb on the surface of copper to form active carbon species $(C_xH_y)_s$, for example, $(CH_3)_s$, $(CH_2)_s$, $(CH)_s$ and C_5 . These species are responsible for produce graphene subject to further reactions. The dehydrogenation reaction



are not thermodynamically favourable on Cu substrate (the reaction will need to overcome a 1.6eV activation barrier at room temperature) and are extremely slow in terms of reaction speed.^{116–118} One way to overcome the barrier is to use excessive amount of methane, but this method proves to produce thick graphite. The more effective way is to add hydrogen gas as a co-catalyst, the catalytic reaction undergoes are shown below.



Hydrogen molecules dissociates on copper rapidly and form active hydrogen atoms.¹¹⁹ These atoms are able to assist the activation of absorbed methane described in Equation (2-12), surface bound radicals $(CH_3)_s$ were formed in that process, subsequently dehydrogenation process lead to a more active surface bound species being formed and thus are of fundamental importance to graphene growth.

As a result, graphene growth is highly dependent on the input of hydrogen due to the complicated double role it plays during the growth process. Excess or limited amount of hydrogen gas will result to either none or partial graphene coverage. The ratio between methane and hydrogen gas is also imperative in terms of obtaining single layer sheet. Low methane concentration require long time period to form continuous sheet while high concentration lead to multilayer. A stepwise increase of methane concentration was also reported to match the reduction in copper catalysts as more copper surface are covered by graphene. This study also gives an indication that not all growth parameters gives a self-limiting single layer graphene growth. Inappropriate growth parameters might lead to double or multi-layer formation in the initial stage of nucleation because second or third layer of graphene tends to form when the amount of

supplied active surface-bound carbon exceeds what can be consumed by small circumference of a graphene grain. This is also the reason for the SEM observation of additional layers of hexagonal graphene on top of a larger hexagonal shaped graphene.

2.4 AC-TEM of graphene

A state-of-the-art HRTEM has provided researchers with a powerful tool to analyse samples at atomic resolution during imaging mode and further provides electron diffraction information while in SAED mode. In an HRTEM, electrons are emitted from an electron gun by thermionic or field emission, an accelerating voltage of 80kV or lower is normally used for graphene samples as this minimises radiation damage. When the electron beams pass through a specimen, the interference of the scattered and un-scattered waves forms an image of the graphene lattice.¹²⁰

Different modes of HRTEM have been adapted for graphene characterisation. Imaging mode is most commonly adopted to directly image graphene – albeit as a weak phase object. It reveals the lattice structure of graphene and allows a study of its defects, dislocation and edge structures.^{121–123} Conversely, dark-field imaging is used as a tool to identify grain boundaries.^{110,112} SAED mode is used in conjunction with sample tilt to identify the number of graphene layers.¹²⁴

2.4.1 Determining the number of graphene layers

There are numerous ways where TEM can be used to determine the thickness of graphene layers. Perhaps the most reliable and frequently used method is to count the number of higher contrast lines at the folded edge.^{12,124,125} As reflected in the HRTEM images in Figure 2-9, the darker contrast fringes arise from the part of the lattice that lies parallel to the direction of beam illumination.^{124,126} Graphene edges similar to those shown in Figure 2-9 are considered to be folded edges; while open edges have a much

lower edge contrast.¹²¹ Those backfolds are used as a powerful tool for enumerating graphene layers.

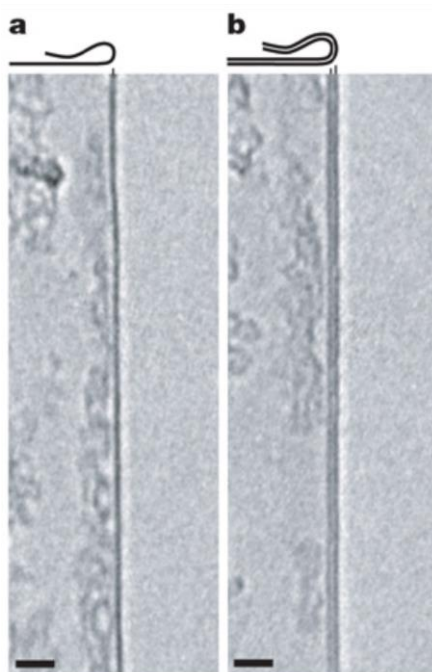


Figure 2-9 HRTEM images of folded edges for monolayer and bilayer graphene, with its corresponding schematic model illustration. Scale bars = 2nm. (Reprinted by permission from Macmillan Publishers Ltd: [Nature] (12), copyright (2006))

The number of layers could also be determined with the diffraction mode of a TEM, this is advantageous in allowing the use of less sophisticated HRTEMs, since SAED could be performed with the majority of TEMs in the market. The latter can also be performed on any part of the specimen instead of being confined to the edges. Figure 2-10 (a,b) show the reciprocal 2D space of monolayer and AB-stacked bilayer graphene. The intensity profile along Z direction of the reciprocal space shows a continuous attenuating rod profile; and bilayer models adopt an alternating contrast Z profile as seen in Figure 2-10 (b). Figure 2-10 (c-h) further demonstrate the intensity of diffraction spots from both the experimental results and simulations obtained from the Fourier transformation of projected atomic potentials.¹²⁷ For monolayer graphene,

the intensity increases by a small margin even though Figure 2-10 (a) reveals a slightly reduced intensity. This is due to more atoms from the lattice being accounted for when the sample is tilted. For bilayer graphene, the intensity alternates in a pattern that is based around the relation between the tilt axis and diffraction pattern. The distinctive tilt behaviour between monolayer and bilayer graphene helps to unambiguously ascertain the number of layers of graphene.

There are several other methods for enumerating graphene layers. The most trivial method is to sputter a hole using the electron beam in a TEM and to count the step edge around the hole. The contrast from atomic resolution AC-TEM images also provides an indication of the number of graphene layers: the atomic contrast of monolayer to six-layered graphene has been compared with experimental data – each has a distinctive contrast profile under fixed defocus and alignment parameters and this allows one to distinguish the number of graphene layers.¹²⁸

2.4.2 Determining stacking order and rotational stacking fault

AB- Bernal stacking is the most common of all stacking orders in natural graphite, and its atomic model is illustrated in Figure 2-11; this property is attributed to the low formation energy of the AB–Bernal configuration, which is 17.31mV/atom lower than the AA–stacking configuration.¹²⁹ The latter also explains the rare occurrence for AA–stacking in natural graphite, as those are only observed on the back folds of graphene edges.^{121,130} ABC stacking, with its atomic model shown in Figure 2-11, was initially reported to form on multilayer graphene that has been epitaxially grown on silicon terminated SiC,¹³¹ but was later shown to also occur on CVD grown graphene – as characterised by HRTEM and Scanning tunnelling microscopy (STM).^{121,130,132}

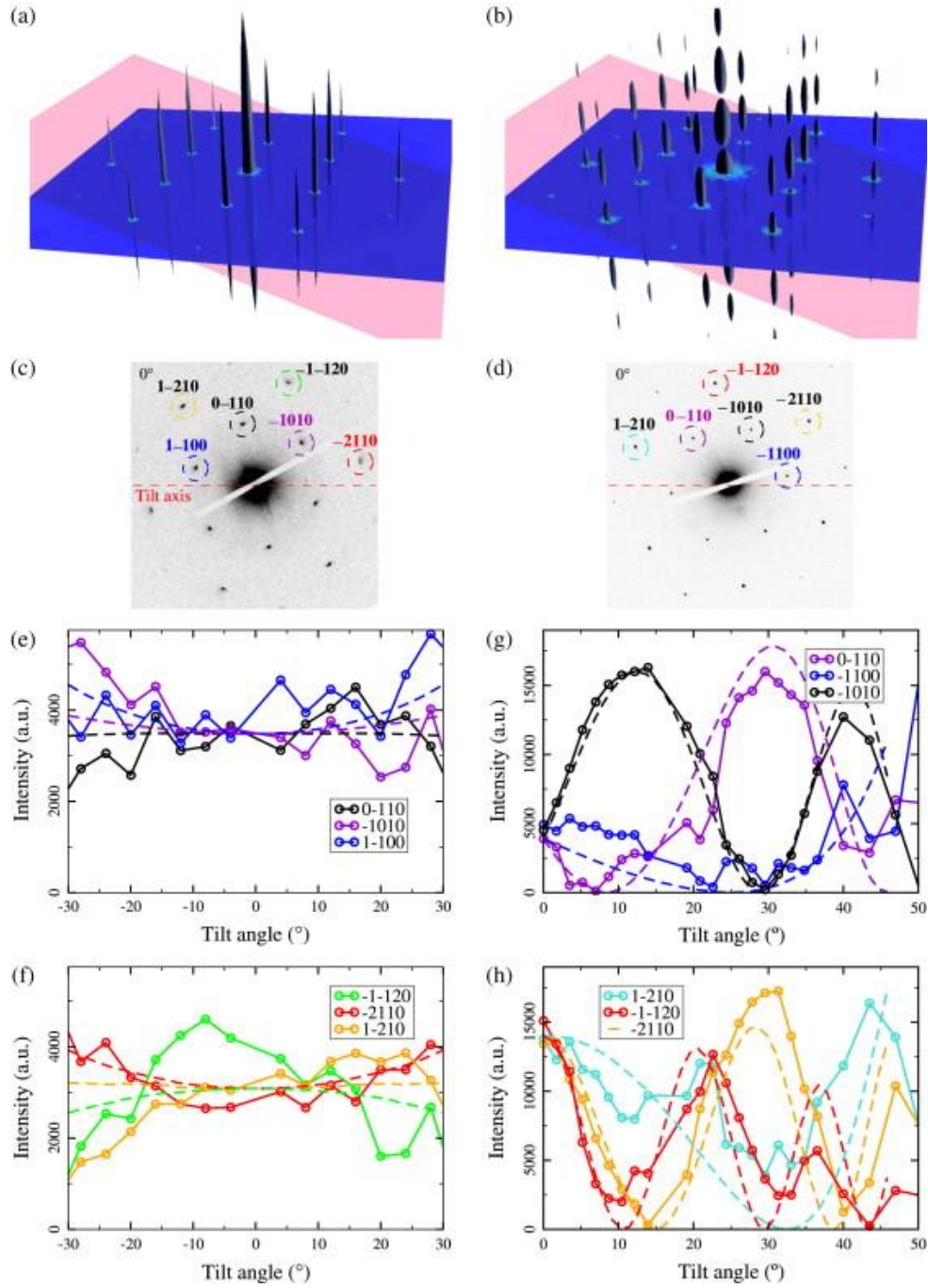


Figure 2-10. (a,b) 3D plot of the reciprocal space for monolayer and bi-layer graphene respectively, blue planes indicates the diffraction plane that would be obtained at normal incidence, the red plane indicates 20° tilt. (c,d) diffraction pattern obtained from normal incidence for monolayer and bilayer graphene. (e-h) Intensity variations of experimental (Solid Lines) and electron diffraction simulation (Dashed Lines) for various diffraction pattern in monolayer (c, e, f) and bilayer graphene (d, g, h) at different tilt angles(-30 – 30°). (Reprinted from ref.[124], with permission from Elsevier)

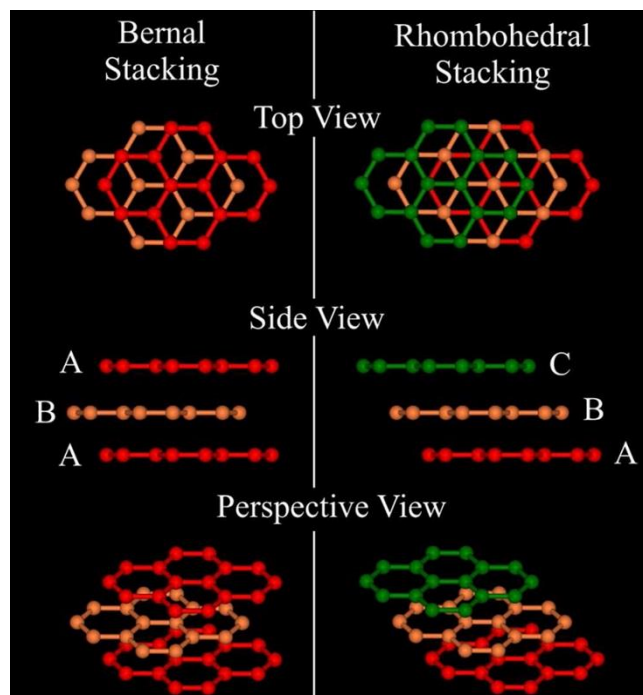


Figure 2-11. Top, side and perspective view of ABA Bernal Stacked and Rhombohedral stacked graphene. (Reprinted with permission from ref.[132], Copyright (2012) American Chemical Society)

2.4.3 Point defects

Defects in graphene can be categorised as intrinsic or extrinsic; the former is a name given to lattice perturbation without the addition of a foreign atom and latter are defects associated with impurities. A unique property of a graphene lattice is the ability to reconstruct itself into various polygonal shapes by adopting various carbon-carbon bonding states. The complexity of intrinsic defects is proportional to the increase in the number of atoms being lost and the number of reconstructions.

I begin with Stone-Wales rotation as the simplest type of effect, where no atom is lost and only bond rotation is observed.¹³⁵ As shown in Figure 2-12 (a,b), four hexagons are transformed into a combination of two pentagons and two heptagons after a 90° bond

rotation. The energy barrier for this transformation is calculated to be 10eV, and the reverse process has a barrier of 5ev.¹³⁶ This type of defects are regularly observed with electron beam irradiation during a TEM experiment.¹³⁷ A 5eV barrier enables a rapid quenching process during electron beam irradiation, but allows a stable structure at room temperature.

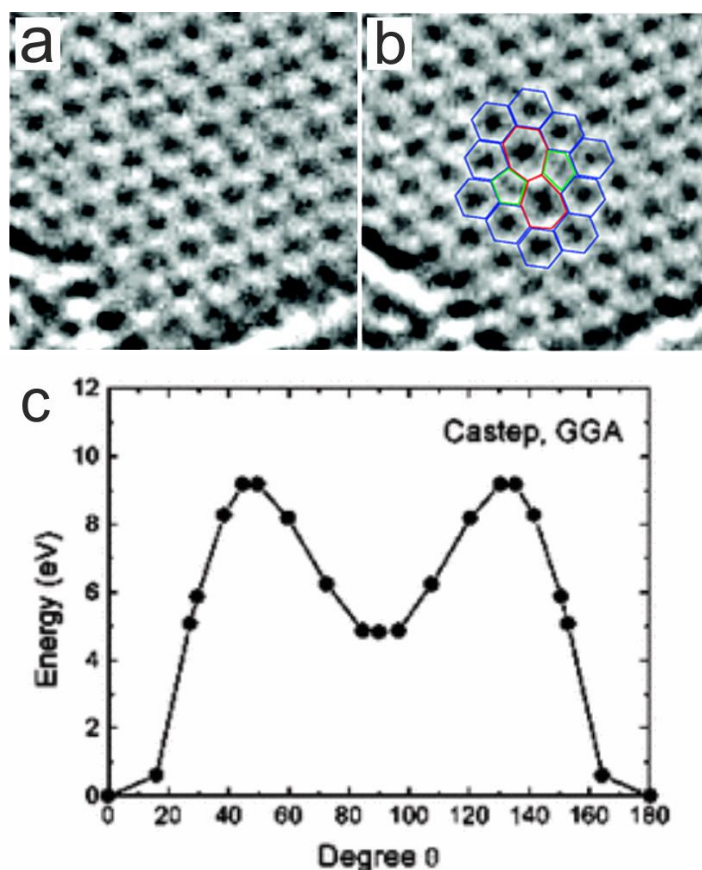


Figure 2-12. (a) and (b) are two AC-TEM frames before and after Stone-Wales rotation. (Reprinted with permission from ref.[137]. Copyright (2008) American Chemical Society) (c) Calculated barrier for Stone-Wales bond rotation. (Reprinted figure with permission from ref.[136], Copyright (2005) by the American Physical Society).

A monovacancy defect describes the situation where a carbon atom is lost, and has been experimentally observed in TEM and STM experiments.^{137–140} When one carbon atom leaves the lattice, three atoms become under-coordinated, as shown in Figure 2-13 (a-

c), resulting in an unstable structure that reconstructs through Jahn-Teller distortion leading to the saturation of two bonds and the formation of the 5-9 structure shown in Figure 2-13 (d-f). In an intrinsic monovacancy three atoms are under-coordinated, they could be saturated by forming a bond between either of the two atoms, and there are three possible ways to form this bond. The low energy of approximately 0.13eV allows the switching between the three possible reconstruction structure to occur readily during electron beam irradiation.¹⁴⁰ The transition between states is believed to occur so rapidly that the structure shown in Figure 2-13 (a) is likely the result of a superimposition of states; the functionalisation of the under-coordinated C atom by a low mass element, such as hydrogen, allows visualisation of the 5-9 structure shown in Figure 2-13 (d). The maximum energy transfer from an electron beam that is accelerating at 80kV to a single layer of graphene is estimated to be 17.9eV.^{141,142} This reading falls below the theoretical first-principles estimates of the minimum energy required for a carbon atom to leave its position in a lattice without recombination – which is between 28-22eV.^{143–146} Nevertheless, a substantial increase in the beam current density (BCD) allows the local sputtering of carbon atoms without surpassing the knock-on damage threshold.¹²² *In situ* point defects could therefore be introduced in a TEM with this method.

Divacancies are formed when two adjacent atoms are lost or when two monovacancies coalesce, and the resulting structure is shown in Figure 2-14 (a). When a divacancy fully reconstructs, a 5-8-5 structure, which lacks a dangling bond, is formed. A similar amount of energy is required to form a monovacancy and a divacancy – around 8eV. In terms of energy per atom, however, the formation of a divacancy (~4eV) is much more thermodynamically favourable than monovacancy – which is therefore more frequently observed.^{147–149} A divacancy could reconstruct into a more complex

structure through a series of Stone-Wales rotations, as shown in Figure 2-14 (b).¹³⁵

Figure 2-14 (c) shows an extended defect along the armchair direction that results from the union between two divacancies.

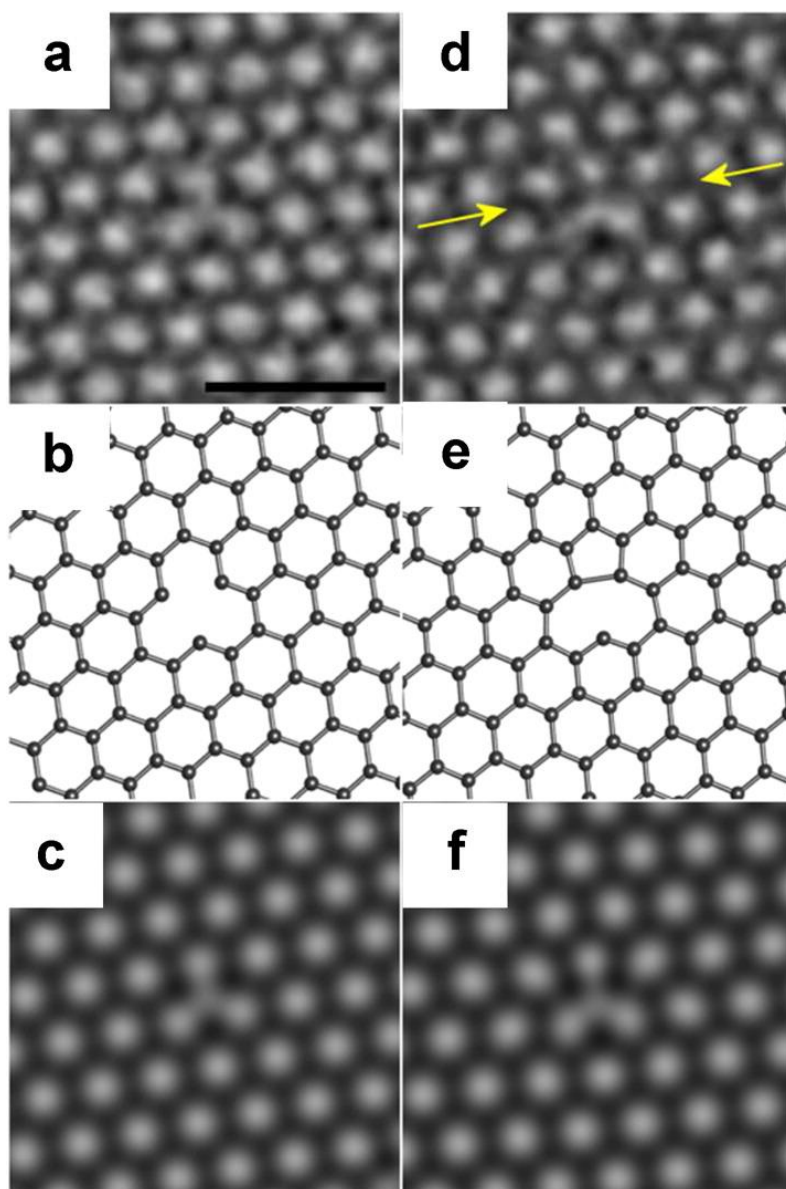


Figure 2-13. Monovacancy (a) Smoothed AC-TEM image of the symmetric monovacancy, s-MV with Density functional theory (DFT) calculated atomistic model shown in (b) and its multislice image simulation in (c). (d) Smoothed AC-TEM image of the reconstructed monovacancy, r-MV with DFT-calculated atomistic model shown in (e) and multislice image simulation in (f). (Reprinted with permission from ref.[140], Copyright (2013) American Chemical Society)

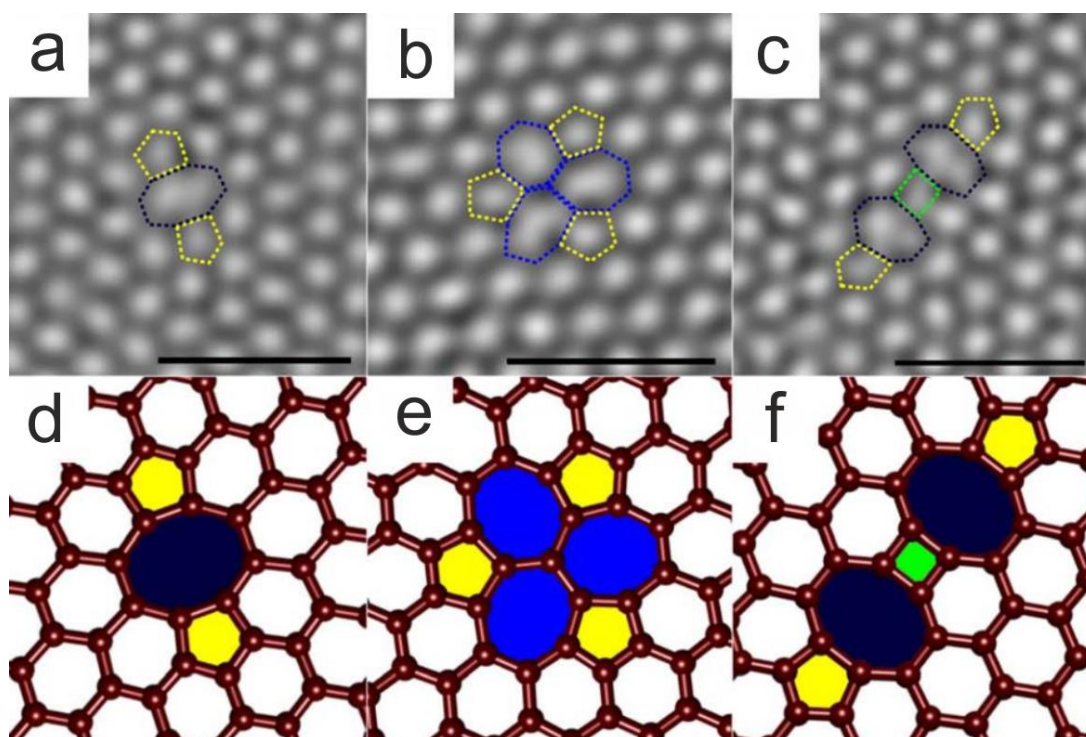


Figure 2-14. Divacancy (a) an AC-TEM frame of a divacancy and its reconstructed form through a single Stone-Wales bond rotation shown in (b). (c) shows the atomic structure when two divacancies linked along the armchair direction. (d-f) are atomic structures corresponding to (a-c) respectively. (Reprinted by permission from Macmillan Publishers Ltd: [Nature Communications] (ref.[122]), Copyright (2012))

The manner in which three atoms are displaced from the the lattice system to form a trivacancy, is reminiscent to the formation of a monovacancy, they both result from an odd number of atoms being lost through Jahn-Teller bond reconstruction, where one carbon atom is left under-coordinated (Figure 2-15 (a)).^{140,147} This structure is however, not frequently observed in when electron beam from a TEM is utilised as a source to sputter carbon atoms, but shows higher occurrence when graphene is being sputtered under ion irradiation.¹⁵⁰ Unlike the case with electron beam irradiation, a single incident ion with sufficient energy can potentially eject three adjacent atoms simultaneously. Under electron beam irradiation, a bridging atom stabilised Trivacancy structure as shown in Figure 2-15 (b) are however frequently observed. The DFT relaxed model

and image simulation are shown in Figure 2-15 (c,d), and the latter fits well with experimental results. The formation energy responsible for this bridging structure, as calculated by DFT, is higher than the reconstructed structure shown in Figure 2-15 (a), but Tight-binding molecular dynamics (TBMD) calculations suggest that this bridging structure is preferred when a monovacancy merges with a divacancy.¹⁵¹ Trivacancies are also found to exhibit a magnetic moment of $1.92 \mu_B$ which is significantly higher than the reconstructed structure shown in Figure 2-15 (c) ($1.02\text{--}1.04 \mu_B$).^{152,153}

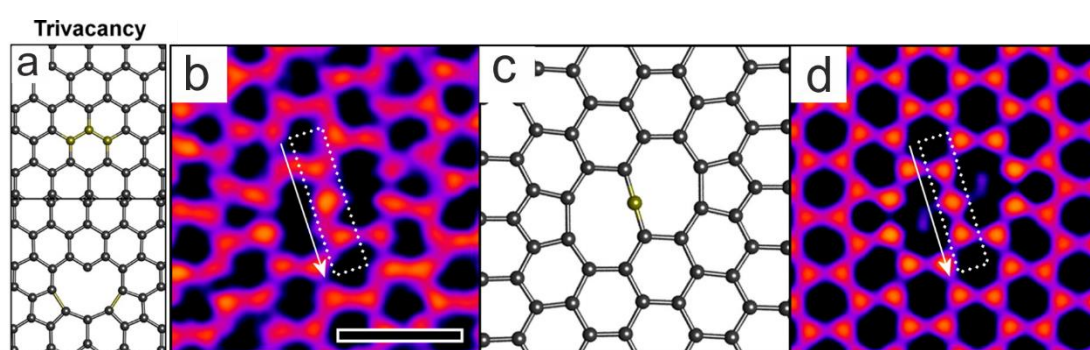


Figure 2-15. Trivacancy (a) Schematic model illustration of reconstructed Trivacancy leaving one carbon atom having one uncoordinated bond. (b) Smoothed AC-TEM image of a bridging atom stabilised Trivacancy. (c) A DFT optimised atomic structure for bridging atom stabilised Trivacancy and its multi-slice image simulation shown in (d). Scale bar is 0.5nm. (Reprinted with permission from ref.[151], Copyright (2014) American Chemical Society)

The complexity of defects that develop in structures scale with the number of atoms being lost: for example, tetravacancy is where four atoms are lost.¹⁵⁴ The possible permutation of structures increase dramatically with the number of atoms being lost. Accordingly, the number of ways that a defect could reconstruct itself by Stone-Wales rotation increase further. Since commonly observed structures are not necessarily the most energetically favourable, it is important to correlate experimental evidence with theoretical calculations when modelling more complex defective structures. These types of complex multivacancies are often observed when graphene is exposed to an

electron beam for an extended period of time in a TEM,¹²⁵ raising the possibility that these structures could expanded from an existing, simpler defect, or that they result from the migration and agglomeration of defects through electron beam assisted diffusion and bond rotation.¹⁵⁵ Likewise, configurations like the extended zig-zag or armchair divacancy chains,^{156–158} and closed loop structures could also be formed through similar processes.¹⁵⁹

2.4.4 Adatoms and dopants

Out of the possible adatom positions, the bridging position shown in Figure 2-16 (a), is the most energetically favourable. The hybridisation state change to form a partially sp^3 -hybridisation bond to incorporate the out of plane adatom in the lattice. The binding energy is between 1.5-2.0 eV.^{160,161} An adatom at the bridging position could also migrate on the surface considering the small energy difference of 0.3eV between the local and global minima.^{161,162} The migration of the adatom on the surface of the graphene lattice occurs rapidly, such that observation under TEM and Scanning transmission electron microscopy (STEM) is not normally possible unless there is a defect.¹⁶³ When an adatom is placed at the centre of a hexagon as shown in Figure 2-16 (b), it is considered to be in the interstitial position; the adoption of such a position in monolayer is prohibitively high in energy cost, and therefore should not exist. The other possible position is the top position, where the adatom is placed directly above another carbon atom, as shown in Figure 2-16 (c) this position is higher in energy than the bridge position by 0.5eV and has a migration barrier of 0.9eV,¹⁶⁴ and is pertinent to the study of bilayer and multilayer graphene.

With the addition of multiple carbon atoms, the formation of atomic carbon blisters with the out of plane buckling of the graphene has been theoretically explored.^{165–169}

The blister defects, for a long period of time, lacks experimentally study. Robertson et al. showed in ref. [170] a detailed study of the blister defect structures up to an addition of six carbon atoms. Figure 2-16 (d) shows a defect structure when 6 extra carbon atoms are incorporated into the lattice structure (C_6), with the atomistic structure shown in Figure 2-16 (e). the misaligned 6- membered ring in the centre of the defect structure is wrapped around by 4 heptagons and 4 pentagons.

The C_4 defect structure, where four extra carbon atoms are added is shown in Figure 2-16 (f), and its atomistic model is represented by Figure 2-16 (g). The result is a triad of dislocation core structures, where each dislocation core 5-7 structure is oriented in the armchair direction, mutually eliminating extra lattice planes, and limiting the number of additional atoms to four. In Figure 2-16 (h), each dislocation core is glided by one lattice plane, which increases the length of each dislocation to better illustrate the mutual elimination effect. The C_2 defect, also known as the inverse Stone-Wales defect (ISW), performed an additional Stone-Wales rotation to form the structure shown in Figure 2-16 (i) (its atomistic model is shown in Figure 2-16 (j)). This structure could also be viewed as a self-contained triad of dislocations with a hexagon in the middle that has been rotated by 30° with respect to the bulk lattice. The study also shows that the blister structures suffer little in-plane lattice strain, as a result of the buckling of the graphene lattice. The adatom defects are rarely seen relative to vacancy defects, which suggests a large formation energy barrier. The relatively short lifespan (~ 35 s for C_4 , and C_6 , and ~ 3 min. for C_2) of these structures during electron beam irradiation should be taken into account when engineering defects through atom addition.¹⁷⁰

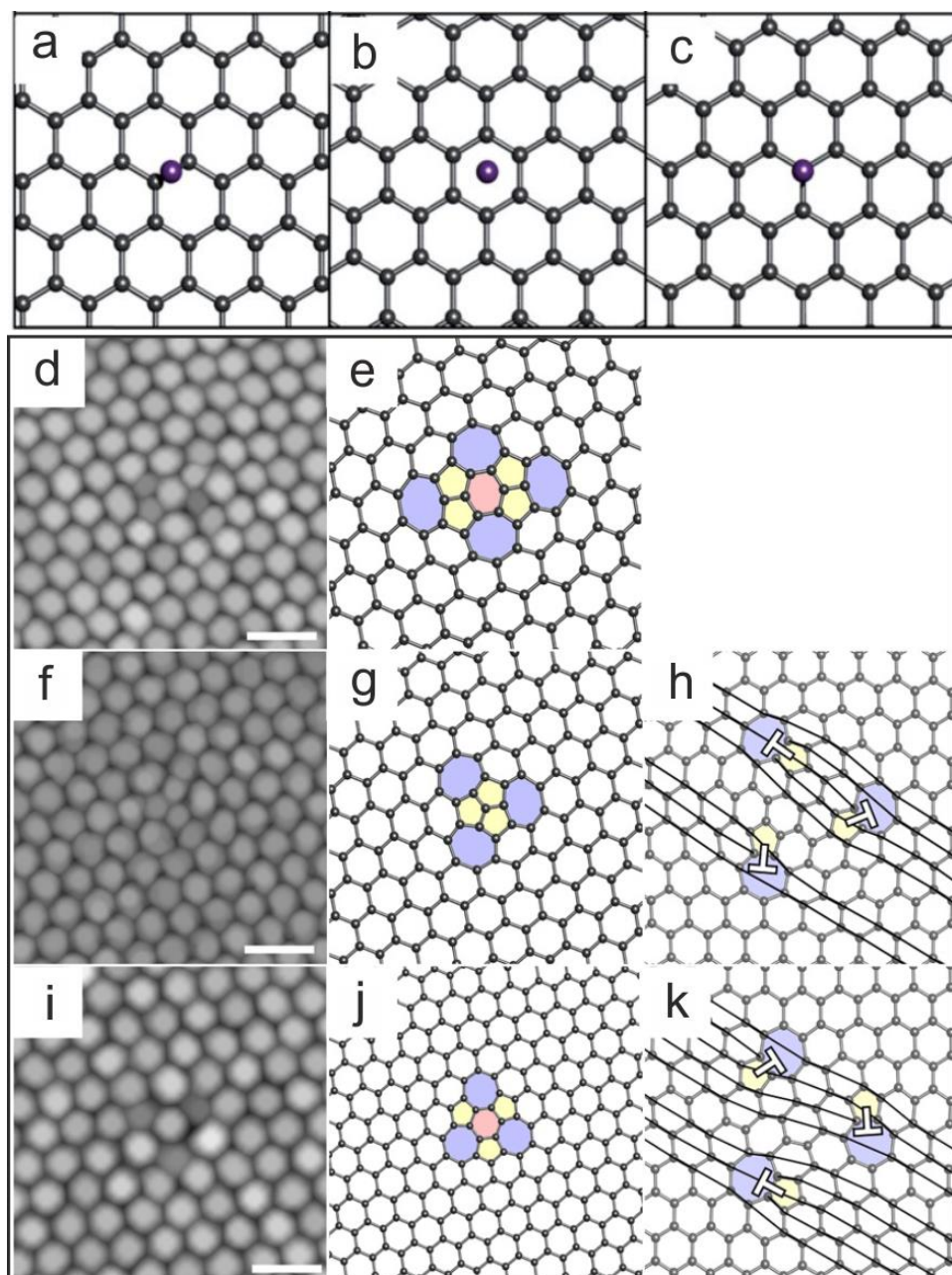


Figure 2-16. Carbon adatoms. The atomistic structure of three possible adatom (blue atoms) positions on a graphene sheet. (Reprinted with permission from ref.[125], Copyright 2013 Nanoscale). (d, f, i) are maximum filtered AC-TEM frames of C₆, C₄, and C₂ adatom defects respectively, with their atomistic models shown in (e, g, j). (h, k) are annotated atomistic model emphasizing the dislocation triad generated by expanding the 5-7 dislocation cores of the C₄ and C₂ defects respectively. Colour coding: yellow, red, blue are for 5-, 6-, and 7- membered rings respectively. (Reprinted with permission from ref.[170], Copyright (2014) American Chemical Society)

The effect that foreign dopants, such as transition metals have on the properties of graphene is largely dependent on the bonding configuration between the atom and graphene.¹⁷¹ Metal dopant atoms could reside on top of the graphene sheet by forming weak van der Waals interactions, and this type of doping is unstable due to chemical reactivity with atmospheric molecules. The migration of dopant atoms is initially employed to study the dynamics and bonding configuration, as it reveals information on the activation energy required for dopant migration, etc.; it is, however, challenging to distinguish between van der Waals and covalently bonded dopant atoms.^{171–179} Covalently bonded dopants offer a more permanent solution to doping, and is therefore more valuable for graphene engineering. Following the development of aberration correction technology TEM, it became possible to reveal the covalent bonding configuration between dopant atoms and bulk graphene.^{180,181} Divacancies (Figure 2-17 (b)) are observed to trap Fe metal atoms within the vacancy location and to form interstitial substitutions.^{150,180} Even the generally considered unstable trivacancy can be filled with a single Pt atom, due to the large size of the atom.¹⁵⁰ Using aberration corrected electron optics, it was also possible to gather information on both the dynamics and spatial resolution of the structure, since this allowed a monitoring of the bonding configuration of vacancies before and after the occupation of metal dopants.¹⁸² The change in electronic structure when dopant atoms are introduced at different bonding configuration can also be revealed with exceptional high signal-to-noise ratios by employing atomic resolution electron energy loss spectroscopy (EELS) in a STEM.¹⁸³

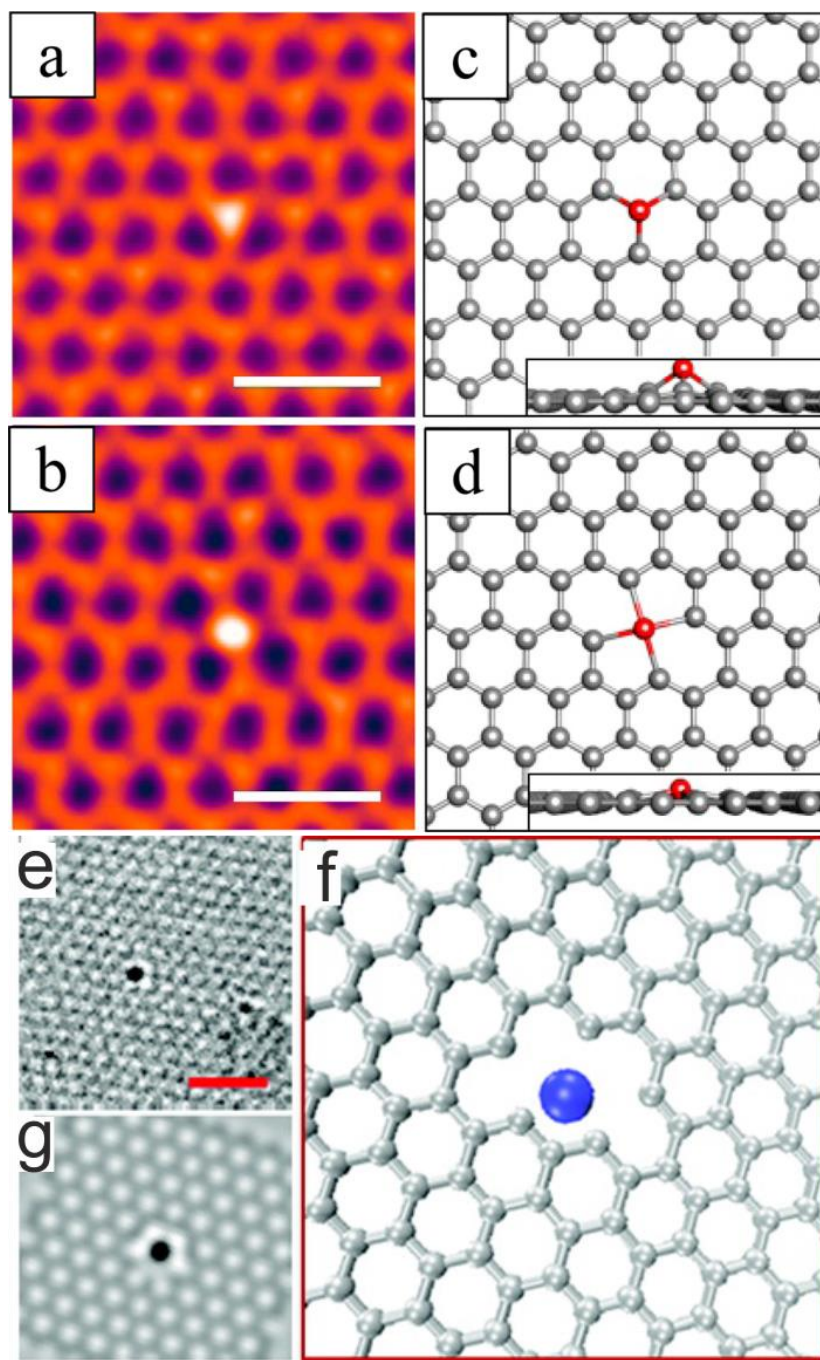


Figure 2-17. Metal dopants. (a,b) are false coloured AC-TEM frames of single Fe atoms residing in a monovacancy and divacancy respectively. (c,d) are DFT optimised atomistic models corresponding to (a,b). Insets are the side views of the optimised structures. Scale bar, 0.5nm. (Reprinted with permission from ref.[181], Copyright 2014 Nano Letters) (e,f,g) are AC-TEM frame, atomistic model and multi-slice image simulation of a Pt atom trapped in a trivacancy. (Reprinted with permission from ref. [150], Copyright (2011) American Chemical Society)

A carbon atom has been replaced by Si, Fe (Figure 2-17 (a)), and N to form a substitutional doping site.^{180,184–186} For lighter atoms, such as N, the substitutional doping is exceptionally stable; and survives local sp^2 bond reconstruction without being sputtered or replaced by a carbon atom. Aberration corrected scanning transmission electron microscope (AC-STEM) is an increasingly popular technique that enables the visualisation of bonding configurations at defective sites and edges of graphene.^{158,182–184,187–189} The combined use of atomic resolution 2D EELS mapping and Angular dark field (ADF)-STEM allow the mapping of local bonding variations, this has allowed direct visualisation of both bonding hybridisation (sp^2 or sp^3) and detailed changes in the carbon K-edge EELS spectrum.

2.4.5 One-dimensional defects

2.4.5.1 Dislocation

Since dislocation was first conceptualised, it has remained an important subject of study for material scientists as it heavily influences both the mechanical behaviour and properties of solid state matter.¹⁹⁰ The imaging of structural dislocations began with low resolution TEM using the weak beam method.^{191,190,192} The discovery of graphene and substantial advancement in the spatial resolution of AC-TEM allowed the study of dislocation with atomic precision, the former because of its monolayer nature, which allowed the direct study of atom arrangements without the need for complex image simulations. The two-dimensionality prohibits the formation of screw dislocation and instead, forms what would be an edge dislocation in 3 dimensional material. The lack of an adjacent atomic layer also allows clear visualisation of out-of-plane corrugations.^{123,163,193–196} Figure 2-18 (a) shows a pair of edge dislocations that are aligned in opposite directions.¹²³ There are five possible ways for dislocations in

graphene to form: during synthesis, from electron beam sputtering in a TEM, surface atom incorporation, reconstruction from multivacancies and multiple Stone Wales rotation.¹²³ In ref.[123] and Figure 2-18 (a-c), the dislocation pair was formed by electron beam sputtering, and the two dislocation cores were observed to have undergone both a climb and a glide process. In this scenario, a climb describes the loss of two neighbouring atoms (marked by two crosses in Figure 2-18 (g)) and then reconstruction that allows the dislocation to propagate in the zig-zag direction. A glide does not involve atom loss, instead, it occurs *via* Stone-Wales rotation involving the two atoms highlighted with an ellipse shown in Figure 2-18 (g). These two motions constitute the fundamentals types of dislocation movements and form the basis for the further understanding of more complicated atomic patterns of behaviour, such as migration, attraction and annihilation, the birth of graphene dipoles.^{193,194,197}

HRTEM offers a significant advantage in that it allows continuous time series imaging to capture the dynamics of atomic movement during the formation of dislocations.^{193,194,197} Geometric phase analysis (GPA) are used on AC-TEM images to show “compression” and “elongation” in the local lattice – based on differences in average bond length measurement in the vicinity of the defect and a pristine area of bulk graphene.^{123,198–200} In corroboration with GPA, multi-slice image simulation of the DFT relaxed structure reveal severe instances of rippling that is associated with dislocation defects which also tend to be longer in range than point defects. When dislocations are found near the edge, the rippling decreases and in-plane rotation occurs more frequently relative to dislocations in bulk graphene, allowing the frequent edge reconstruction to relax the strain.²⁰¹

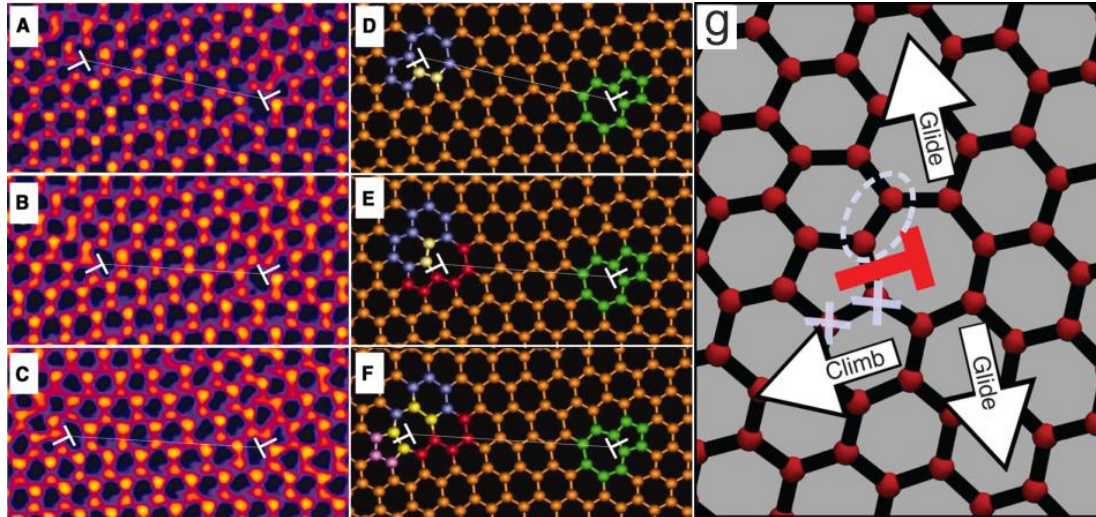


Figure 2-18 Dislocation Dynamics. HRTEM image of graphene dislocation movement under continuous electron beam irradiation with time. (a)0s (b) 141s (c) 321s. (d-f) atomistic models illustrating the atomic structure of (a-c) respectively. (From ref.[123], Reprinted with permission from AAAS) (g) Schematic illustration of possible routes for graphene movements – climb and glide. (Reprinted by permission from Macmillan Publishers Ltd: [Nature Communications] (ref.[193]), Copyright (2013))

2.4.5.2 Grain boundary

Given a large enough sample area, grain boundaries (GB) inevitably exist in graphene. They are known to affect the properties of polycrystalline graphene greatly – reducing electronic mobility,^{74,75,94,101} lowering thermal conductivity,²⁰² and reducing mechanical strength.^{203,204} The GB of graphene have been studied with STM initially,^{205–208} and more recently performed on epitaxially grown graphene on single crystal substrates.^{90,156,209–212} However, this imaging process is time consuming, requires a graphene sample to be on special substrate, and is not appropriate for large area characterisation. AC-TEM, SAED in STEM mode, and dark field imaging was later proved to be a powerful tool to resolve the atomic structure of the grain boundary, and also map out the grain size on a sufficiently large area.^{110,112,204} Figure 2-19(a) is

an attempt to map out the domain structure of graphene on SiN grid, based on the diffraction pattern shown in Figure 2-19(b), the highlighted circles shown are the apertures used to isolate individual diffraction spot for the dark field imaging.

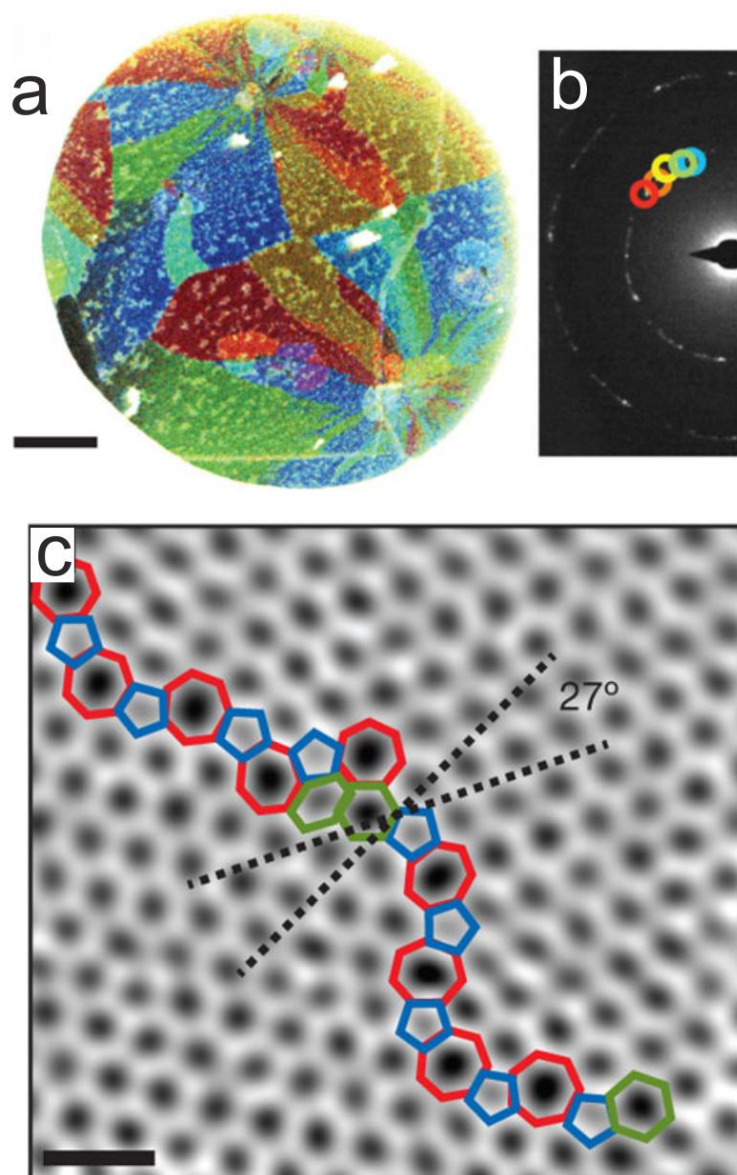


Figure 2-19. Grain Boundary. (a) Grain structure mapped out with dark-field TEM with each colour corresponding to the aperture selected in the diffraction pattern shown in (b). Scale bar, 500nm. (c) Two grains intersect with a 27° relative rotation, an aperiodic line of defects stitches the two grain together, with the pentagons highlighted in blue and heptagons in red and the distorted hexagons in green. Scale bar = 0.5 nm. (Reproduced by permission from Macmillan Publishers Ltd: [Nature] (ref.[110]), Copyright (2011))

The atomic structure was later imaged using AC-TEM in ref.[110] to show the alternating pentagon-heptagon chains expected from a grain boundary between two mismatched domains. The electron beam irradiation effect also causes the GB to migrate; under long enough irradiation time (depending on the length, usually > 20 minutes), it is also possible to observe the total collapse of nanometre scale GB, and form a close looped structure (also known as the flower defect).^{213,214} By increasing the defocus in TEM, it was possible to differentiate between two grains atomically stitched or overlapping each other, which are the two possible ways graphene could merge during CVD growth, and are therefore important.²¹⁵

2.4.6 Edges

As mentioned in section 2.2.3, the field of graphene edge research has expanded rapidly due to the motivation of obtaining clean, atomically sharp graphene edge especially on nano-constraint structures, such as GNRs. The renaissance of TEM and STEM technology mainly contributed by the advancement in aberration correction technology, and monochromation instrumentation has allowed the possibility to image and obtain spectroscopic information down to atomic resolution even for light element such as carbon.

The following sections will attempt to review some of the most important discoveries of graphene edge behaviour obtained from TEM, STEM and EELS, enabling a more thorough understanding and a better control of the edge behaviour. Inspired by these studies, Chapter 4-8 reports on novel sciences that have been investigated on the topics of atomic resolution studies on graphene edges. These studies try to address some of the issues still remain unsolved in this specific field.

2.4.6.1 Open and closed edge

The differences between open and closed edge graphene is schematically illustrated in Figure 2-20 (a), where a closed edge in bilayer graphene describes the situation where the top and bottom layer form bonds to eliminate the dangling bonds; open edge occurs where the edges stay in its intrinsic form without bonding to adjacent layers. As can be seen in the HRTEM image shown in Figure 2-20 (b), open and closed edges can co-exist, even along the same edge. The ability to experimentally distinguish open and closed edges is important as the presence of open edges in graphene could produce significantly large differences in electronic features when compared to other sp^2 based nano-carbon structures, such as carbon nanotube, and fullerene, which have minimal edge effect. The properties are indeed different compare to closed edge bilayer graphene.^{216–220} It is therefore necessary to investigate the atomic structure of graphene edges under various environments to correlate peculiar electrical properties with atomic structure. The technique of Scanning Tunnelling microscopy (STM) was used to study graphene edges that terminate with hydrogen in ultrahigh vacuum conditions.^{221,222} HRTEM was later employed to study folded graphene edges, i.e. closed edge.^{124,223,224} In ref.[121], the thermally treated graphene (2000°C for 3 hours in vacuum) have sufficiently clean edges for the lattice to be revealed under a HRTEM; closed and open edge can be distinguished based on the contrast difference.

On a similar topic, my results in Chapter 8 follow the development of a method where a closed bi-layer structure could be formed with a pristine single layer graphene sheet as the starting block, they are shown to be more stable and resistant to back filling. The study sheds light on the use of graphene as sensors and even potentially for direct DNA sequencing.

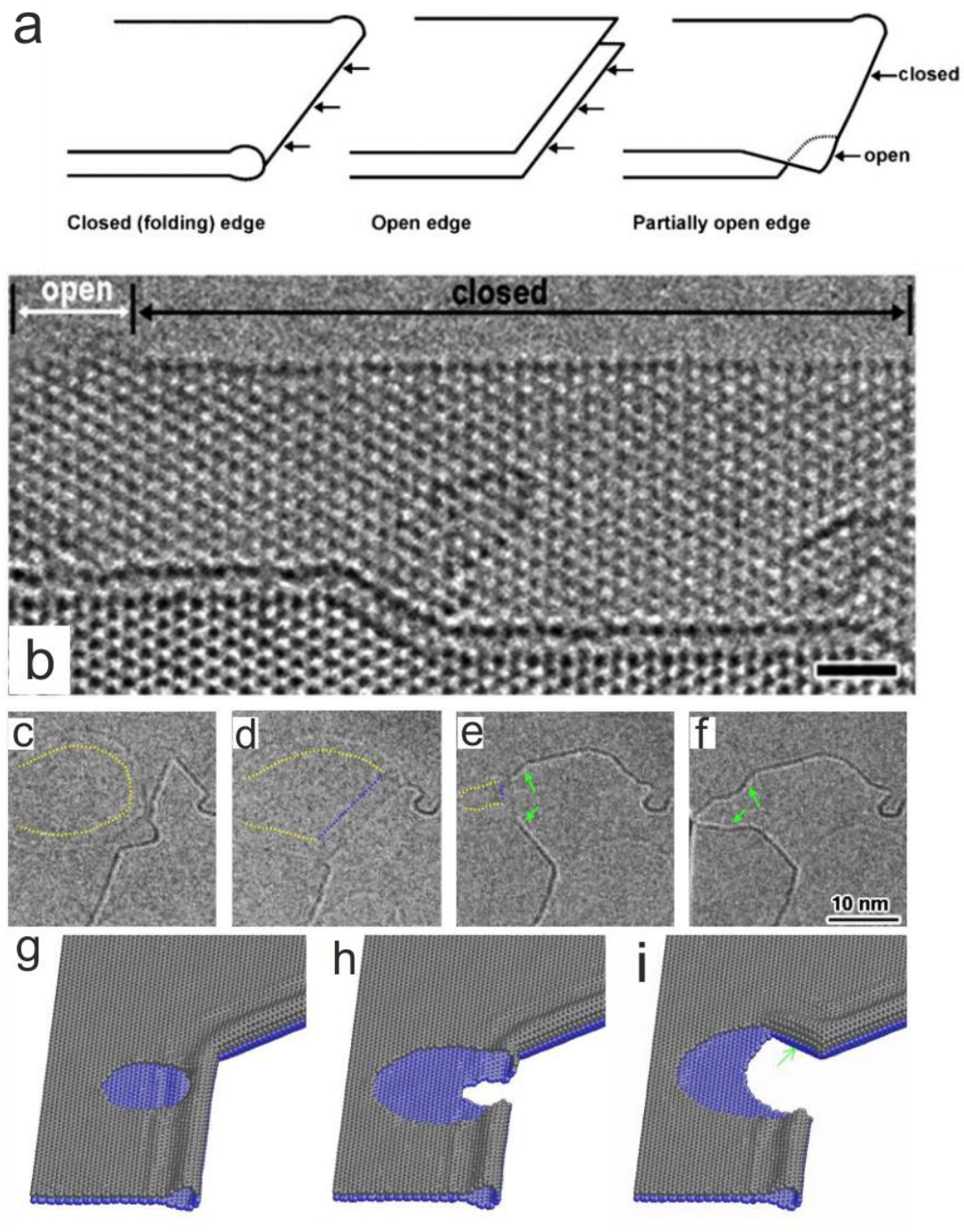


Figure 2-20. Open and Closed Edge. (a) Schematic illustration of open, closed, and partially closed bilayer graphene. (b) An HRTEM image of a partially closed edge along the armchair direction. (Reprinted figure with permission from ref. [121], Copyright (2009) by the American Physical Society) (c-f) Sequential HRTEM image showing the formation process of bonded bilayer graphene and its schematic illustration shown in (g-i). (Reprinted with permission from ref.[225], Copyright (2009) National Academy of Sciences, USA.)

Joule heating provides an alternative solution to edge cleaning and tailoring and is shown in ref. [225] In Figure 2-20 (c-i), carbon atoms on the edge vaporises as the applied voltage is increased to $\sim 2.5\text{V}$. Graphene lattice were imaged simultaneously with the application of voltage, and it is observed that $>99\%$ of the bilayer edge are in a bonded edge configuration, which means that the top layer and bottom layer are linked by covalent bonds. This is thermodynamically favourable as it eliminates the dangling bond (capillary energy), and by doing so, is more resistant to etching and is a more stable form of the bilayer edge. The bonding process is captured with time series HRTEM imaging, as shown in Figure 2-20 (c-f), it is also schematically illustrated in Figure 2-20 (g-i).

2.4.6.2 Edge configuration

Because of the honeycomb structure of the graphene lattice, by cutting graphene along its two directions, two intrinsic edge structures could form, namely armchair (Figure 2-21 (b)) and zig-zag (Figure 2-21 (d)). Cutting along other directions introduces step edges, and the chirality of the edges are characterized with a chiral vector (n,m) , which defines the edge orientation.^{226,227} Graphene nanoribbons (GNR), which introduced a bandgap in graphene, offer promising properties for graphene electronic design.^{37,38,228,229} Depending on the chirality, tuneable energy gaps,^{38,230} one-dimensional edge states,^{231–233} and unusual magnetic structure could be introduced.^{46,234} By going through a Stone-Wales like bond rotation,^{135,235} edges could reconstruct themselves into different configurations, some have a higher energy state than the original structure.

A zig-zag edge could rearrange into a 5-7 membered ring structure, namely rec. 5-7 (Figure 2-21 (a)). As seen in Figure 2-21 (f), the reconstructed form are calculated to

have lower edge energy compare to the original zig-zag form and has been reported to be observed under HRTEM as a transient structure.^{125,141,236–238} Kim et al. has reported in ref.[141] the transition of that zig-zag edge into rec. 5-7 edge under electron beam irradiation in a collective manner and flips between the two states. Statistical measurements indicate that the zig-zag configuration is preferred 66% of the total time and, this is attributed to the higher thermodynamic and electron beam irradiation stability of the rec. 5-7 configuration.^{237,239} The Armchair edge has two reconstructed states, also through bond rotation ac(677) shown in Figure 2-21 (c), and edge atom sputtering ac(56), shown in Figure 2-21 (e). The two structures have 1.1 and 1.5 eV/Å in energy respectively, both higher than the original armchair edge, 1.0 eV/Å. They are therefore only observed on occasional basis in HRTEM, and soon been sputtered away by electron beam.²³⁶

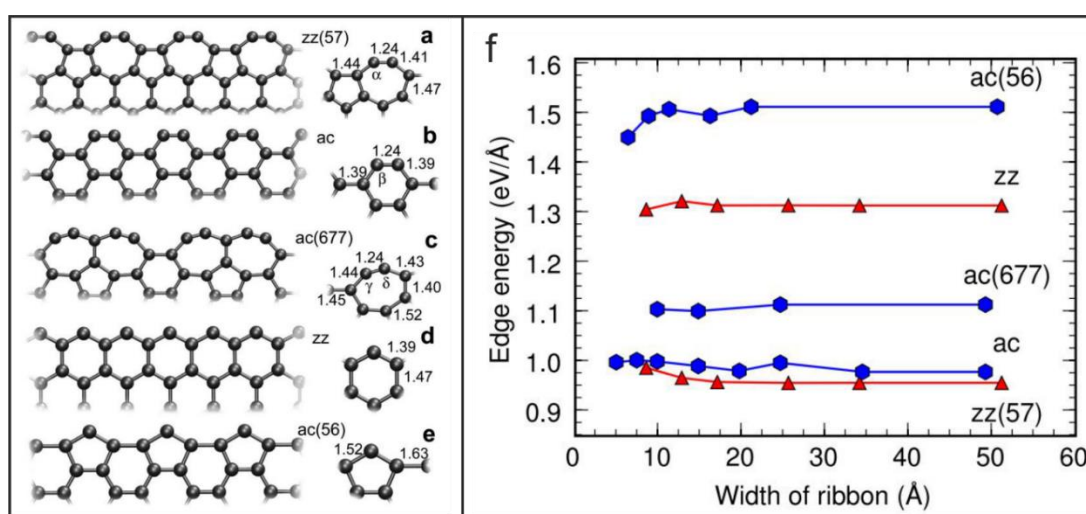


Figure 2-21. Possible graphene edge configurations. (a) reconstructed zig-zag (zz(57)), (b) armchair (ac), (c) reconstructed armchair (ac(677)), (d) zig-zag, (e) pentagonal armchair (ac(56)). The structure was optimised with a tight binding method, some bond lengths (in Å) and bond angles are shown: $\alpha = 143^\circ$, $\beta = 126^\circ$, $\gamma = 148^\circ$, and $\delta = 147^\circ$. (f) edge energies of carbon nanoribbon plotted against width of the ribbon. (Reprinted figure with permission from ref.[240], Copyright (2008) by the American Physical Society)

The subject of tailoring graphene edges with precise controllability is highly desirable. Attempts are made with electron and photolithography on selected crystallographic direction, unzipping of carbon nanotubes, and metal particle assisted etching to gain control of the edge configuration.^{37,72,241,242} More recently, the anisotropic etching of graphene with the assistance of metal nanoparticles and hydrogen at elevated temperatures are employed to produce predominately zig-zag edges.^{243,244} Characterising the atomic configuration at a graphene edge has also been the focus of this report. Atoms at the edge have lower sputtering barrier, as they are only bonded to two atoms, therefore either have a dangling bond attached to it, or adopt other hybridisation states than the native sp^2 . The dynamics could therefore easily be studied by taking time series imaging sequence. Chapter 4 described a novel method to combine the precise bond length measurement along armchair direction and DFT calculation to determine the hydrogenation states. With the monochromation of electron beam turned on, a fourth periodic structure of graphene edges was reported in Chapter 5. They are rarely observed under normal conditions due to both electron beam irradiation effect and resolution limit. A temperature dependent study of edges is carried out in Chapter 7, aiming to understand the nature behind drastically different edge behaviour under different temperatures.

2.4.6.3 One-dimensional atomic carbon chain

Linear carbon chains formed just before the breakage of a carbon nanotube have previously been observed.²⁴⁵ A similar structured carbon chain can be formed by relentless sputtering of a GNR in a TEM, which in itself is produced by sputtering two holes in close vicinity to each other on a piece of graphene, shown in Figure 2-22 (a-c).^{246,247} It was observed that normally a double wire structure often forms before the formation of a single wire. As is analysed in Figure 2-22 (d-o), when the double wire

are connected to two different aromatic rings, it tends to attach to a hexagon and pentagon combination; if the two chains are connected to one aromatic ring, it prefers to connect to a pentagon, rather than a hexagon ring. When the two chains are both attached to one aromatic ring, they are more curved than if they are connect to two different aromatic rings.

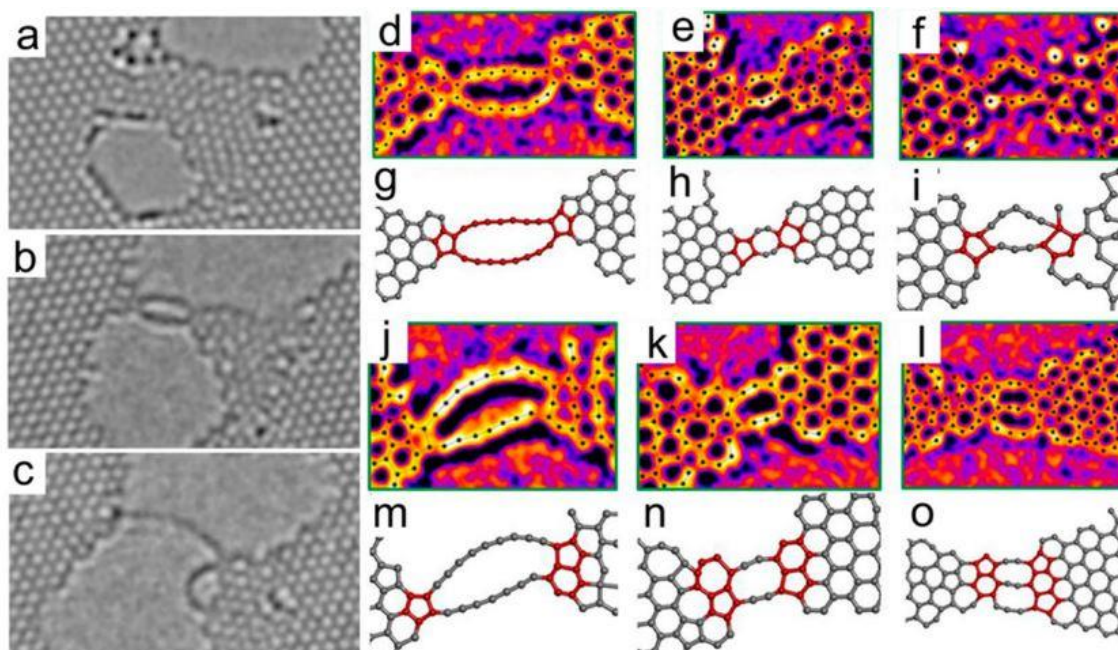


Figure 2-22. Atomic carbon chains. (a-c) sequence of AC-TEM images of graphene at 80kV electron-beam irradiation, showing the narrowing of GNR and eventually forming a linear carbon atomic wire. (d-f) are false colour AC-TEM frames showing double carbon chains interconnected bonded to the same aromatic rings on both sides, with its atomistic model shown in (g-i). (j-l) are double carbon chains attached to the same aromatic rings on both side with the atomistic models shown in (m-o). (Reproduced with permission from ref.[246], Copyright (2014) American Chemical Society)

The bonding configuration for the chain has not been thoroughly studied, it is suspected that either a polyyne $C-C\equiv C-C\equiv C$ or cumulene $C=C=C=C$ structure could be formed. Theoretical calculations predict that cumulene is a more stable structure out of the two, ref.[246] measured the bond length of the chain by fitting double Gaussian equations

to the intensity profile acquired on the monochromator improved AC-TEM atomic resolution images, proving there is a bond length variation between the centre of the chain and the two bonds that connects to graphene lattice.

2.4.6.4 Edge state

With the advancement in STEM and electron energy-loss spectroscopy (EELS) technique, it is now possible to combine the use of annular dark field imaging with atomic resolution EELS measurement to associate the local electronic properties with the geometrical position of the carbon atom.^{248–250} Suenage et al. was able to obtain site-specific EELS spectrum on graphene edges, enables the determination of electronic and bonding configuration of single-, double-, and triple- bonded carbon atoms.¹⁸⁷ This was achieved by simultaneously taking ADF-STEM images with EELS spectrum at an accelerating voltage of 60kV, below the sputtering threshold. An example is shown in Figure 2-23, an ADF image of graphene edge is shown in Figure 2-23 (a), with the possible carbon atom positions derived from the local maxima. Three possible bonding configurations, triple-, double-, and single- bonded carbon atoms are identified and shown in green, blue, and red. The EELS spectrum are shown in Figure 2-23 (d), where all three spectrum show typical sp^2 bonded carbon atoms feature – the exciton peak of σ^* at 292 eV, and π^* peak at around 286eV.²⁵¹ The spectrum in blue was recorded from an edge atom located at the edge, coordinated with only two other atoms, and surprisingly, there is an extra peak at $283.6 \pm 0.2\text{eV}$ (labelled D), with π^* peak has a reduced intensity. The spectrum in red is taken on a Klein edge (single- coordinated), shows a similar feature, with the extra peak S occurring at $283.6 \pm 0.2\text{eV}$. By taking line profiles and mapping the EELS signal, the delocalisation of the edge effect could

also be estimated.¹⁸⁷ Detailed EELS information from single atoms are highly desirable. The acquired EELS can be compared with existing reference spectra to determine the electronic and bonding states of an unknown element in the lattice.²⁵² From the above studies, I have understood that EELS from edge of graphene have distinctive spectrums, they cannot be compared directly with reference EELS from bulk of graphene. The reference spectra of carbon atoms at the edge and within bulk should be catalogued differently.

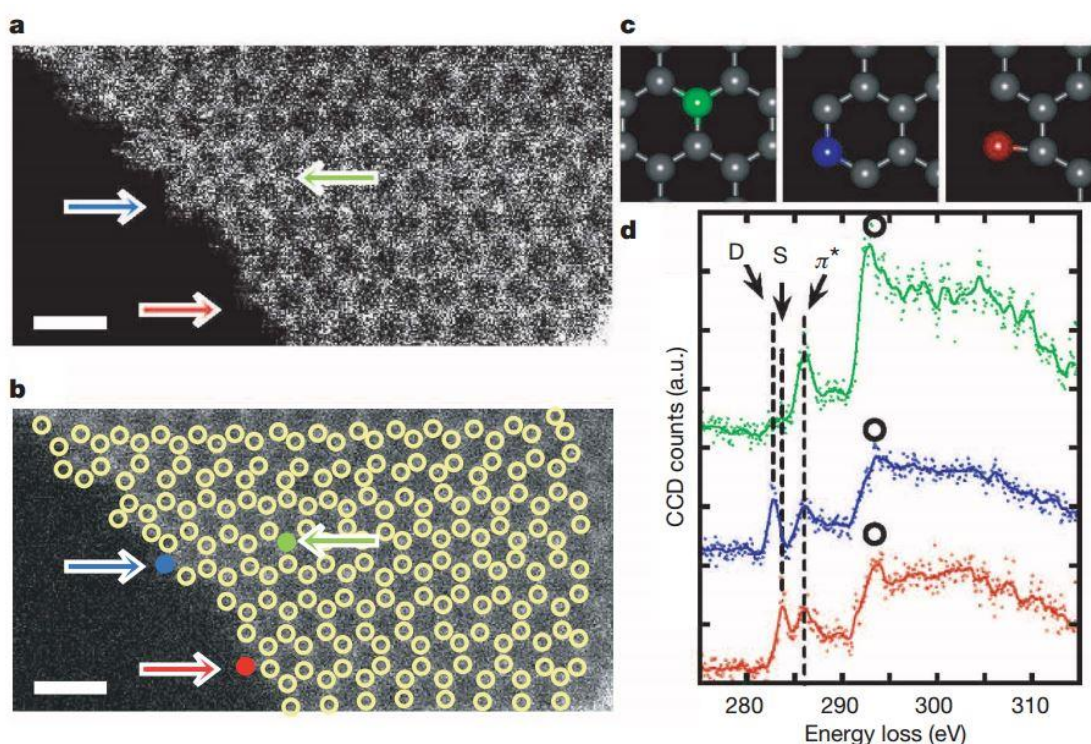


Figure 2-23. Graphene edge electron energy-loss spectroscopy. (a) ADF image of single layer graphene at the edge area. The position of carbon atoms are marked with open circles in (b). Scale bars 0.5nm. The Energy-loss near edge structure (ELNES) of the green, blue, and red circle highlighted atoms are shown in (d) with the same colour coding. They represent normal sp^2 bonding, double-coordinated, and single-coordinated carbon atoms respectively as shown in (c). (Reprinted by permission from Macmillan Publishers Ltd: [Nature] (ref.[187]), Copyright (2010))

By investigating the bonding configuration of graphene edges further with EELS., one recognises that even though both rec. 5-7 and armchair both form a dimer where the two atoms are double coordinated, they still have different EELS spectra, indicating the variation in the energy states.²⁵³ By generating 2D spectroscopic images based on EELS from a single element at atomic resolution and overlay it on a ADF image taken from the same area as shown in an example in Figure 2-24, one can visualise the variation in energy states across the lattice and near edge.²⁵³ This technique is also widely adopted to study light atom doping, such as N, both on the edge and within bulk lattice.^{183,188,189}

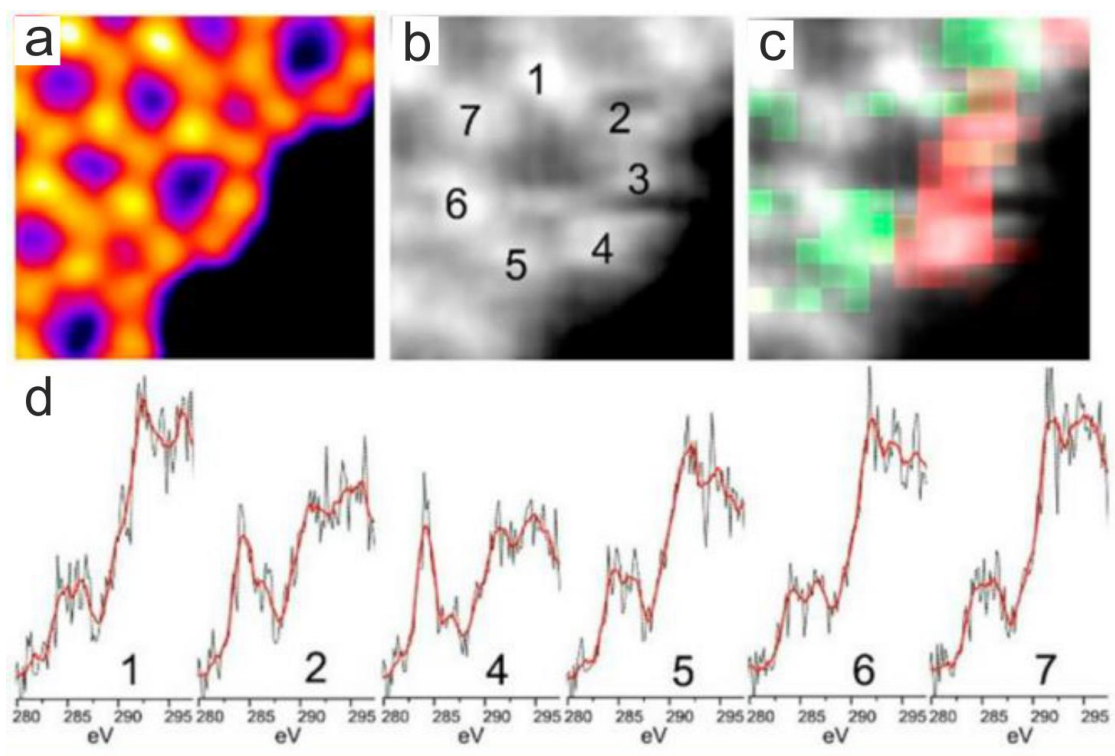


Figure 2-24. (a) An ADF image of rec. 5-7 graphene edge with coded with false colour. The carbon atom positions of the 7 membered ring is labelled in (b) and the EELS spectra of them are shown in (d). (c) Spectrum images extracted from the 2D EELS overlaid onto ADF image. Red areas indicate the location where extra EELS peak exist, green area indicate bulk bonding characteristic. (Reproduced with permission from ref.[253], Copyright (2014) American Chemical Society)

2.5 Conclusion

With the attractive properties of graphene that have fascinated the scientific research field now for more than 11 years since its discovery; and the increasing awareness of the possible ways that graphene could revolutionaries our day to day life, it is of huge interest to both the scientific and industrial field that at least some of the graphene's most promising applications are translated to real life applications. As the science of graphene matures, it is application-driven research that begins to take precedence. However, it is still difficult to predict where graphene's biggest impact would lie in the future. In the roadmap for the implementation of graphene as described by Novoselov *et al.*,²⁵⁴ the development of a synthesis route that could produce graphene with properties surpassing existing materials such as silicon on an industrial scale remains a primary goal. A prerequisite for its fruition include controlled layer formation and a synthesis process that is defect free and allows the production of a continuous graphene sheet, which has not been achieved yet. Nevertheless, it is reasonable to predict a new group of technologies that will emphasize on the inherent properties of graphene rather than solely attempt to surpass the record that previous materials have set. It is with this intention that this project was conceived, to give due attention to the unique edge behaviour of graphene.

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Chapter 3

Methodology

3.1 Introduction

This chapter describes the experimental and analytical techniques employed over the course of the research project. This includes graphene synthesis, characterisation, and transfer to TEM grids as well as image processing and the relevant atomic model construction and simulation techniques that were used. The majority of the methods have already been briefly introduced in the literature review section as some of the methods have applied by other research groups. This chapter explains how these techniques have been specifically used in this project to help answer the scientific question this thesis aims to address. For example, contrary to the traditional CVD graphene synthesis route, where solid copper is used as a catalyst, we have increased the reaction temperature to 1090 °C, beyond the copper melting temperature. This allows the growth of large domain size, monolayer graphene – ideal for HRTEM characterisation. This chapter will also focus on the technicalities of the HRTEM experiment: for example, the specifications of the TEM instrument used, sample pre-treatment and acceptable residual aberration values.

3.2 CVD

The CVD system used to prepare graphene samples was established by Dr. Alex Robertson prior to the experiments that were carried out in this thesis. In the CVD experiments that will be discussed below. The solid copper growth method was

developed by Dr. Alex Robertson. The liquid copper growth on Molybdenum substrate was co-developed by Dr. Yimin Wu and Fan Ye. The liquid copper growth on Tungsten substrate and the two stage growth mechanism was developed by me. The setup is shown in the photograph with a schematic illustration in Figure 3-1, this is also the original status of the experimental setup before I have started my CVD experiment: a split furnace was used to heat the reaction chamber within the quartz tube to the desired temperature (furnace max. temp. 1200 °C). The tube was connected to three gas supplies: argon, methane, and hydrogen, as well as an exhaust outlet which is regulated through a valve, allowing the scroll pump to evacuate the reaction chamber if necessary. The scroll pump was, however, not used in this project as all the experiment was carried out at atmospheric pressure. The gas supplies were controlled through three digital mass flow controllers (MFCs), which controlled the amount of each gas in the reaction chamber.

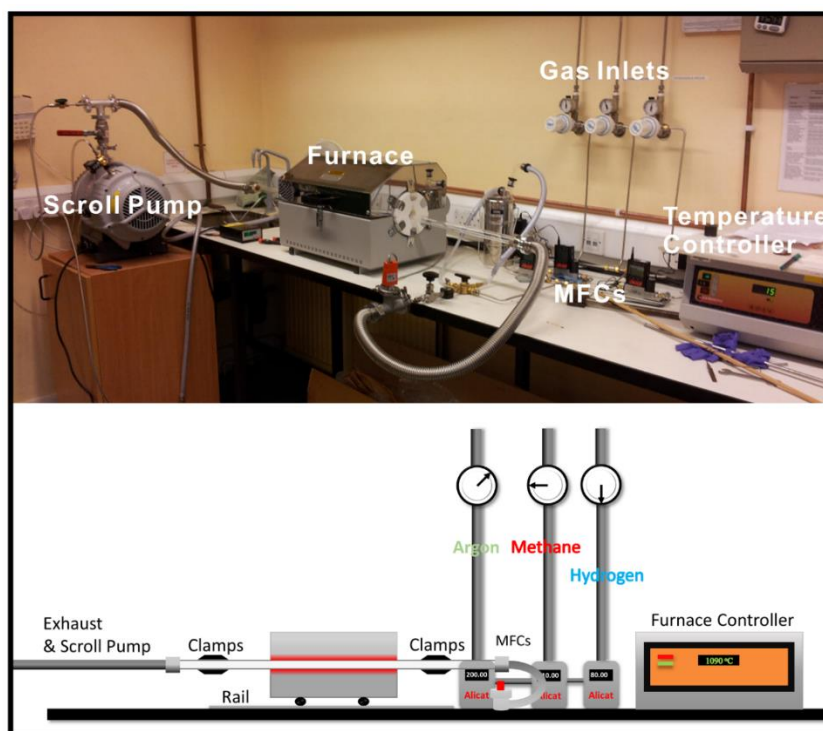


Figure 3-1 A photograph and schematic illustration of the CVD experimental setup used to prepare samples for the graphene results obtained in this project.

A growth method using melted copper as a catalyst to grow monolayer, large grain size, high quality, clean graphene was initially developed by Mr. Fan and Dr. Wu.¹ A piece of 1 x 1 cm copper (Alfa Aesar, Puratonic 99.999% pure, 0.1 mm thick) rested on a similarly sized molybdenum sheet (Alfa Aesar, 99.95% pure, 0.1 mm thick). Under atmospheric pressure, the reaction chamber was heated up to 1090 °C under argon flow (200 sccm) and then reduced in hydrogen (100 sccm, 1:3 H₂/Ar mix) at 1090 °C for 30 min. The flow rate of hydrogen was reduced to 80 sccm for the growth period while the 200 sccm argon flow was maintained. After this, 10 sccm of CH₄ (1:99 CH₄/Ar mix) was added in the gas mix for 90 min. The sample was rapidly cooled to room temperature by removing the copper/molybdenum sheet from the hot zone after the reaction and then turning the CH₄ flow off.

There are, however, two drawbacks with the use of this approach as a routine method to prepare graphene samples for HRTEM experiments. Firstly, hexagonal shaped impurities form on the surface of copper during the reaction: SEM and Energy-dispersive X-ray spectroscopy (EDX) reveals that the impurities are molybdenum rich and, as a result, this affects the continuity of the graphene sheet grown on top. Secondly, the drastic deformation of copper that occur during the solidification process of copper imposes stress on graphene and causes cracks, as shown in Figure 3-2 (a-d), and (h). A combined effort was made by myself and Ye Fan to address this issue, by altering the substrate materials and synthesis parameters.² Tungsten was used instead of molybdenum: tungsten does not form any alloy with copper at 1090 °C and therefore helps to eliminate the impurity issue.

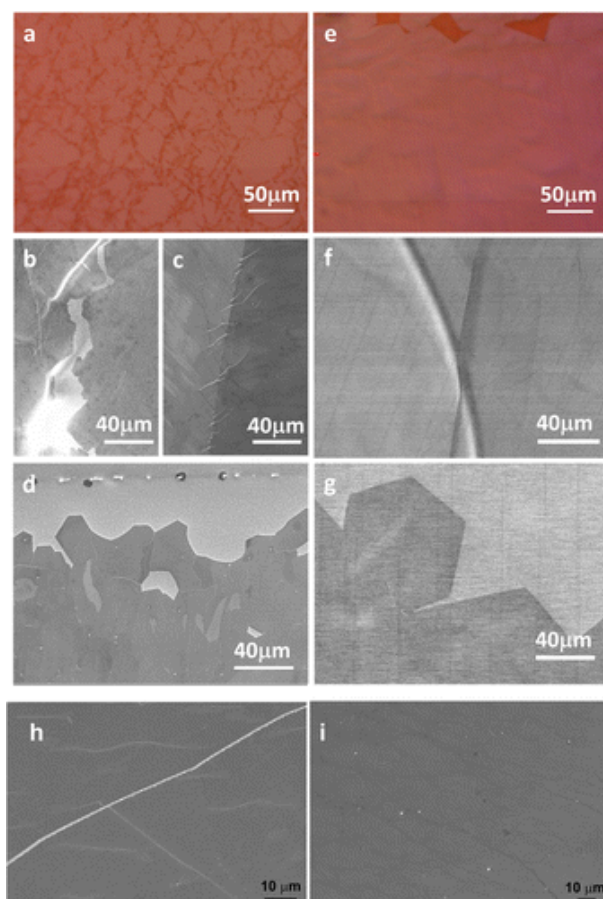


Figure 3-2 Morphology of graphene grown using different cooling processes. (a) Optical images of graphene grown on copper with the fast cooled method (sample was baked in air at 150 °C for 15 min to oxidise the Cu substrate that did not have graphene coverage). The oxidised Cu appears as a dark red colour, while graphene-protected Cu appears as a light orange colour. (b) and (c) are SEM images of a large crack and the “boundary tears” that exist in fast-cooled samples. (d) SEM image of long cracks from the graphene edge. (e) Optical image of a two stage grown graphene on Cu: the edge is purposely included in this image so as to provide a contrast with the bulk of the sheet. (f) and (g) are SEM images of crack-free two-stage grown graphene covering the copper GB and graphene edge. (h) and (i) are high magnification SEM images comparing a long crack in the fast cooled sample and a smooth surface grown using the two-stage process, respectively. (Reproduced with the permission from ref. [2]. Copyright American Chemical Society 2014.)

A two-stage graphene growth process, with the second stage acting as a re-growth process, was developed by myself to address the cracking issue. After the initial 90 min growth process, the temperature was gradually decreased from 1090 °C to 1060 °C, enabling enough time for Cu to solidify and to release the thermal stress between the graphene and Cu. CH₄ was supplied continuously during this period, allowing graphene to continue grow and occupy the crack areas. This resulted in a smooth, crack-free, continuous film as seen in Figure 3-2 (e-g), and (i). This improved technique guaranteed the quality of the as-grown graphene, providing a stronger material; it therefore increased the likelihood of graphene being successfully transferred onto other substrates in the subsequent experiments.

3.3 Anodic etching transfer method

The side etching method described in section 3.5 was initially adopted. The most noticeable disadvantage of the side etching method is its protracted reaction process. The stress that originates from the drag force of the tungsten weight and the harsh highly acidic environment with which graphene has to be in contact during the conventional side etching method are factors that deteriorate the quality of graphene during the transfer process. A stress-free anodic etching method has therefore been developed by Mr. Fan, and this was used to prepare the graphene TEM sample subsequently.

A PMMA scaffold (8% wt. in anisole, 495k molecular weight) was spin cast on to the graphene side of the graphene/copper/tungsten sample at 4700rpm for 60 seconds, and then cured at 180 °C for 90 seconds. As illustrated in Step 1, Figure 3-3, the W substrate was electrochemically etched in a 2 M sodium hydroxide electrolyte solution. The PMMA/Graphene/Cu/W sample was connected to the anode, and a 2.4 V potential

difference was applied between the anode and cathode (Cu foil). The tungsten on the back of the sample was slowly etched away, after which the sample was floated on FeCl_3 or ammonium persulfate solution to dissolve the remaining Cu, to leave a transparent layer of PMMA/graphene ready to be transferred onto a desired substrate or TEM grid.

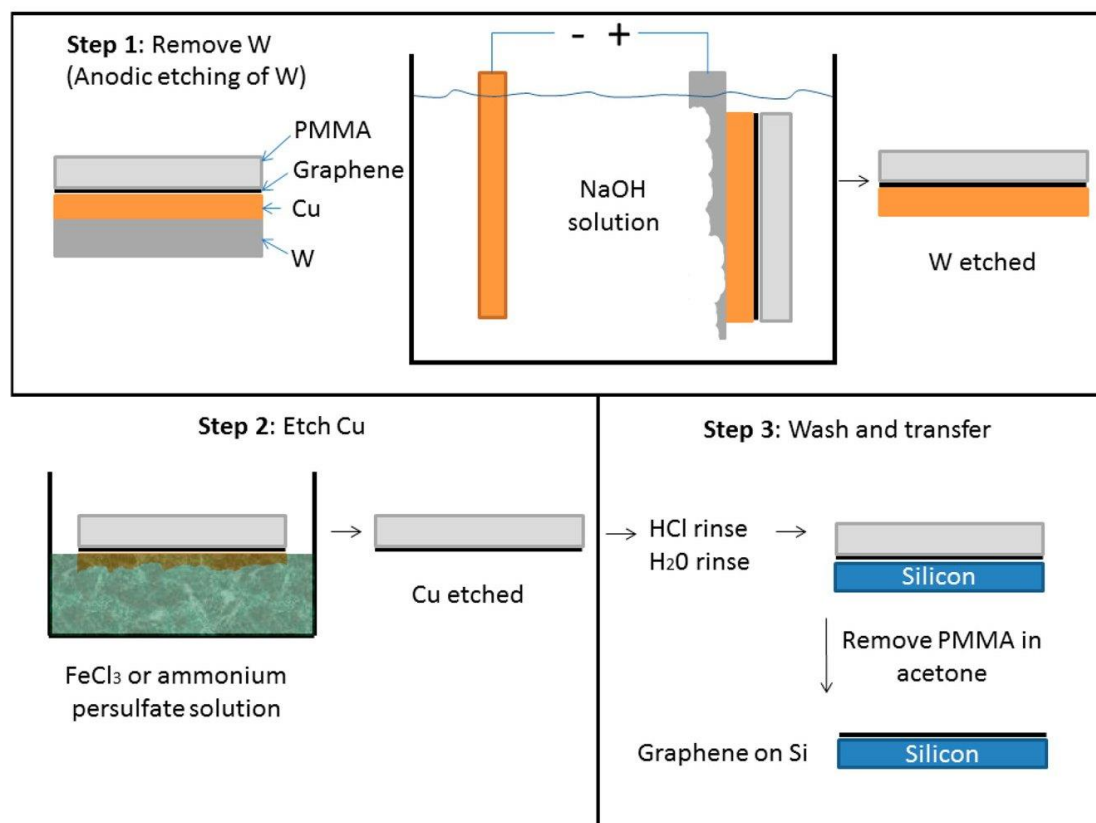


Figure 3-3 Schematic illustration of the anodic etching transfer method. In step 1, Tungsten is etched by an electrochemical process. Cu is then subsequently etched away by either FeCl_3 or ammonium persulfate solution. (Reproduced with the permission of ref. [2]. Copyright American Chemical Society 2014)

3.4 SEM/focused ion beam

The graphene samples grown by CVD and those that were transferred to SiO₂ substrate and TEM grids were routinely checked by SEM in order to characterise the grain size, continuity, and variation in layers. Two SEM instruments were used in this project: the Hitachi S-4300 field-emission gun (FEG) and the ZEISS NVision 40 FIB-SEM focussed ion beam (FIB) dual system. Both instruments operate at low voltage (2 – 5 kV) to ensure sufficient contrast when imaging graphene samples. The NVision, which is equipped with an in-lens secondary electron detector, provides enhanced contrast when imaging thin film samples, such as graphene.

The FIB, with which the NVision was equipped, was utilised to fabricate windows on platinum-resistive coil-embedded TEM chip (DENS Solutions DENS-C-30), which were then mounted on the commercially available *in-situ* heating holder (DENS Solutions SH30-4M-FS). Windows of $0.2 \times 2.0 \mu\text{m}$ in size were fabricated as shown in Figure 3-4 (e). The windows allowed atomic resolution lattice imaging of the transferred graphene.

SEM samples were prepared by attaching the graphene/copper/tungsten, graphene/TEM grids or graphene/SiO₂/Si specimen to a sample stub with carbon sticky pads. Great care was taken to ensure the samples were not strongly pressed against the carbon pads, especially for the TEM grids samples, as they could be easily damaged during the dismounting process.

3.5 Transfer to TEM grids

A side etching method was originally employed to remove the substrate. A PMMA scaffold (8% wt. in anisole, 495k molecular weight) was spin cast on to the graphene side of the graphene/copper/tungsten sample at 4700rpm for 60 seconds, and then cured at 180 °C for 90 seconds. The sample was floated on FeCl₃ solution, due to the chemical inertness of tungsten, the etchant could only etch away Cu from the side; this process usually took three to five days, depending on the concentration of FeCl₃. When Cu was fully etched, tungsten detached from the sample automatically, leaving PMMA/graphene floating on the surface. This was thoroughly cleaned by transferring it to clean DI water several times, where it was floated, and then transferring it to a 30% Hydrochloric Acid (HCL) solution for 5 minutes, rinsed again in Distilled Water (DI) water for 30 minutes. This process has been reported to be critical, in order to clean the residual contamination from the etching process.³⁻⁵ TEM grids (Agar Scientific number Y5385) were usually placed on a silicon wafer during the transfer process, for ease of practical operation. This sample preparation technique was employed for the experiments carried out as described in Chapter 4 and 5. The anodic etching method described in Section 3.3 was subsequently used to transfer graphene onto the platinum-resistive coil-imbedded TEM heating chip. The results set out in Chapters 6-8 were obtained from graphene samples transferred using this method.

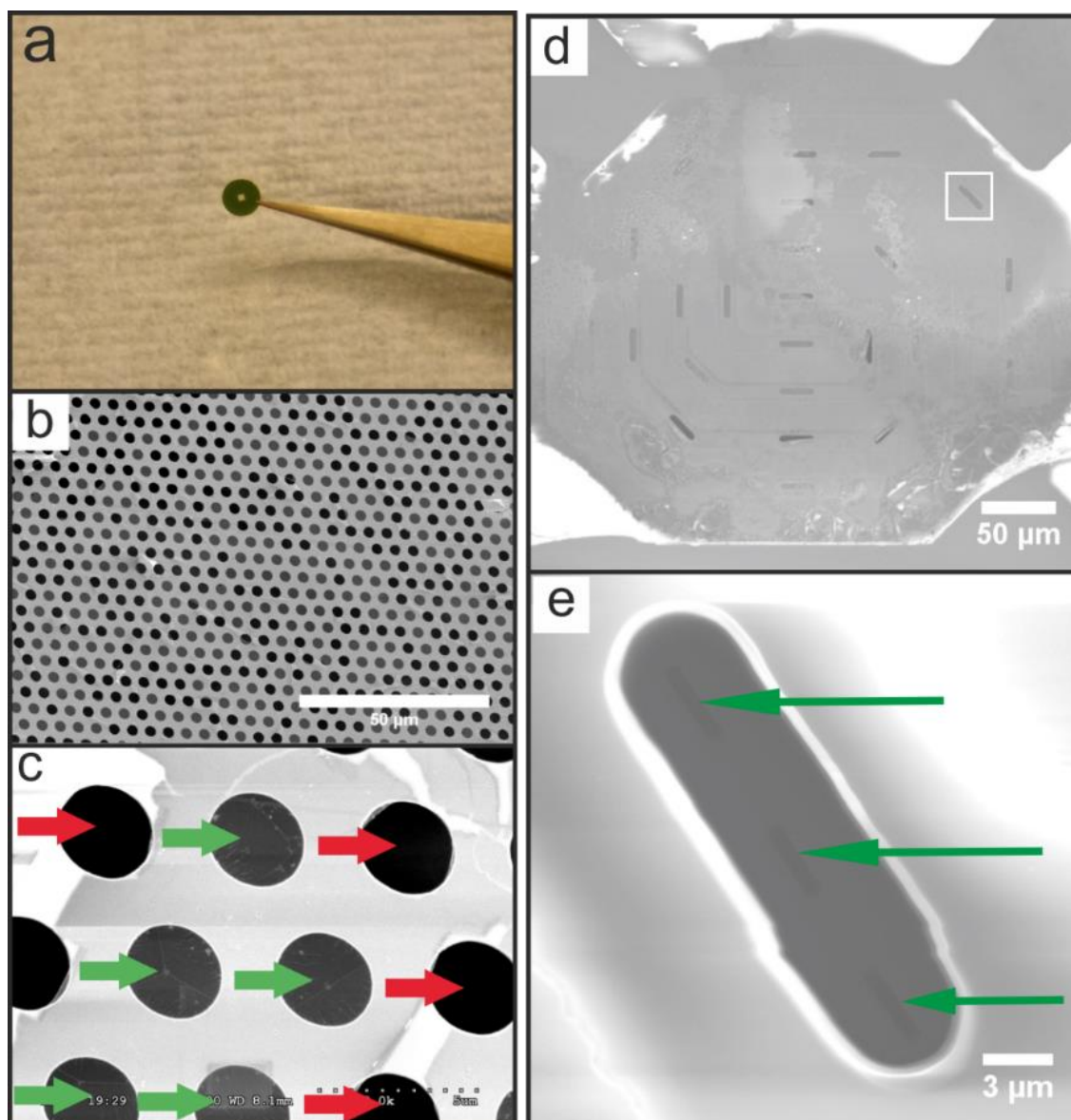


Figure 3-4 Sample transferred onto TEM grids. **Agar Scientific Y5385 SiN grid** (a) An optical micrograph of the SiN grid after graphene has been transferred onto it. (b) SEM revealing the zoomed in area of the window on the SiN grid. (c) shows the graphene coverage rate after graphene transfer: the green arrows indicate covered holes and the red arrows indicate uncovered holes (vacuum). **Platinum resistive coil imbedded TEM heating chip (DENS Solutions DENS-C-30)** (d) An SEM micrograph of a heating nano-chip with graphene transferred onto it. (e) shows the thick SiN membrane that is situated in the viewing windows; the green arrows indicate long vacuum strips fabricated by FIB, which allows graphene imaging.

3.6 TEM

TEM characterisation of CVD grown graphene formed the majority of the research activities presented in this thesis. Several TEM instruments were used to serve different experimental areas. JEOL JEM-4000EX HREM with a lanthanum hexaboride (LaB_6) filament, JEOL 2010 TEM with a tungsten tip, and JEOL 2100 TEM with a LaB_6 tip were all operated at 80kV in order to examine graphene specimens synthesised with CVD and transferred onto an SiN grid. These three instruments were all used extensively to screen graphene samples, in order to optimise the sample preparation process. This was a crucial characterisation step that was required in order to repeatedly be able to transfer graphene onto TEM grids and to obtain a sufficiently clean surface for further experiments. It was found, following the transfer steps described in Sections 3.3 and 3.6, that a further overnight annealing under vacuum at 180°C was required in order to remove the majority of the surface amorphous carbon adsorbates, so that a sufficiently large clean area could be exposed to allow lattice imaging. The lattice of graphene, including all the atomic resolution images were taken on the OJ 2200 MCO TEM, this microscope is equipped with double aberration correctors (pre- and post-specimen), double Wien Filter monochromator and a schottky FEG electron source to limit the profile of electron energy spread.

3.6.1 TEM background

The imaging theory introduced below are based on the text book written by David Williams and Barry Carter.⁶ The aberration correction theory are based on chapter 1 of the book *Science of Microscopy*.⁷

The optical system in the microscope transforms each point on the specimen into an extended region on the final image in a circular disk shape. The specimen are described

by a specimen function $f(x, y)$; the extended region in the image that is correspond to the point (x, y) in the specimen is described as $g(x, y)$, which could also be written as $g(r)$. The $g(x, y)$ that corresponds to two close vicinity points in the specimen could overlap, each point in the image therefore has contributions from many points in the specimen; the result is then expressed as

$$g(r) = \int f(r')h(r - r')dr' \quad (3-1)$$

$$= f(r) \otimes h(r - r') \quad (3-2)$$

$h(r)$ describes how a point spreads into a disk, it is therefore known as the point-spread function or the smearing function, and $g(r)$ as seen in Equation(3-2), is the convolution of $f(r)$ with $h(r)$. $h(r - r')$ is a weighting term that contains information on how much each point in the specimen contributes to each point in the final image. The $g(x, y)$ function, when written in two dimensions, is a result of the sum of sine waves.

$$g(x, y) = \sum_{u_x u_y} G(u_x - u_y) \exp(2\pi i(xu_x + yu_y)) \quad (3-3)$$

$$g(x, y) = \sum_{\mathbf{u}} G(\mathbf{u}) \exp((2\pi i \mathbf{u} \cdot \mathbf{r})) \quad (3-4)$$

Here, $\mathbf{u}$ is known as the reciprocal lattice vector, the spatial frequency for the particular direction. In Equation (3-4), $g(r)$ is expressed in terms of $G(\mathbf{u})$, where $G(\mathbf{u})$ is known as the Fourier transform of $g(r)$, and is the frequency domain representation of that function. In analogue to the above analysis $F(\mathbf{u})$ and $H(\mathbf{u})$ are the Fourier transform of $f(r)$ and $h(r)$ respectively. Since $h(r)$ is a function that describes how information is transferred from specimen to the image, $H(\mathbf{u})$ therefore describes information transfer at $\mathbf{u}$ space, and are known as the contrast transfer function (CTF). These three Fourier transforms are related by

$$G(\mathbf{u}) = H(\mathbf{u})F(\mathbf{u}) \quad (3-5)$$

A convolution in real space shown in Equation (3-2) is the equivalent of multiplication in reciprocal space. There are three factors that contribute to the CTF $H(\mathbf{u})$: the apertures, described with an aperture function $A(\mathbf{u})$; attenuation of the wave, described with an envelope function $E(\mathbf{u})$; and the aberration of the lens, described with an aberration function $B(\mathbf{u})$. $H(\mathbf{u})$ is therefore the product of the three terms

$$H(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})B(\mathbf{u}) \quad (3-6)$$

The aperture function cuts off all values of spatial frequency higher than the radius of the selected aperture. The envelope function is the intrinsic property of the electron source, lens and detector themselves, which will be discussed further subsequently. The aberration function is expressed as

$$B(\mathbf{u}) = \exp(i\chi(\mathbf{u})) \quad (3-7)$$

To derive an expression for $\chi(\mathbf{u})$, we first consider the effects of spherical aberration C_s and the defocus Δf of the objective lens, the imaging disk has a radius of

$$\delta(\theta) = C_s \theta^3 + \Delta f \theta \quad (3-8)$$

Due to spherical aberration of the objective lens, the rays that pass through the objective lens with an angle θ are not focused on the Gaussian image plane, which is the perfect spherical electron wave front. The average of all the angles are

$$D(\theta) = \int_0^\theta \delta(\theta) d\theta = \frac{C_s \theta^4}{4} + \Delta f \frac{\theta^2}{2} \quad (3-9)$$

Bragg's law state

$$2d \sin \theta_B = n\lambda \quad (3-10)$$

When θ_B is small

$$2\theta_B \cong \lambda g \quad (3-11)$$

Because the scattering angle is $2\theta_B$, we could replace the θ in Equation (3-9) with $\lambda \mathbf{u}$, where $\mathbf{u}$ is a general reciprocal lattice vector. We can then write the phase shift

$$\chi(\mathbf{u}) = \text{phase shift} = \frac{2\pi}{\lambda} D(\mathbf{u}) = \frac{2\pi}{\lambda} \left(C_s \frac{\lambda^4 \mathbf{u}^4}{4} + \Delta f \frac{\lambda^2 \mathbf{u}^2}{2} \right) \quad (3-12)$$

$$= \pi \Delta f \lambda \mathbf{u}^2 + \frac{1}{2} \pi C_s \lambda^3 \mathbf{u}^4 \quad (3-13)$$

$\chi(\mathbf{u})$ is also known as the phase distortion function that has a form of phase shift affected by spherical aberration C_s , defocus Δf , and astigmatism C_a , the phase shift value are normally $2\pi/\lambda$ times the path difference.

If I now reconsider the specimen function $f(\mathbf{r})$, it could be represented by a model

$$f(x, y) = A(x, y) \exp(-i\Phi_t(x, y)) \quad (3-14)$$

Where $A(x, y)$ is the amplitude and $\Phi_t(x, y)$ is the phase which depends on the thickness of the specimen. If the incident wave amplitude is set to be unity, $A(x, y) = 1$. The phase shift therefore only depends on the potential $V(x, y, z)$ which the electron sees as it passes through the specimen. If the specimen is thin, the projected potential

$$V_t(x, y) = \int_0^t V(x, y, z) dz \quad (3-15)$$

This allows the two dimensional projection of a 3D crystal structure to be created, which is important in the interpretation of HRTEM images. The wavelength λ of the electrons are related to its energy as

$$\lambda = \frac{h}{\sqrt{2meE}} \quad (3-16)$$

When electrons are in the crystal, the wavelength λ changes to λ'

$$\lambda' = \frac{h}{\sqrt{2me(E + V(x, y, z))}} \quad (3-17)$$

When passing through a slice of material of thickness dz , the electrons experience a phase change of

$$d\Phi = 2\pi \left(\frac{dz}{\lambda'} - \frac{dz}{\lambda} \right)$$

$$\begin{aligned}
&= 2\pi \frac{dz}{\lambda} \left(\frac{\sqrt{E + V(x, y, z)}}{\sqrt{E}} - 1 \right) \\
&= 2\pi \frac{dz}{\lambda} \left(\left(1 + \frac{V(x, y, z)}{E} \right)^{\frac{1}{2}} - 1 \right) \\
&= 2\pi \frac{dz}{\lambda} \frac{1}{2} \frac{V(x, y, z)}{E} \\
&= \frac{\pi}{\lambda E} V(x, y, z) dz \\
&= \sigma V(x, y, z) dz
\end{aligned} \tag{3-18}$$

The total phase shift is dependent on $V(x, y, z)$

$$d\Phi = \sigma \int V(x, y, z) dz = \sigma V_t(x, y) \tag{3-19}$$

The σ is known as the interaction constant, and tends to be a constant value as V increases. If we now consider the absorption effect as electrons pass through the specimen by including a function $\mu(x, y)$

$$f(x, y) = \exp[-i\sigma V_t(x, y) - \mu(x, y)] \tag{3-20}$$

If the specimen is thin enough that we could neglect the absorption effect, we have estimated the specimen as a ‘phase object’, this is known as the phase object approximation or POA. If the specimen is very thin, then $V_t(x, y)$ is $\ll 1$, Equation(3-20) could then be expanded with Taylor expansion and, neglecting the $\mu(x, y)$ term and the higher order terms

$$f(x, y) = 1 - i\sigma V_t(x, y) \tag{3-21}$$

This is known as the weak phase object approximation or the WPOA. This approximation essentially says that for very thin specimen, such as monolayer or bilayer graphene, the amplitude of a transmitted wave function is linearly dependent on the

projected potential of the specimen. If we apply WPOA to HRTEM imaging, the wave function of electrons is given by

$$\psi(x, y) = [1 - i\sigma V_t(x, y)] \otimes h(x, y) \quad (3-22)$$

If $h(x, y)$ is represented as $\cos(x, y) + i\sin(x, y)$, then

$$\psi(x, y) = 1 + \sigma V_t(x, y) \otimes \sin(x, y) - i\sigma V_t(x, y) \otimes \cos(x, y) \quad (3-23)$$

The intensity is given by the multiplication of the wave function and its complex conjugate

$$I = \psi * \psi^* \quad (3-24)$$

Because the interaction constant σ is small, the σ^2 term could be neglected, we therefore have

$$I = 1 + 2\sigma V_t(x, y) \otimes \sin(x, y) \quad (3-25)$$

If this result is compared with the aberration function in Equation (3-7), only the imaginary part of the aberration function contributes to the intensity shown in Equation (3-25), we can therefore simplify

$$B(\mathbf{u}) = 2\sin\chi(\mathbf{u}) \quad (3-26)$$

The factor of '2' in Equation (3-26) is the same as the '2' in Equation (3-25). A new quantity $T(\mathbf{u})$, the intensity transfer function is given as

$$T(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})2\sin\chi(\mathbf{u}) \quad (3-27)$$

It must be made clear that $T(\mathbf{u})$ is not the same as the CTF; when $T(\mathbf{u})$ is negative, phase contrast result in a positive value, meaning that atoms would appear dark, and vice versa. When $T(\mathbf{u}) = 0$, there is no detail in the image for this value of $\mathbf{u}$. If WPOA applies to a specific sample, which is the case in our graphene experiment, $T(\mathbf{u})$ is called the CTF, because there is no amplitude contribution, and the output of the optical system is an observable quantity, the image contrast. If we ignore the attenuation function $E(\mathbf{u})$ for now and assume that all astigmatism can be properly corrected. Then

if $T(\mathbf{u})$ is a large value, it means information with a periodicity or spatial frequency correspond to that specific $\mathbf{u}$ value can be transmitted. We also need the contrast to be uniform across the image, therefore the ideal form of $T(\mathbf{u})$ would be a constant value with increasing $\mathbf{u}$ over large ranges of $\mathbf{u}$.

$T(\mathbf{u})$ is zero when $\mathbf{u} = 0$, it becomes zero again at $\mathbf{u} = \mathbf{u}_1$; it is preferable to have $\mathbf{u}_1$ as large as possible, more spatial frequency information is included in this way. If $T(\mathbf{u})$ crosses the $\mathbf{u}$ axis, the sign of the transfer function flips, it therefore defines the limit to which one could directly interpret an HRTEM image. In Figure 3-5, different values of spherical aberration C_s and defocus Δf are explored for a microscope with an acceleration voltage of 200kV as an example to demonstrate the effect they have on the transfer function. It could be seen from Figure 3-5 (a-c) that if defocus is set to a fixed value, then smaller C_s values result in larger $\mathbf{u}_1$, therefore higher spatial resolution could be achieved. If instead the spherical aberration is now a fixed value, as seen in Figure 3-5 (d-f), the initial increase in defocus results in an increase of $\mathbf{u}_1$ value. The bump at $\mathbf{u}_2$ in Figure 3-5 (f) also increases and will eventually cross the $\mathbf{u}$ axis, which result in the sudden drop of $\mathbf{u}_1$. Therefore a balance between the spherical aberration and defocus needs to be achieved in order to optimise the imaging performance. Scherzer noticed back in 1949 that the best combination to achieve optimum imaging capability is

$$\Delta f_{Sch} = -1.2(C_s \lambda)^{1/2} \quad (3-28)$$

At this defocus value, all the beams are out of phase by a constant value up until of $\mathbf{u}_1$, and is the best performance to be expected from a microscope without image processing.

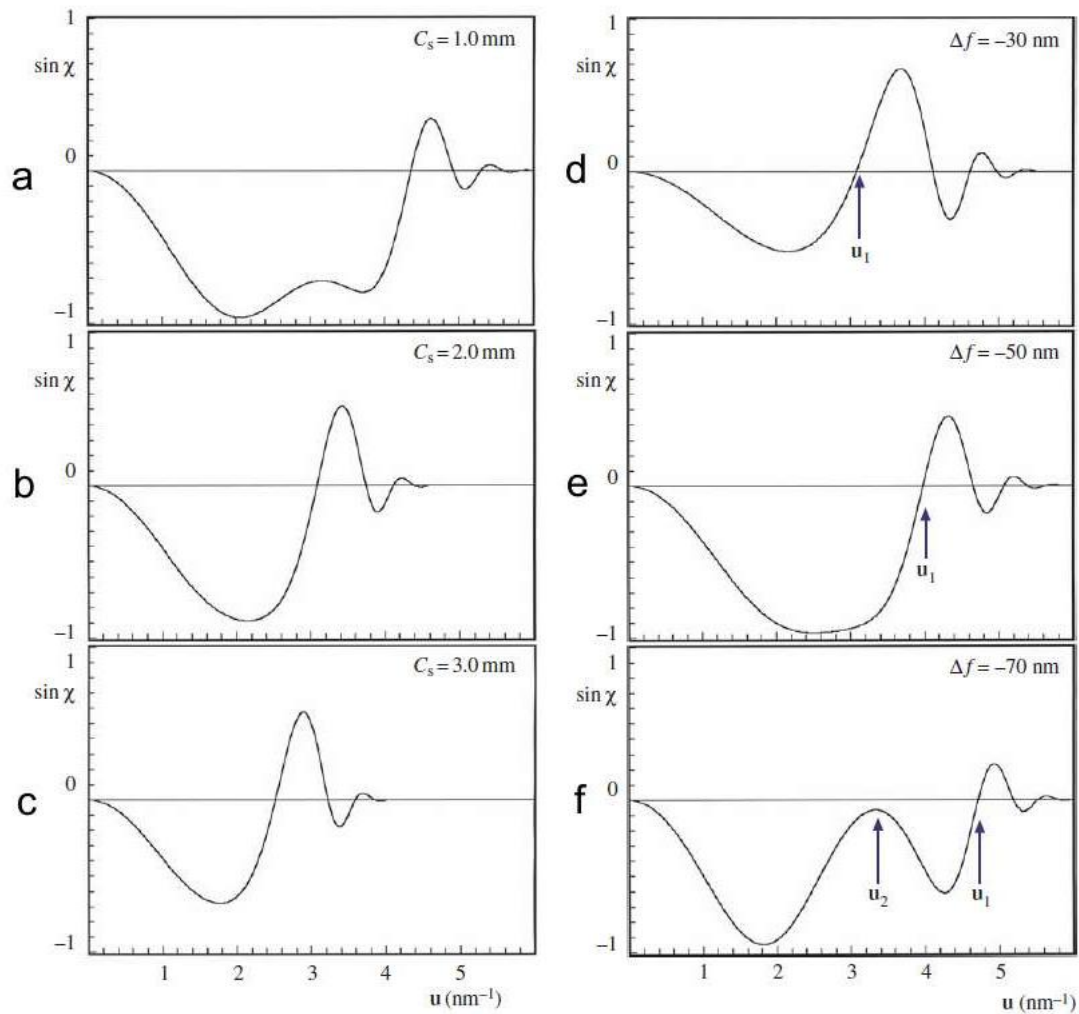


Figure 3-5. (a-c) are a series of $\sin\chi(u)$ curves calculated for different values of spherical aberration C_s under an acceleration voltage of 200kV and a defocus value $\Delta f = -60\text{nm}$. (d-f) are a series of $\sin\chi(u)$ curves calculated for different defocus values Δf under an acceleration voltage of 200kV and spherical aberration value $C_s = 1.0\text{mm}$. (Reprinted figure with permission from ref. [6], Copyright (2009) by the Springer publishing group)

3.6.2 Information limit and partial coherence imaging

The transfer function could theoretically extend forever. In practice, the phase distortion function terminates at a point, in another world, is unable to resolve the finest details for reasons other than the transfer characteristics of a linear system. All the above

discussions on the imaging theory assumes that electron source of the microscope has the same intrinsic energy and they are emitting at the same direction. This is hardly true even for field emission gun (FEG) electron source. The coherency of the electron source impose a large effect on the envelope function, therefore could influence the information limit of a microscope to a large extend, especially on an aberration corrected TEM.

The total envelope function is the product of all the separate terms

$$E_T(u) = E_c(u)E_s(u)E_d(u)E_v(u)E_D(u) \quad (3-30)$$

Each individual terms are described in the table below

$E_c(u)$	Chromatic aberration
$E_s(u)$	The source dependence due to the small spread of angles from the probe
$E_d(u)$	Specimen drift
$E_v(u)$	Specimen vibration
$E_D(u)$	The detector

Table 1. The description for each individual terms in the envelope function.

Each term in Table 1 contribute differently to the envelope function; in this section, we mainly discuss the effect of chromatic aberration in this section. The envelope function $E_c(u)$ of the chromatic aberration is expressed as

$$E_c(u) = \exp \left[-\frac{1}{2} (\pi \lambda \delta)^2 u^4 \right] \quad (3-31)$$

Where δ represents defocus spread caused by the aberration

$$\delta = C_c \left[4 \left(\frac{\Delta I_{obj}}{I_{obj}} \right)^{2h} + \left(\frac{\Delta E}{V_{acc}} \right)^2 + \left(\frac{\Delta V_{acc}}{V_{acc}} \right)^2 \right]^{1/2} \quad (3-32)$$

C_c is the chromatic aberration coefficient and the $\frac{\Delta E}{V_{acc}}$ term is the intrinsic energy spread of the electron source, these two values could be reduced by the use of a FEG over traditional thermionic emitter and also by installing a monochromator. A FEG helps to reduce the instrumental contribution to chromatic aberration and extends information cut-off of the envelope function to a larger value, and result in higher spatial frequencies to be included in the final image. The $\frac{\Delta I_{obj}}{I_{obj}}$ and $\frac{\Delta V_{acc}}{V_{acc}}$ terms represent the instabilities caused by the objective lens current and high voltage supply respectively. These two terms could be improved by adopting a more stable current to the magnetic lenses.

The effect of an envelope function is to create a virtual aperture at the back focal plane of the objective lens in a microscope. The presence of this virtual aperture prohibits the access to higher order passbands as seen in the example shown in Figure 3-6. The cut-off of information imposes a new resolution limit on the microscope, and is known as the ‘information limit’.

As mentioned in previous texts, HRTEM images are directly interpretable up to the instrumental resolution, this limit is set by the Scherzer resolution. However, if the information limit is beyond the Scherzer resolution limit, then image processing techniques need to be employed to resolve more details.

The classical two-point resolution theory proposed by John William Strutt and Lord Rayleigh, also known as the Rayleigh criterion, says that when the intensity profiles of two points are plotted, if the lowest point between the two peaks is $< 81\%$ of the maximum peak intensity, the two points are said to be resolved. The context of Rayleigh criterion was originally used in the diffraction points of two light sources, when adopted in the analysis of atomic resolution TEM images, the intensity profile is usually fitted with 2D Gaussian curves. The point resolution is the distance between the two peaks when the central valley position is exactly 81% of the of the maximum peak intensity.

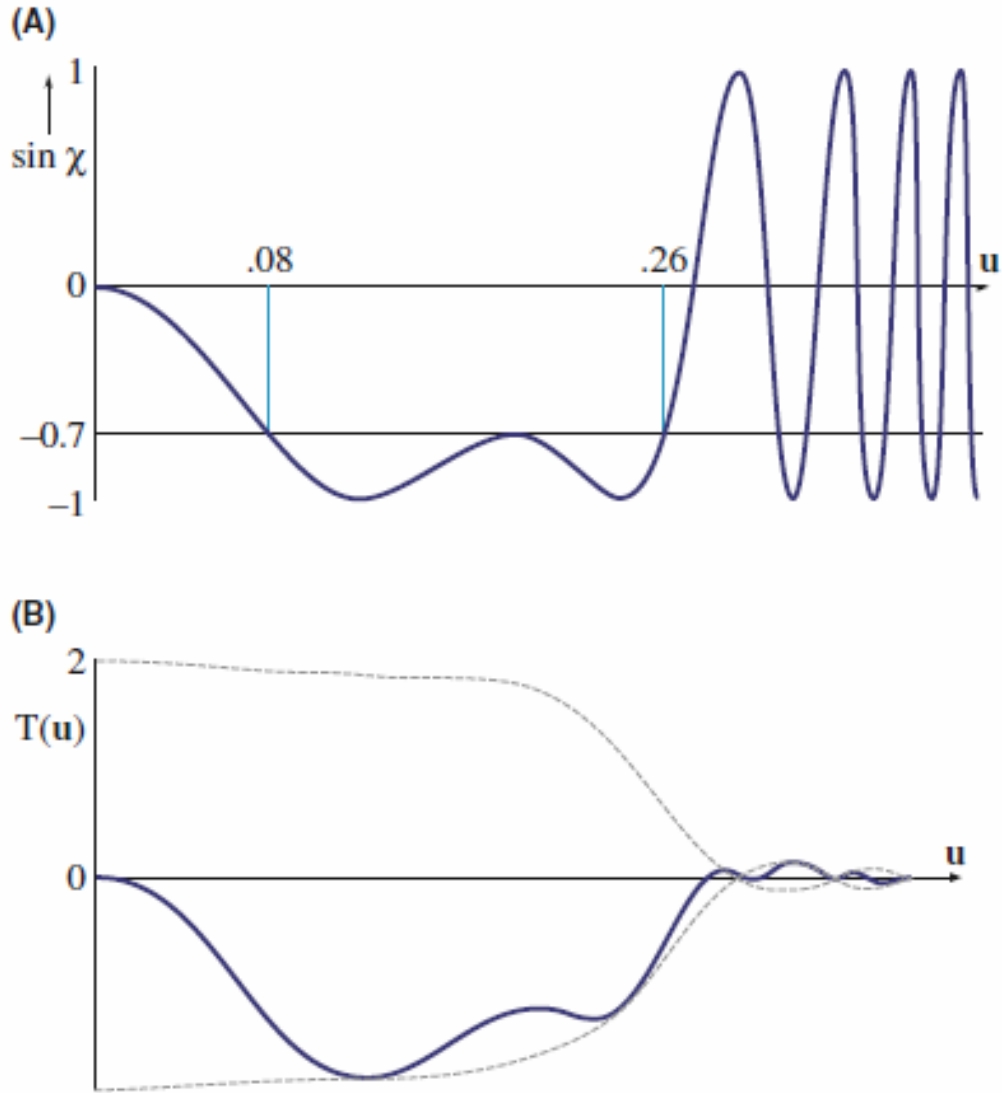


Figure 3-6. (a) $\sin\chi(\mathbf{u})$ versus $\mathbf{u}$ without damping of the higher spatial frequencies. (b) $T(\mathbf{u})$ versus $\mathbf{u}$ imposed by the damping envelope. Both curves are taken under the condition of $\Delta f = -100\text{nm}$, $C_s = 2.2\text{nm}$ at an acceleration voltage of 200kV. (Reprinted figure with permission from ref. [6], Copyright (2009) by the Springer publishing group)

If resolution in frequency domain is considered, the cut-off frequency f_c in the transfer function is defined as the diffraction limit for resolution measurement. This cut-off value can be limited by the wave aberrations in the lens and partial coherence envelope function discussed in Equation (3-30). It is helpful to define a concise equation for the linear imaging process.

$$G(u) = \Psi(u) \left[\exp \left[-\frac{2\pi i}{\lambda} W(k) \right] \right] E_T(u) \quad (3-33)$$

Where $W(k)$ is the wave aberration function, $E_T(u)$ is the total envelope function. When pursuing the ultimate resolution in a TEM, it is important to recognise the primary restriction factor of the transfer function. The range of the envelope function can be improved by using a FEG and a monochromator, but if the spherical aberration at the object lens is not corrected, the transfer function would oscillate severely between positive and negative before the information cut-off. The aberration correction of electron wave at the object lens could cause the move of first crossing point u_1 to a higher spatial frequency, but if the first crossing is beyond the information cut-off imposed by the envelope function, the transfer function would drop to zero before reaching u_1 and is therefore cost ineffective. It is important to balance the two effects to achieve the highest resolution of a given TEM.

3.6.3 Aberration correction

Two types of aberrations exist in a TEM: spherical and chromatic. Spherical aberration usually inherently exists in the objective lenses, and arises when the outer part of the electrons are focused more strongly by the optics than the inner part. For an ideal lens, a point object in the object plane leads to a spherical wavefront in the diffraction plane. However, all electromagnetic lenses suffer from aberrations caused by the deviation from the ideal spherical wavefront as seen in the schematic diagram shown in Figure 3-7. This reduces the sharpness of an image and deteriorates the imaging capabilities much more severely than the diffraction limit. The wave aberration function $w(u, v)$ is therefore as outlined in Figure 3-7, the distance between the perfect spherical and actual wavefront in the diffraction plane as a function of the position (u, v) of the point object in the diffraction plane.⁸

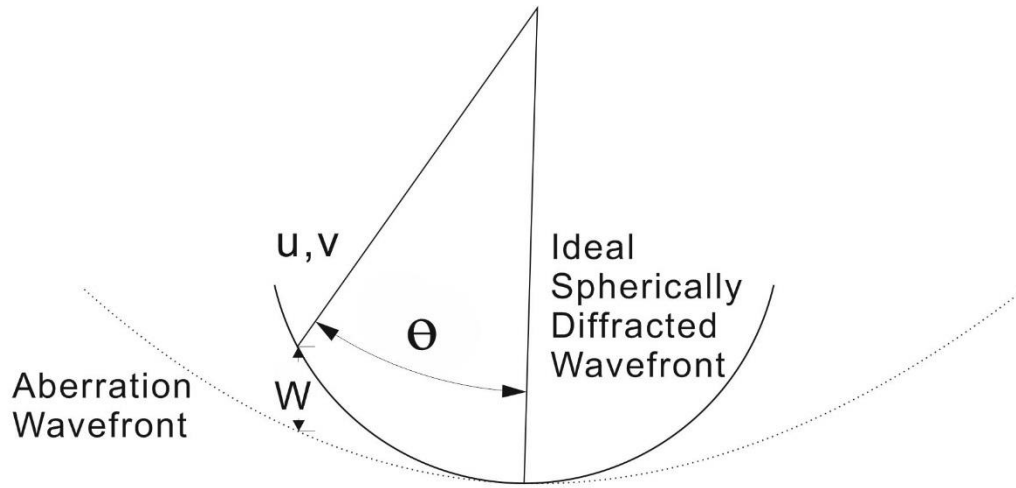


Figure 3-7. Schematic diagram illustrating the origin of wave aberration function, $W(u, v)$, which is the deviation from an ideal spherical diffracted wave front. (Reprinted figure with permission from ref. [7], Copyright (2007) by the Springer publishing group)

The wave aberration function, $W(\omega)$, where the complex number $\omega = u + iv$ can be Taylor expanded to 3rd order in terms of the axial aberrations

$$\begin{aligned}
 W(\omega) = \Re \left\{ \frac{2\pi}{\lambda} \left\{ A_0 \lambda \omega^* + \frac{1}{2} A_1 \lambda^2 \omega^{*2} + \frac{1}{2} C_1 \lambda^2 \omega^* \omega \right. \right. \\
 + \frac{1}{3} A_2 \lambda^3 \omega^{*3} + \frac{1}{3} B_2 \lambda^3 \omega^{*3} \omega \\
 + \frac{1}{4} A_3 \lambda^4 \omega^{*4} + \frac{1}{4} S_3 \lambda^4 \omega^{*3} \omega + \frac{1}{4} C_3 \lambda^4 \omega^{*2} \omega^2 \\
 \left. \left. + \dots \right\} \right\}
 \end{aligned} \tag{3-34}$$

Converting to polar notation, where $\omega = k e^{i\phi}$, $A_n = |A_n| e^{i\alpha_n}$ and $B_n = |B_n| e^{i\beta_n}$.

Therefore Equation (3-34) can be rewritten as

$$\begin{aligned}
W(k, \phi) = & \frac{2\pi}{\lambda} \left\{ |A_0| \lambda k \cos(\phi - \alpha_0) \right. \\
& + \frac{1}{2} |A_1| \lambda^2 k^2 \cos 2(\phi - \alpha_1) + \frac{1}{2} C_1 \lambda^2 k^2 \\
& + \frac{1}{3} |A_2| \lambda^3 k^3 \cos 3(\phi - \alpha_2) + \frac{1}{3} |B_2| \lambda^3 k^3 \cos(\phi - \beta_2) \\
& + \frac{1}{4} |A_3| \lambda^4 k^4 \cos 4(\phi - \alpha_3) + \frac{1}{4} |S_3| \lambda^4 k^4 \cos 2(\phi - \alpha_3) \\
& \left. + \frac{1}{4} C_3 \lambda^4 k^4 + \dots \right\} \quad (3-35)
\end{aligned}$$

This way the azimuthal and radial dependence of the aberration terms are made more apparent. There are several nomenclature systems that can be used to name different modes of aberrations. For the CEOS (Haider) system we are use:

Aberration	Order in ω	Azimuthal	Description
		Symmetry	
A_0	1	1	Image Shift
A_1	2	2	Two-fold Astigmatism
A_2	3	3	Three-fold Astigmatism
A_3	4	4	Four-fold Astigmatism
B_2	3	1	Axial Coma
S_3	4	2	Axial Star
C_1	2	∞	Defocus
C_3	4	∞	Spherical Aberration

Table 2. Aberration coefficients that are important for HRTEM

This provides a measurement for the tilted aberrations as compare to the normal axial ones. The two-fold astigmatism, and defocus, can be directly measured from the diffractogram, and from them, the third-order aberration can also be derived by recording a tilt tableau. If the illumination is tilted by an angle τ , the new aberration coefficients up to C_3 are given by

$$\begin{aligned} A'_0 &= A_0 + A_1\tau^* + A_2\tau^{*2} + C_1\tau + \frac{1}{3}B_2^*\tau^2 + \frac{2}{3}B_2\tau^*\tau^2 + C_3\tau^*\tau^2 \quad (3-36) \\ A'_1 &= A_1 + 2A_2\tau^{*2} + \frac{2}{3}B_2\tau + C_3\tau^2 \\ C'_1 &= C_1 + \mathcal{R}\left(\frac{4}{3}B_2\tau^*\right) + 2C_3\tau^*\tau \\ B'_2 &= B_2 + 3C_3\tau \\ C'_3 &= C_3 \end{aligned}$$

Some aberration coefficients could be measured directly, others needs to be derived from the measureable ones. As could be seen in Equation (3-36), the shift $A'_0 - A_0$ between the two images taken at a beam tilt of τ depends on all other aberration coefficients. Therefore, by measuring image shifts on multiple set of tilt angles, it is possible to calculate all coefficients. The alternative is to measure the tilt-induced changes in defocus ($C'_1 - C_1$) and two-fold astigmatism ($A'_1 - A_1$) from the diffractograms, they depend on A_1 , C_1 , A_2 , B_2 , and C_3 , with enough diffractogram measurements from different angles, it is possible to calculate all of the above coefficients.

Inspired by Scherzer's theorem(1947), the design of a multi-pole system or a time-varying field emerged to try and correct the aberration in TEM images.^{9,10} Only after 50 years was a multiple lens design used to realise a spherical aberration corrector that could actually improve the spatial resolution in a TEM.¹¹ There has been a continuous improvement in instrumentation. For example, the OJ 2200MCO microscope, which was heavily used throughout this project is one of the early double aberration corrected TEMs that was developed as a joint project between Japan Electronics and Oxford

University (hence the name). In this system, two hexapole lenses and two transfer lenses doublets are fitted to manage the aberrations. The first hexapole deviates the beam to the radial distance from the electron optics axis, creating a negative C_s , which is desired. However, this also gives rise to three-fold aberration, which is compensated for by the second set of hexapoles. With a CEOS aberration corrector fitted in the system, the correction is achieved by means of the Zemlin tableau method. A series of diffractograms generally on amorphous materials, are taken, with known beam tilts. The acquired thin rings corresponds to the oscillations of the contrast transfer function. In practice this is done firstly by finding an amorphous area on the sample, usually an area where surface adsorbates are dense on the surface of graphene, or a very thin area of SiN (which inherently exists on the heating holder TEM grid). The diffractogram or a power spectrum of an image of an amorphous specimen area is a measure of the contrast transfer; this is achieved *via* a Fast Fourier Transform (FFT) of the underlying real space image. The diffractogram is normally represented in the form of concentric ellipses of high and low intensities. The high intensity area reflects passbands of the phase contrast transfer function, which are extrema, whereas the vanishing contrast intensity region represents areas where the phase contrast transfer function approaches zero. The spacing and sequence between these ellipses depend on the applied defocus, C_1 and the spherical aberration, C_3 . Moreover, the ellipticity is directly affected by the two-fold astigmatism A_1 . We zoomed into the targeted area (the thin amorphous region) to 500,000 X magnification, and then roughly adjusted the defocus and A_1 manually, until there were seven to eight rings within the field of view and the rings were as circular as possible. This process is often where most problems occur: it is important to find a uniform and thin enough area for the diffractograms to work at their optimum capacity. Especially when using surface contamination as a source of amorphous

materials, it is also crucial to make regular checks during the correction process, to ensure that the continuous electron beam irradiation has not damaged the amorphous area.

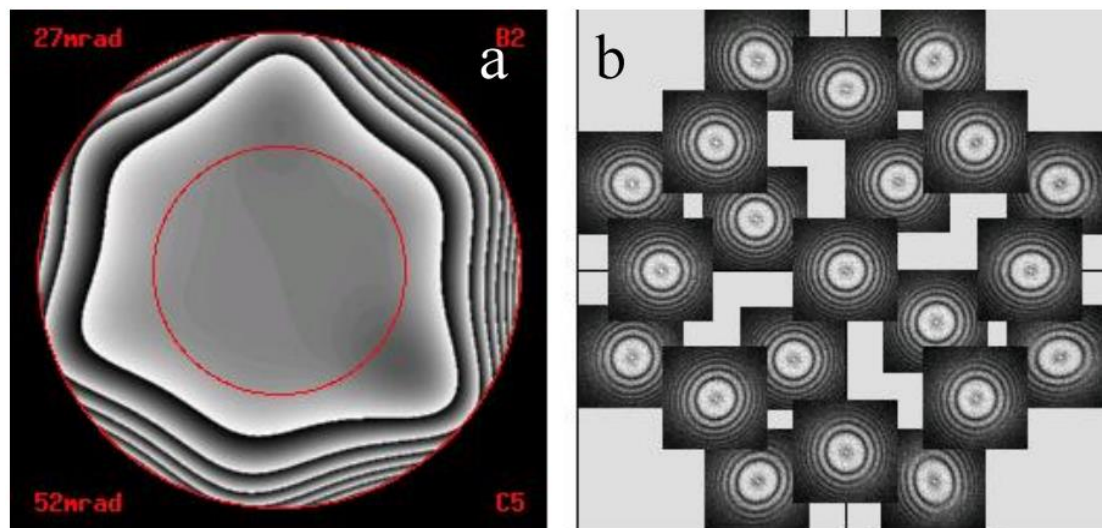


Figure 3-8 A Zemlin tableau taken at 36 mrad tilt angle on the OJ2200 MCO, (a) is the resultant phase plate and (b) is the diffractogram taken at enhanced mode.

The Zemlin tableau can be taken automatically in the software by a user predefined tilt angle: this process normally starts with 18 °of tilt angle and fast tableau, so as to roughly adjust all the aberration values first. The tilt angle is brought up to 26 ° if the monochromator is on, the instrument is changed to enhanced tableau mode in order to take more measurements. This tilt angle is only a practical guideline for my graphene samples, if the microscope is performing well, I would take it to a higher value to restrict the residual aberration further. The results of this process will be similar to those shown in Figure 3-8, with the diffractogram and readings of the actual quantification of the individual aberration coefficients are also given. The software also generates a phase plate calculated to the fifth order, as shown in Figure 3-8 (a), and gives out the type of aberration that needs correction. This process is iterated until a convergent in aberration coefficient values are reached. AC-TEM images can now be acquired by taking the

microscope to an appropriate magnification and setting the sample stage to the appropriate defocus value by adjusting the piezo control.

Apart from the quantification of each individual aberration coefficients, the characteristics of the Zemlin tableau can also provide qualitative measure of the type of aberration that is present. If the automated correction does not reach a convergence, and manual correction needs to be carried out, one can refer to the aberration characteristics for each aberration type as shown in Figure 3-9. The impact of first-order aberrations, such as defocus and two-fold astigmatism can be identified from a single diffractogram as they affect the number of thon rings and the elliptical distortion of the diffractogram without tilt. For aberrations of order ≥ 2 , such as B_2 , A_2 , C_3 , S_3 , and A_3 , no more elliptical distortion will be observable for the non-tilted case. Only by applying illumination tilt, are the characteristic distortions of each aberration observable.

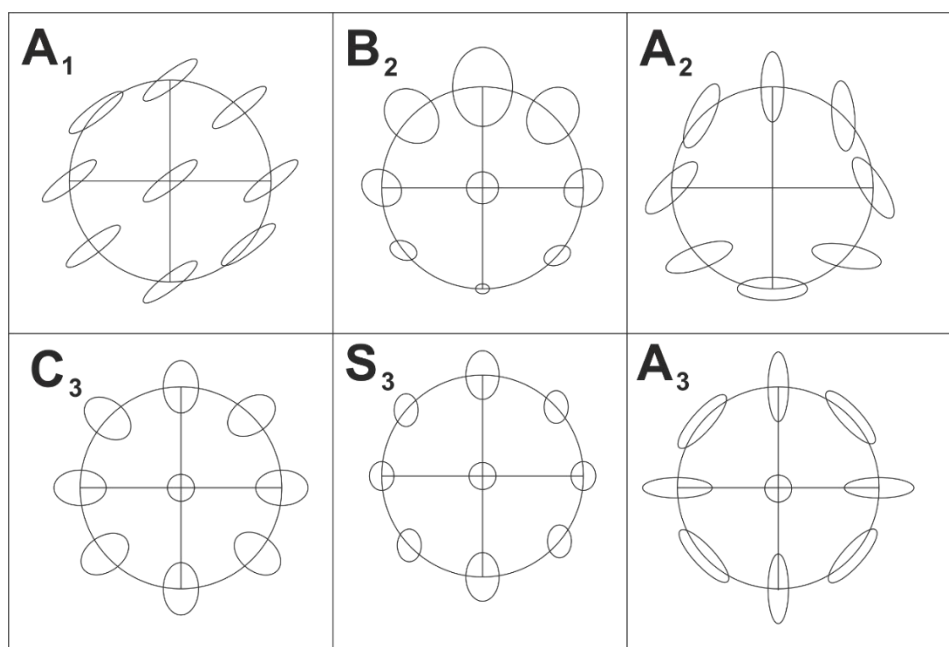


Figure 3-9. Schematic illustration of the Zemlin tableau characteristics for up to third order.

The name of the aberration that corresponds to the specific shape of the tableau is also given.

All atomic resolution AC-TEM data presented in Chapters 4 – 8 were captured with the JEOL JEM-2200MCO microscope, which operates at an accelerating voltage of 80kV. Aberrations up to third order can be corrected with the CEOS corrector fitted on this microscope, allowing routine sub-Angstrom resolution of graphene lattice to be imaged. It is also equipped with a double Wien Filter monochromator¹² with 5 and 9 μm slits used to limit the FEG source energy width to within a $\sim 0.2\text{MeV}$ profile, allowing for single atom resolution ($\sim 80\text{pm}$). Since imaging in a monochromation environment requires protracted alignment time, and fine manual adjustments to the aberration values are also constantly required to keep the high level of image quality. The aberration free areas are also smaller ($\sim 8 \times 8 \text{ nm}$), there is therefore a trade-off between image quality and practical operation. For experiments that required a large even aberration area, or those that required a long image period without aberration drift, we operated the microscope under mono-off mode. The results in this regard are discussed in Chapters 7 and 8. For experiments where highest image quality was needed to measure the bond length variation and also those that did not require an extensive period of imaging time, mono-on mode was activated. These data are discussed in Chapters 4, 5, and 6.

3.7 AC-TEM image processing

Various image processing techniques were employed to improve the signal-to-noise ratio and visual effect of the AC-TEM images. As shown in Figure 3-10 (b), a FFT band-pass filter between 100 to 1 pixels was used to remove the broad uneven illumination variation. The image was then Gaussian blurred with a sigma radius value of 3.0 pixels to remove further noise. This value can be individually adjusted according to the specific signal-to-noise level and the resolution of the AC-TEM frame.

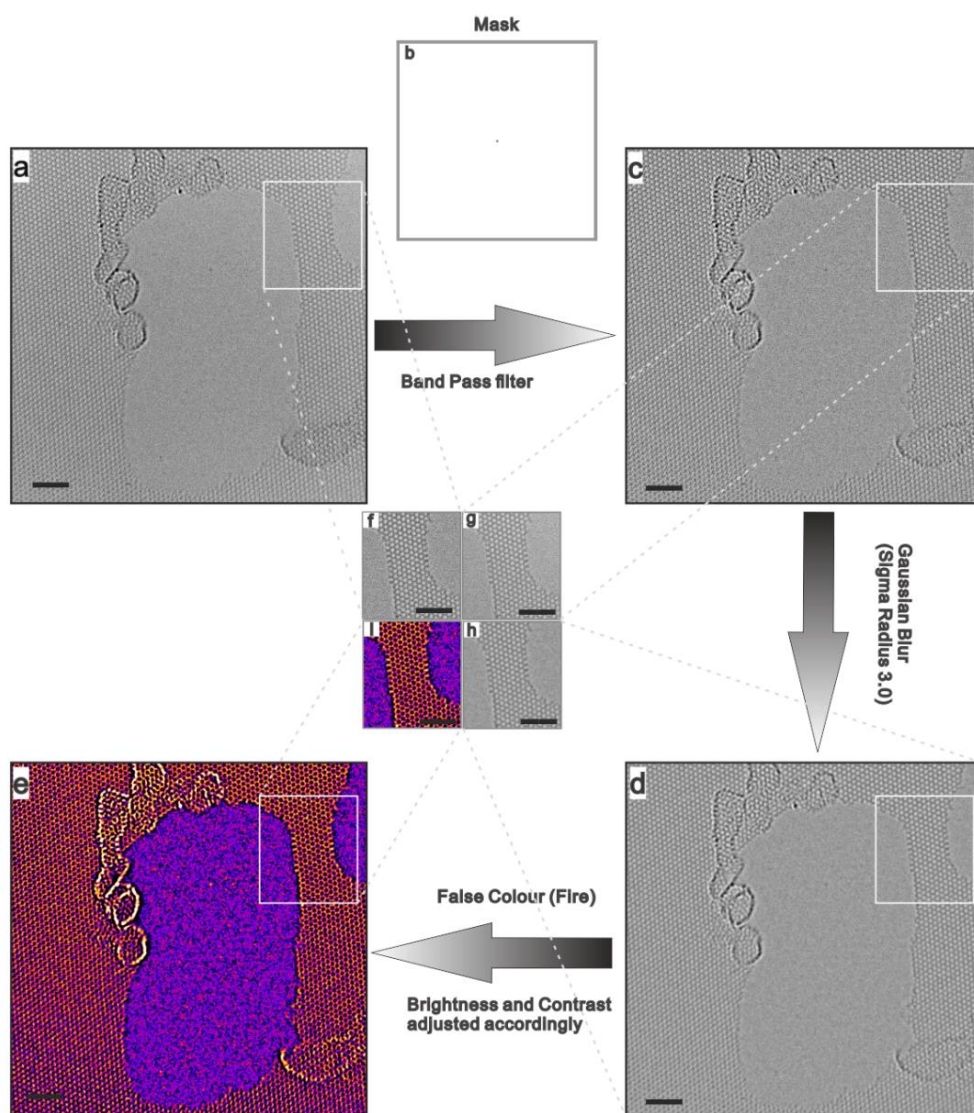


Figure 3-10 The various image processing techniques employed. (a) An unprocessed AC-TEM frame. (c) AC-TEM images were initially subjected to a band-pass filter (ImageJ, filter large structures at 100px and small at 1px) to remove brightness variations. The filter mask is shown in (b). (d) Gaussian blur with a sigma radius of 3.0 was applied to the image. (e) A LUT table (fire) was applied to the image and brightness and contrast adjusted to enhance visual contrast. (f – h) show the magnified images of the white box highlighted area in (a, c, d, e) respectively. Scale bars = 2nm

A colour look-up table (LUT), ‘Fire’ in the ImageJ software, was used to improve visual contrast if necessary. The brightness and contrast were adjusted to create the best visual

contrast. Great care was taken to ensure the parameters used in these processes did not introduce artefacts into the final images. The magnified images of a nanoribbon area that is highlighted with white boxes in Figure 3-10 (a,c,e,d) are shown in (f-i) respectively to demonstrate the effect image processing have on the raw TEM images.

3.8 Discovery Studio and JEMS simulation

Atomic models of graphene were broadly used, as described throughout this thesis, to prepare a corresponding atomic structure of an AC-TEM frame; provide a figurative illustration; and as an initial position to perform density functional theory (DFT) or tight binding molecular dynamics (TBMD) calculation.

Atomic models were prepared in Accelrys Discovery Studio 3.5 Client. The geometry was usually optimised using the built-in “Clean Geometry” function: a fast, Dreiding-like forcefield was used to optimise the geometry. The lighting and camera positions for figurative illustrations were usually optimised in the Persistence of Vision Raytracer v3.6 (POV-Ray) software. All the DFT and TBMD calculations performed in this thesis were carried out by Professor Gun-Do Lee at Seoul National University, readers should refer to the specific publication outlined in the publication section for the calculation details, such as the simulation package code used, the pseudopotential chosen, and the cut-off energy selected for each experiment.

The multislice approach used utilises the basic principle of section the specimen into many slices, which are normal to the incident beam. The process is schematically illustrated in Figure 3-11. The potential of a slice is projected onto a plane, and this is also called the phase grating. The amplitudes and phases for all the beams that will be generated by interacting with the first projection plane are calculated. These beams are then allowed to propagate down free space until they meet the next projection plane

(phase grating). The scattering calculation is then repeated for this new projection plane, this calculation produces a new set of beams which propagate through free space to the next phase grating. This process is repeated until all the slices have been calculated.

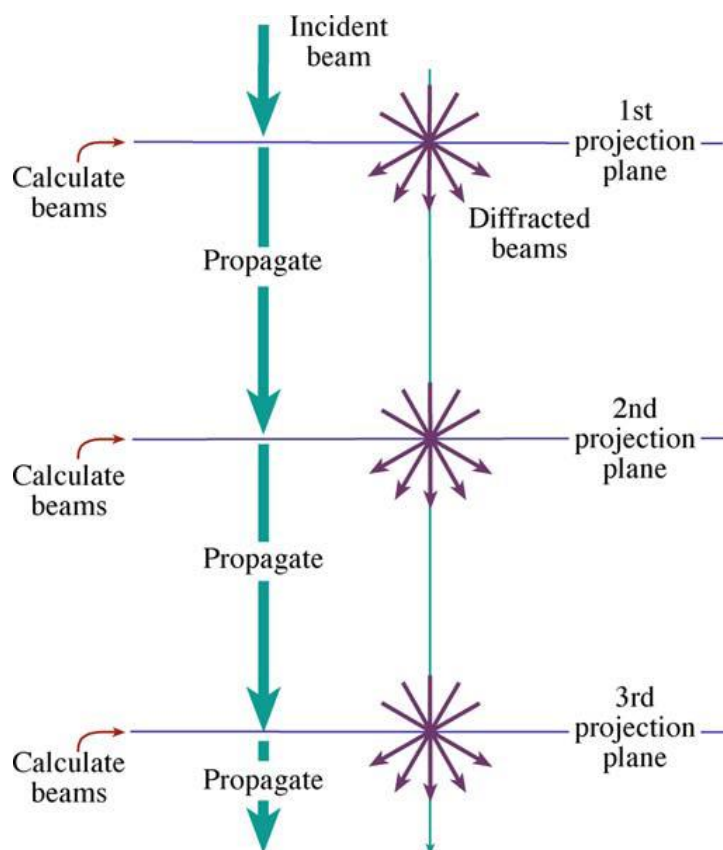


Figure 3-11. The potential within a slice is projected onto the first projection plane, this is the phase grating. The amplitudes and phases for all the beams are generated by interacting with the plane and propagate all the diffracted beams until the next projection plane. This process is repeated for the number slices created. (Reprinted figure with permission from ref.[6], Copyright (2009) by the Springer publishing group)

Image simulation of a given atomic structure can be compared to an AC-TEM frame to allow accurate determination of the geometrical structure. The simulated TEM images were generated using the multislice simulation software, JEMS (available at <http://cimewww.epfl.ch/people/stadelmann/home.htm>) by importing an appropriate coordinate file. This file can be generated from Discovery Studio 3.5 Client and then

converted to a JEMS compatible format by a Java programme. JEMS uses a multislice method to simulate TEM images, where the molecule is disassembled into sub-nanometre slices, which obeys the weak phase object approximations.^{13,14} Graphene is inherently a weak-phase object as it is only one atomic layer thin. It is also possible to include different aberration profiles, defocus spread and defocus in order to match the simulation images with the captured AC-TEM frames. Typically, The defocus spread correspond to δ in Equation (3-32) and would affect the point resolution; two-Fold, three-Fold astigmatism and axial coma can also be adjusted to adopt the distortion in the AC-TEM images. The alignment file for OJ2200 MCO microscope was loaded into the simulation software; the parameters are: accelerating voltage of 80kV, $C_c = 0.560$ mm; $C_s = -0.005$ mm; $C_5 = 1.000$ mm; Energy spread = 0.30eV; Lens stability = 0.00 ppm; Voltage stability = 0.00 ppm; these values were used for multislice image simulation in this thesis. To simulate monochromated TEM images, the defocus spread values of 3-5 nm⁻¹ are often chosen, for non-monochromated images, this value increases to 6-9 nm⁻¹ to represent the reduced point resolution. The point resolution depends largely on the microscope setting (the use of monochromator and the choice of energy slit) and the alignment conditions are different for each experiment. The precise defocus and defocus spread values used are chosen by comparing the simulated images at different settings with the HRTEM frame. The simulation setting at which the simulated images are closest in point resolution is then chosen, this process is done for all the simulation images carried out in this thesis.

3.9 References

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Chapter 4

Hydrogen-Free Graphene Edges

4.1 Introduction

The functionalisation and structural engineering of edges are reported to greatly influence the properties of mesoscopic graphene structures.¹⁻⁷ A variety of elements are known to attach to the edge of graphene, such as N, O, H, Fe and Si. However, to date hydrogen has been the most elusive element as regards studies, due to its small atomic mass. The attachment of hydrogen to graphene edges and its influence on the properties of graphene has been extensively studied theoretically.^{1,8-14} Experimentally, the localised energy states at the edges of graphene have been probed at the atomic level by STM combined with scanning tunnelling spectroscopy (STS), as well as scanning transmission electron microscopy (STEM) combined with EELS. STM and STS with sub-nanometre resolution have revealed the dependence of the electronic structure on local edge atom configurations.¹⁵⁻²⁰ STEM with EELS from single carbon edge atoms in graphene showed the existence of unique energy states not found in the bulk.²¹ Several energy states have been identified and associated with different edge terminations such as Klein, zig-zag and armchair edges. However, it is not possible to obtain an EELS signal from a single H atom at the edge of graphene. Furthermore, when the EELS is acquired at the edge of graphene, the atomic structure may have changed from the initial STEM image used to determine the EELS acquisition region, and this makes exact correlations between edge atomic structure and EEL spectra

challenging. The edges studied by Suenaga and Koshino²¹ were created by electron beam irradiation under vacuum in the TEM and a similar approach to creating edges in graphene has been used in several other studies,^{22–24} but the issue of whether hydrogen is attached to the edge atoms has not been probed experimentally.

The attachment of hydrogen to either zig-zag or armchair edges of graphene changes the local charge density within bonds and should lead to modifications of the C–C bond lengths of the edge atoms relative to non-hydrogen attachment. Kawai and Koga²⁵ in their theoretical study suggested H-free armchair edges reconstruct and form a triple bond at the arm-rest position. This reconstruction gives a predicted bond length reduction from 1.38 to 1.23 Å, which is close to the triple bond of acetylene (1.20 Å).

Despite the progress made in scanning probe microscopy (STM and atomic force microscopy) and AC-TEM,^{26–30} detecting bond length changes at the edges of graphene has been extremely difficult due to the need to fully resolve individual carbon atoms. Recent advances in monochromation of the electron source have enabled AC-TEM with ~80 pm spatial resolution at the low accelerating voltage of 80 kV.³¹ It was recently demonstrated how this leads to the ability to fully resolve individual atoms in graphene, permitting the precise measurement of C–C bond changes within 5–7-membered ring dislocations and monovacancies.^{32,33}

The irradiation of graphene with an electron beam with an energy of 80 keV is known to cause the opening of holes through chemical etching from surface impurities.³⁴ Once a hole has been opened in graphene the edge atoms are susceptible to further sputtering because the 80 keV energy electrons have sufficient energy to knock out the edge atoms. This results in the subsequent expansion of these holes by sputtering of edge atoms. Carbon atoms at the edge of graphene can also be mobile, and move rapidly between

positions of fixed stability leading to edge reconstruction. The rate of edge sputtering is dependent upon the beam current density (BCD). Here I have reduced the BCD sufficiently such that the rate of hole expansion was very slow, $\sim 1.4 \text{ pm s}^{-1}$, and therefore the atomic configuration of the edge structures were stable enough to be sequentially imaged multiple times and an average image formed with high signal to noise contrast from individual atoms. This has enabled the observation of several different types of edge terminations such as zig-zag, Klein edge, armchair and reconstructed 5–7 edge structures.

In this chapter, I will discuss our use of sub-Angstrom imaging of graphene edges by monochromated AC-TEM at an accelerating voltage of 80 kV, combined with DFT calculations to examine armchair edge structures that were predicted to have shortened C–C bond lengths when they are not functionalised by hydrogen or other atoms.^{12,25} Time-dependent images capturing a single atom attaching to the armchair graphene edge were obtained and revealed real-time changes in bond length due to functionalisation.

4.2 Armchair edge bond length mapping

Figure 4-1 (a) shows a TEM image of a hole being sputtered on a pristine sheet of graphene by 80-kV electron beam irradiation. This image was formed by averaging three successive frames where the position of atoms had not altered. This indicates that this specific edge configuration was stable under electron beam irradiation for at least 30 s. Figure 4-1 (b) shows the measured bond lengths obtained from analysis of the TEM image in Figure 4-1 (a), presented as a ratio that is calculated by dividing each measured bond length by a standard C–C bond length value measured in a non-perturbed region of graphene. Colour scale representation is used in Figure 4-1 (b) to

display the bond length ratios on the atomic models for ease of visual inspection. The bond lengths were determined by fitting boxed line profiles of two atoms forming the bond with two Gaussians, shown in Figure 4-1 (c) whereby the peaks of the Gaussians were used as the centre of the atomic positions. Contraction of the bond lengths is observed for the three armchair bonds at the graphene edge, indicated in blue. The ratio between these three bonds and the average bond lengths from the bulk lattice in our images are within the range of 0.86–0.88, matching the theoretical predictions found in Kawai and Koga²⁵ for hydrogen-free armchair edges of graphene. I have conducted geometrical optimisation using DFT for an atomic structure based on the TEM image in Figure 4-1 (a). The unit cell was constructed by removing 52 carbon atoms from pristine graphene composed of 448 carbon atoms to make a hole and edges. In the case of hydrogen-terminated edge structures, 18 hydrogen atoms were attached at the edge of the hole. In constructing the supercell for simulation, we contained a vacuum region of 30 Å in the z direction. The Brillouin zone was sampled using a $(2 \times 2 \times 1)$ Γ -centred mesh. When structural relaxations were performed, the structure was fully relaxed until the force on each atom was smaller than 0.02 eV/Å. Bond lengths were measured on both the DFT atomic model shown in Figure 4-1 (e) and from the multi-slice simulated image shown in Figure 4-1 (d). Both images show the same shortening of the C–C bond distance, which matches the results from the TEM image in Figure 4-1 (a). This confirms that the significant shortening of the C–C bond at the armchair edge is due to bond reconstruction rather than being an artefact of the TEM imaging.

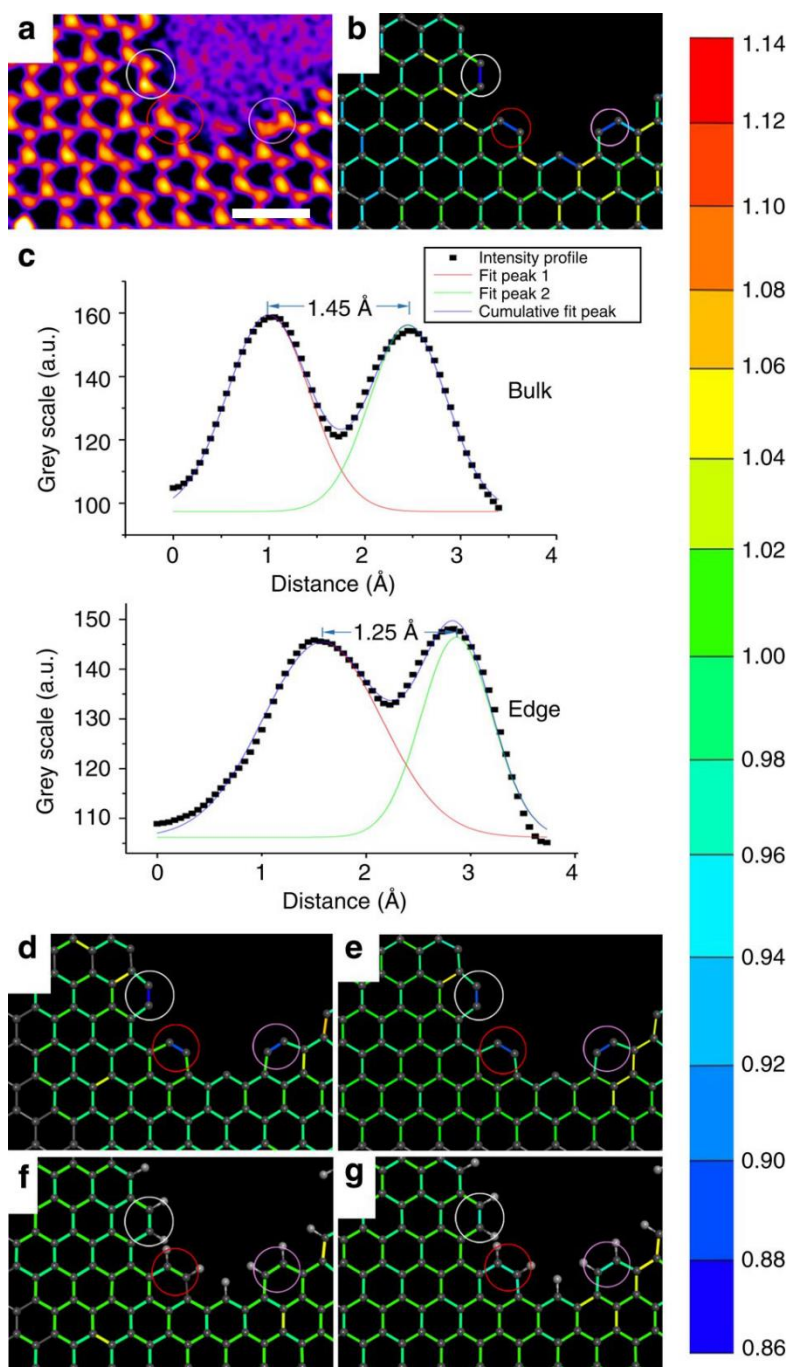


Figure 4-1. (a) AC-TEM image from averaging three consecutive frames with identical structure. The scale bar on the right expresses the amount of compression or elongation of a C–C bond in the form of different colours; the blue end of the spectrum is compression and the red end elongation. The amount of compression or elongation is expressed as a ratio (R) determined by measuring each individual bond length (B_i) and dividing it by a non-perturbed pristine C–C bond length value (B_{C-C}). The results show that contracted bonds have a ratio <1 , elongated bonds have a ratio >1 , and non-perturbed bonds have ratio ~ 1 . (b) Measured bond

lengths expressed in ratio value (R) and represented using the colour scale, from the AC-TEM image in (a). (c) Measurement of bond lengths at the edge (red circled bond in Figure 4-1 (a)) and in the bulk of graphene by fitting the boxed line profile from two atoms forming a C–C bond with two Gaussians. (d) Colour representation of measured bond length ratios from multi-slice simulated image (including residual aberrations discussed in Figure 4-3 to Figure 4-6) based on the DFT-calculated atomic structure shown in (e). (e) Colour representation of bond length ratios calculated using DFT. (g) Colour representation of measured bond length ratios from DFT calculations of a hydrogen-terminated structure. (f) Colour representation of measured bond length ratios from a multi-slice simulated image based on the DFT-calculated atomic structure shown in (g) (including residual aberrations discussed in Figure 4-3 to Figure 4-6). Scale bars = 0.5 nm

Prior theoretical work suggests that graphene edges should be very easily passivated with hydrogen, as this lowers the edge energy.¹² For comparison, another set of DFT studies was performed, but this time with the graphene edges terminated by hydrogen atoms. Analysis techniques similar to those used in Figure 4-1 (d,e) for the hydrogen-free case were applied to the hydrogenated case. Figure 4-1 (f) shows the measurements of bond lengths from the multi-slice TEM image simulation based on the DFT model and Figure 4-1 (g) presents the bond lengths determined from the DFT-calculated atomic structure. The most significant changes occur for the bonds circled with different colours in Figure 4-1 (b,d-g). The armchair edge bonds for the hydrogen attached to the edge of graphene, circled in Figure 4-1 (f,g), show no apparent shortening, with one bond even showing a slight elongation in panel (f). Overall, our experimental data from AC-TEM shown in Figure 4-1 (a,b) match the case of hydrogen-free edge terminations and I can rule out the presence of hydrogen within these bonds.

The standard deviation (s.d.) for the TEM bond length ratio measurement was 0.03 Å. This was obtained by measuring >20 C–C bond length values in pristine regions of

graphene that were unperturbed and calculating the mean and then the s.d. of the data set relative to the mean value. It is therefore not abnormal to see the slight colour variation in the bulk of the lattice. The bond length ratio of the arm-rest position on the armchair edge relative to pristine graphene is at the level of 0.86–0.90, which is well above the noise level. The s.d. values for the DFT model are 0.002 Å and 0.004 Å for hydrogen-free and hydrogen-terminated structures, respectively. These values are calculated in a similar way to the TEM bond ratios, but reflect the uncertainty in the DFT calculation. The values are low and thus there is much less colour variation in Figure 4-1 (e,f). The s.d. values for the multi-slice image simulations based on the DFT models are 0.015 Å and 0.013 Å, respectively, for Figure 4-1 (e,g), primarily due to the experimental uncertainty introduced in Figure 4-1 (d,f) into the measurement of the atom positions by line profile analysis.

In order to ensure our measurements in Figure 4-1 were valid, I have repeated the same analysis on a second newly created edge structure, shown in Figure 4-2. The TEM image in Figure 4-2 (a) is the average from three images, and Figure 4-2 (b) shows the Gaussian fits to line profiles. In Figure 4-2 (c), the bonds of interest are circled and, as in Figure 4-1, they too show shortening. This further confirms that the outermost bonds for the armchair edge structure in sputtered graphene edges show C–C bond compression of ~0.86–0.9, which is consistent with the predicted bond lengths for triple bonded C≡C and indicates they are free from hydrogen attachment.

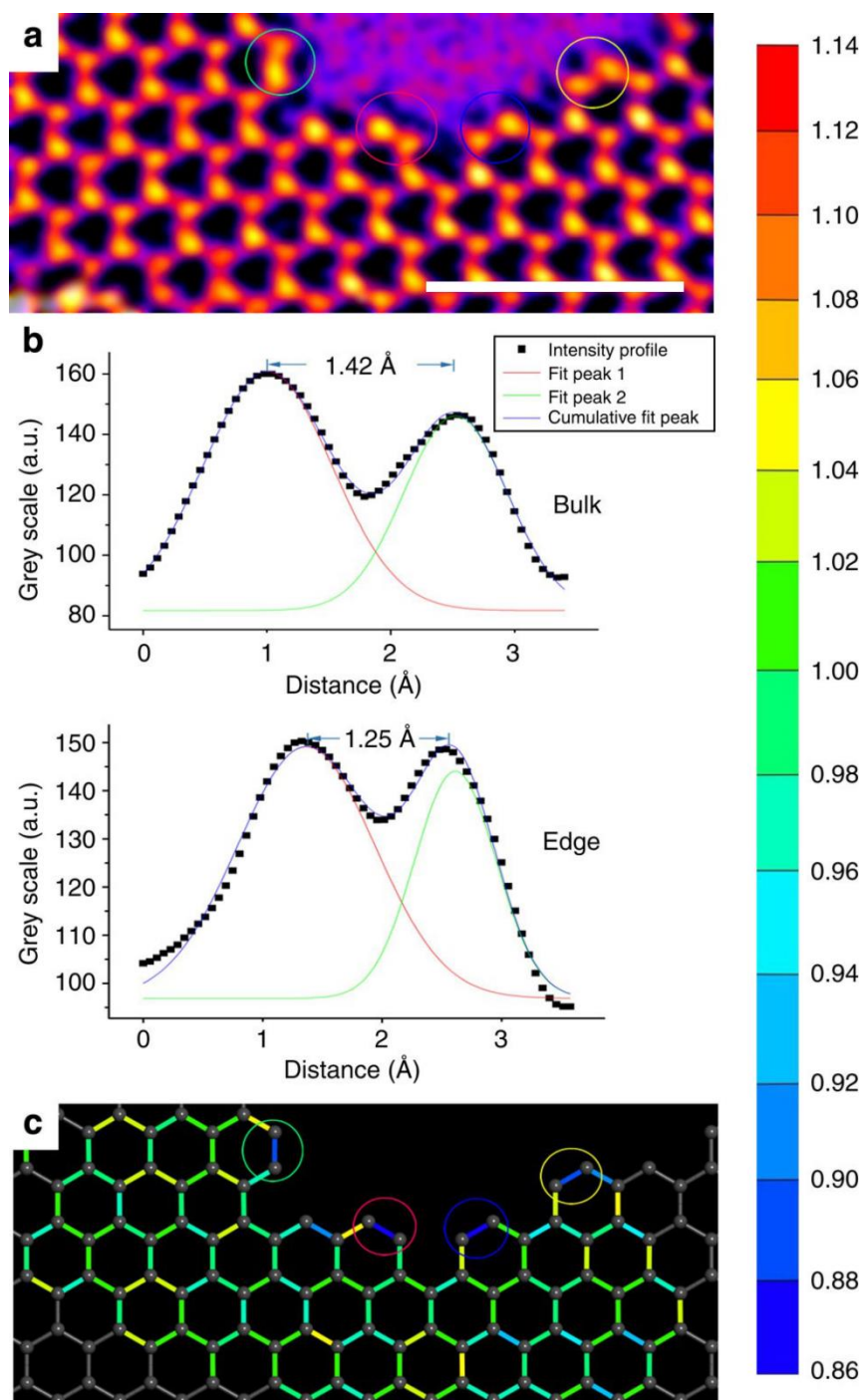


Figure 4-2 (a) Averaged AC-TEM image from three consecutive frames having identical structures. The scale bars on the right-hand side have an identical meaning to those used in Figure 4-1 (b) Measurement of bond lengths for bulk C–C pairs and for a pair of atoms at the edge in armchair configuration using two Gaussian fits to a boxed line profile. (c) Colour representation of bond length ratios for the experimental AC-TEM image in (a). Scale bar = 1 nm

4.3 Characterising residual aberrations in the AC-TEM images.

Aberrations caused by the objective lens are the main cause of information limitation in an HRTEM image.³⁵ The post-specimen hexapole CEOS aberration corrector corrects up to third-order aberrations: this dramatically improves resolution and reduces astigmatism. However, the techniques I have developed, as shown in Figure 4-1 and Figure 4-2, involving examining the bond length variation near the edge and then comparing it with simulated images from atomic models calculated using DFT method, is highly sensitive to second and third-order aberrations as they cause an extensive amount of distortion at the atomic level with even a modest amount of aberration. Furthermore, the aberration-free area is limited to the centre of an AC-TEM image: therefore lattice afield from this area still experiences aberration. It is therefore considered to be indispensable to characterise the residual aberration, to ensure it is below the noise level.³⁶

Figure 4-3 presents a series of multi-slice image simulations with variation in the amount of two-fold astigmatism. Figure 4-3 (a–f) demonstrate the impact different astigmatism amplitudes have on the resultant image, the values range from 0 to 1.0 nm with an interval of 0.2nm. Based on the study, two-Fold astigmatism eventually degrades the resolution of the image and care must be taken to minimise its impact through continual correction. It also possesses a uni-directionally stretching effect on graphene lattice. Comparison of Figure 4-3 with the AC-TEM image shown in Figure 4-1 (a) enables an estimated value of 0.2nm to be obtained. A study of the direction of the astigmatism was carried out, shown in Figure 4-3 (g–o), to accurately define a full

and detailed profile of the astigmatism, a direction value of 225° was estimated for Figure 4-1 (a).

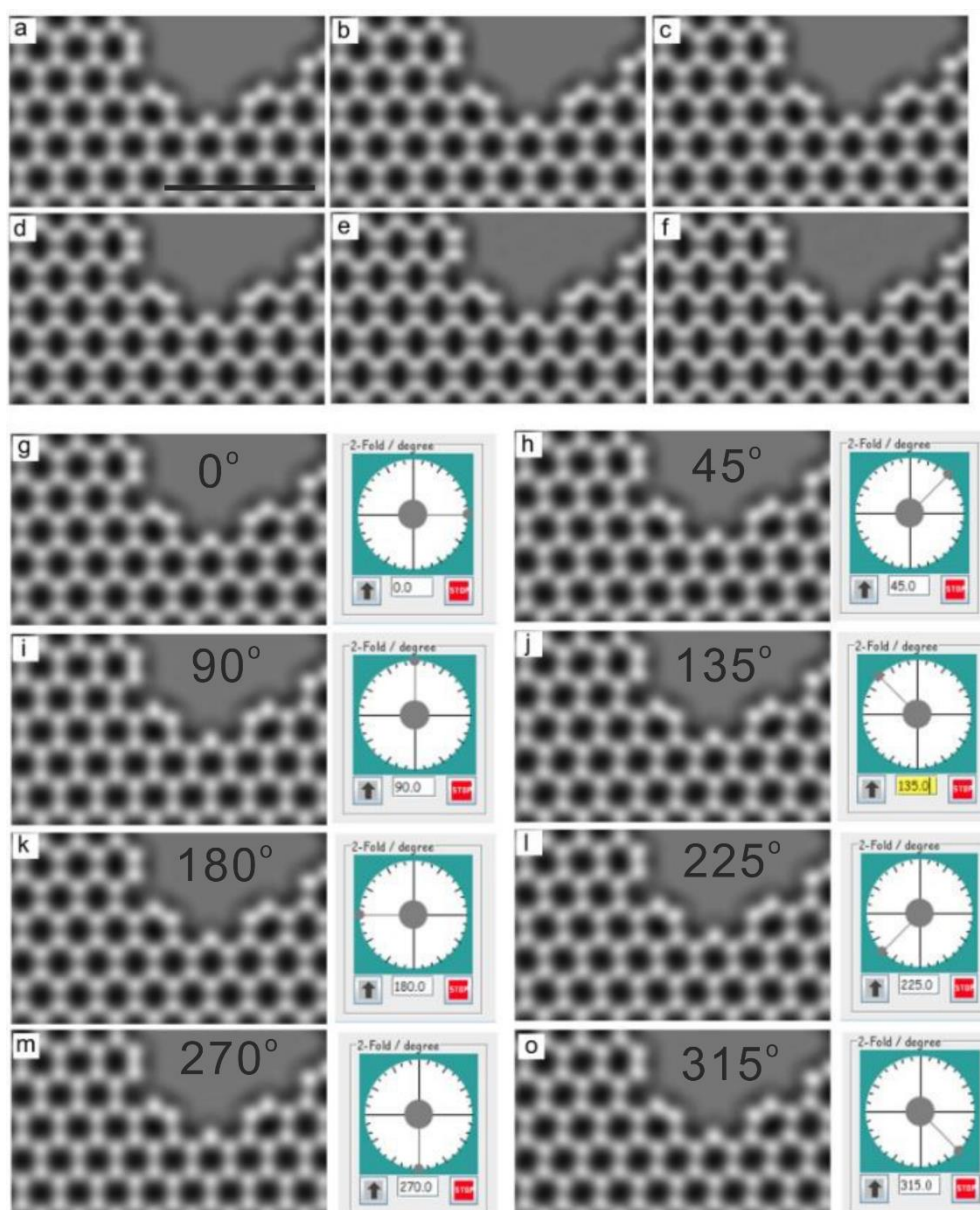


Figure 4-3. Two-Fold astigmatism. (a–f) Multi-slice image simulations of graphene structure with variation of the level of two-fold astigmatism increasing from 0 to 1.0 nm with an interval of 0.2nm. (g–o) Direction studies of the two-fold astigmatism with a value of 0.2 nm. The angle of the directions increases from 0° to 315° , with an interval of 45° (in practice, 0° is equivalent to 360°) The inset to the right of each figure demonstrates the direction of the astigmatism which the simulation adopts. Scale bar = 1 nm

Figure 4-4 presents multi-slice image simulations of graphene lattice for different values of three-fold astigmatism, but with the two-fold astigmatism set at 0.2nm and a direction of 225° , as previously estimated from Figure 4-3. From analysis of these images and comparison with Figure 4-1 and Figure 4-2, I will estimate an amplitude and direction of the three-fold astigmatism to be 40 nm and 315° for the AC-TEM images in Figure 4-1 and Figure 4-2.

Figure 4-5 shows multi-slice image simulations with different values of axial coma, including two-fold astigmatism of 0.2nm and three-fold astigmatism of 40 nm. As can be seen from Figure 4-5 (f), which is an extreme example of a highly misaligned image, adjacent atoms have very different contrast levels – as if the two atoms are different elements. This effect is also directionally sensitive as the contrast of two atoms varies along with the change in coma directions. Values of 60nm and 315° were estimated for the axial coma amplitude and directions.

Having carefully examined the three major first and second order aberrations individually, I have combined all aberrations into one simulation, Figure 4-6, to demonstrate the overall effect on the atomic resolution imaging of graphene. Figure 4-6a shows the TEM image of Figure 4-1 and Figure 4-6 (b) shows the multi-slice image simulation of the representative atomic structure with all aberration values set to 0. Figure 4-6 (c) shows the new multi-slice image simulation that contains aberration values (two-fold = 0.2 nm at angle 225° , three-fold = 40nm at angle 315° , and axial coma = 60nm at angle 315°) estimated by comparing Figure 4-1 with the set of simulations performed in Figure 4-3 to Figure 4-5. The image simulation in Figure 4-6 (c) now shows an excellent agreement in terms of defocus and contrast differences between two adjacent C atoms with Figure 4-1, illustrated again as Figure 4-6 (a).

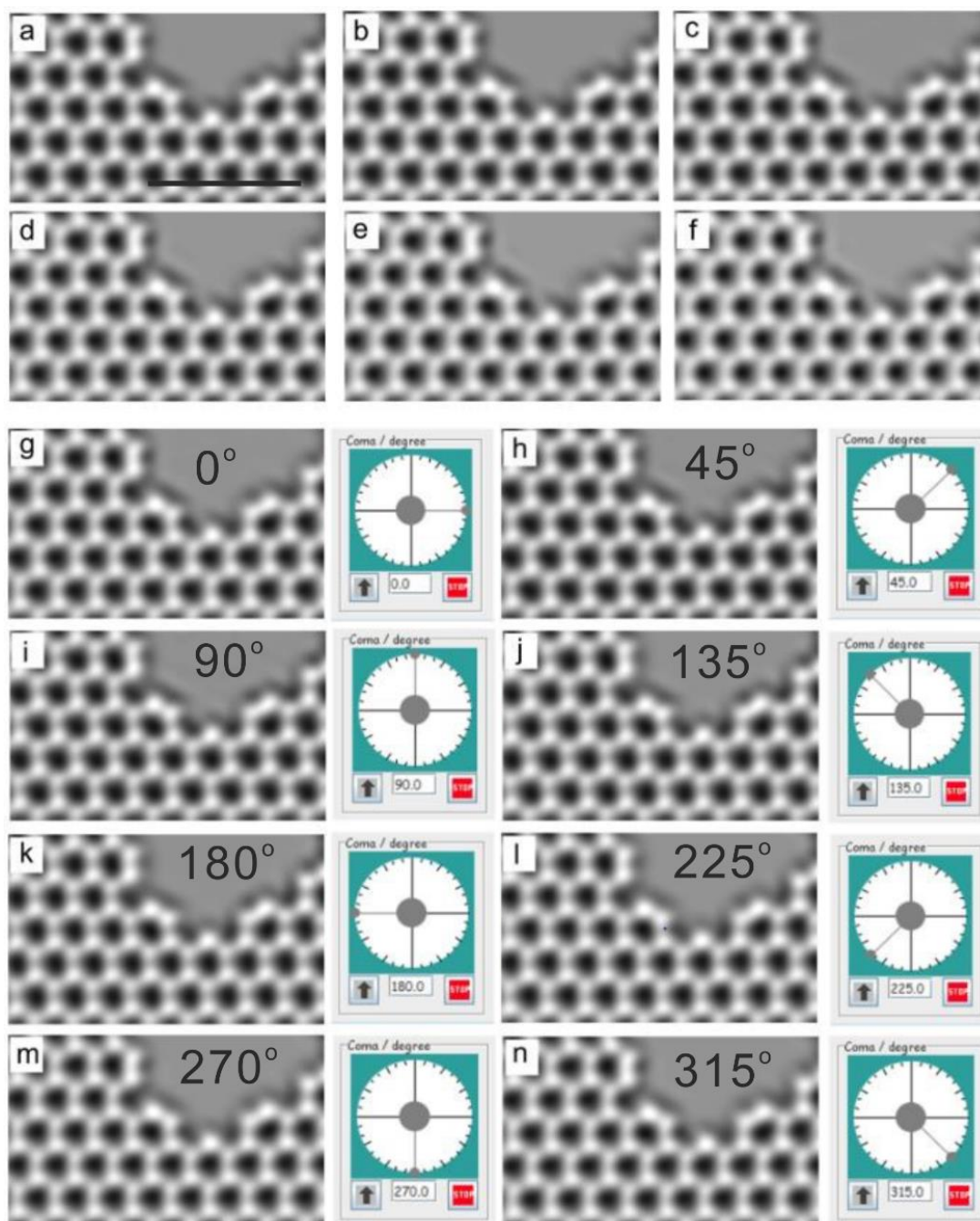


Figure 4-4. Three-fold astigmatism correction with a pre-set two-fold astigmatism value of 0.2 nm and a direction of 225°. Multi-slice image simulations of graphene structure with (a–f) different levels of three-fold astigmatism increasing from 0 to 50 nm with an interval of 10nm. (g–o) Direction studies of the three-fold astigmatism with a value of 40 nm. The angle of the directions increases from 0° to 315°, with an interval of 45° (in practice, 0° is equivalent to 360°). The inset to the right of each figure demonstrates the direction of the astigmatism which the simulation adopts. Scale bar = 1 nm

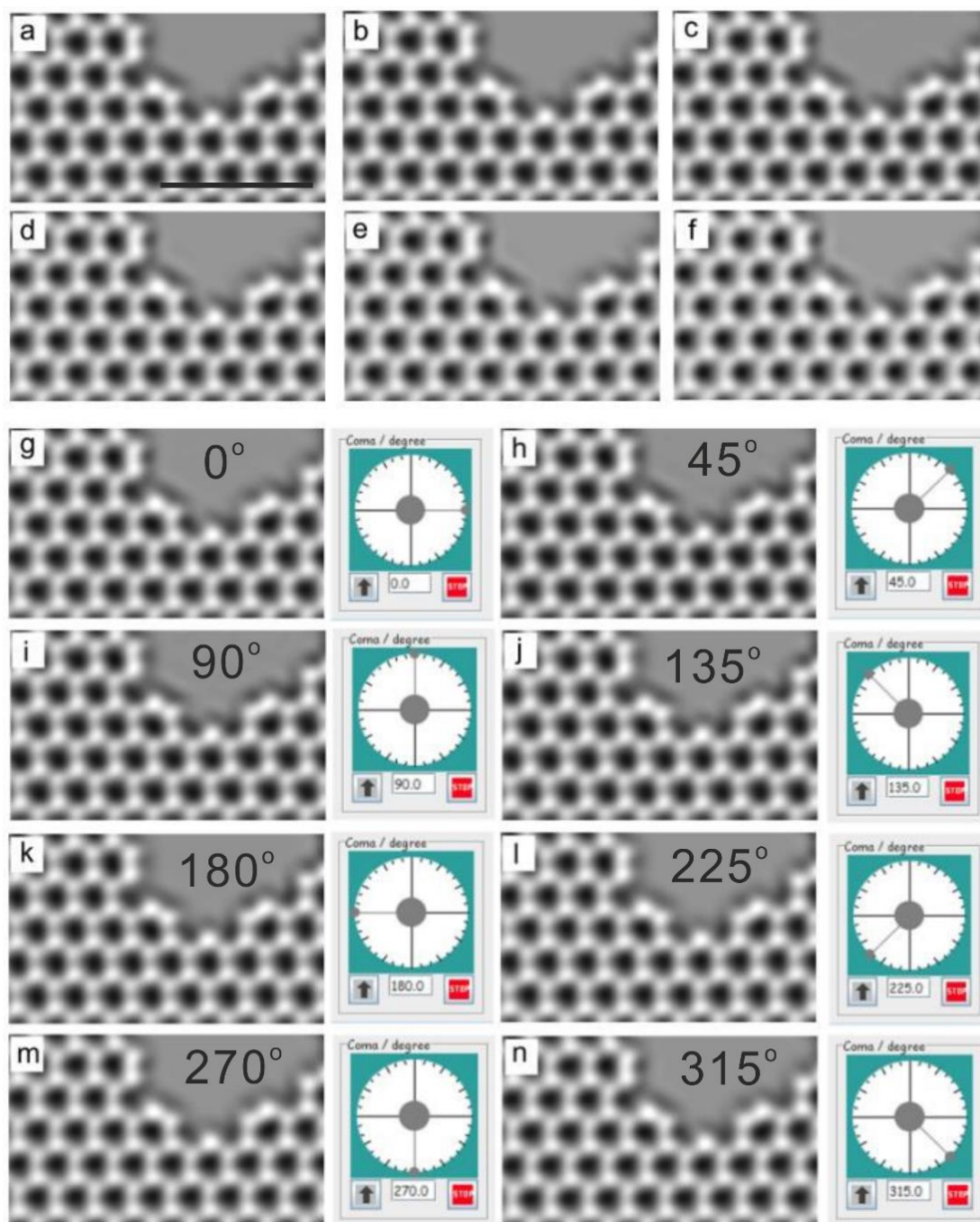


Figure 4-5. Axial coma correction with a pre-set two-fold astigmatism value of 0.2nm and a three-fold astigmatism value of 40 nm. (a–f) Level of axial coma increasing from 0 to 150 nm, with an interval of 30nm. (g–n) Direction studies of the axial coma with a value of 60 nm. The angle of the directions increases from 0° to 315° with an interval of 45° (in practice 0° is equivalent to 360°) The inset to the right of each figure demonstrates the direction of the astigmatism which the simulation adopts. Scale bar = 1 nm

This simulation result, based on a DFT-relaxed geometry combined with appropriate residual aberrations, was then used to calculate bond lengths across the image as in Figure 4-1. Comparison between the bond length values in Figure 4-6 (a-c) shows excellent agreement and demonstrates that the presence of the minor residual aberrations does not affect the measured bond lengths.

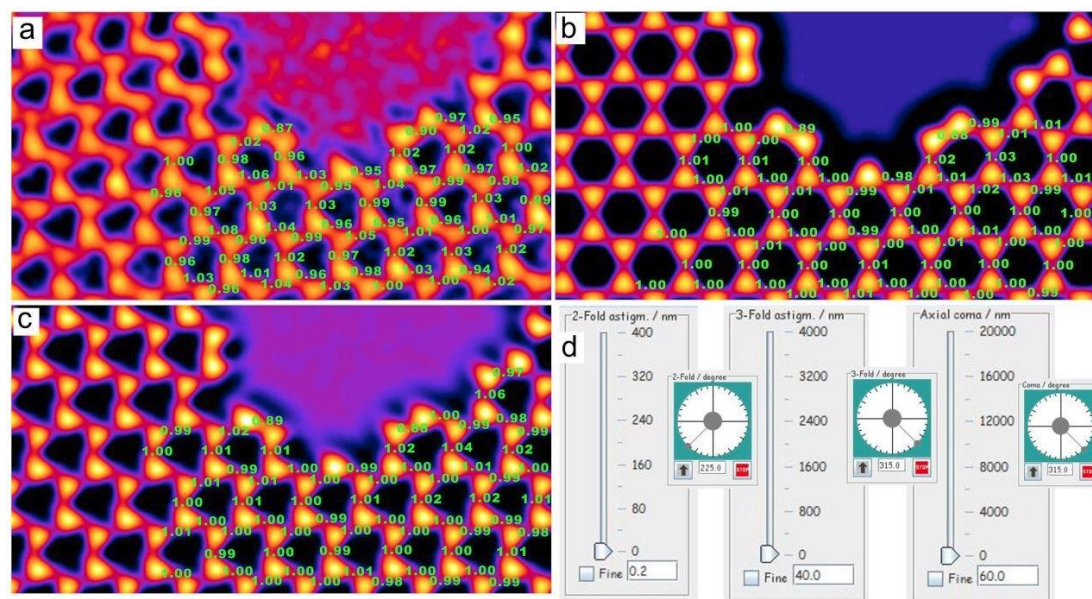


Figure 4-6. (a) A frame of an AC-TEM image with the bond length measurements of the interested region superimposed on the lattice. (b) Multi-slice image simulation of the DFT optimised geometry with appropriate defocus and defocus spread values, the bond length measurements are superimposed on the lattice. (c) Multi-slice image simulation of the same geometry as (b) but with two-fold, three-fold and axial coma astigmatism values set to represent the actual AC-TEM image. The bond length measurement values are superimposed on the lattice. (d) Parameters of the astigmatisms used to generate the multi-slice image simulation in (c).

4.4 Functionalisation-induced bond length changes

TBMD simulations revealed that a transient single carbon atom can temporarily functionalise the armchair graphene edge to form a unique triangular edge state – shown

in the calculations in Figure 4-7. Functionalisation of the armchair edge should perturb the $C\equiv C$ bond and therefore modify the bond length. Figure 4-7 (a–c) shows three frames from the TBMD simulation, as atomic models, that reveal the triangular edge state formation, along with corresponding multi-slice image simulations in Figure 4-7 (d–f). All simulations were started at a temperature of 2,500 K under the canonical control of temperature. The temperature was gradually increased to 3,200 K, under linear temperature control, to accelerate the dynamics so that structural changes at the edge could be observed during the simulation time. The velocity scaling method was also used to control the temperature. In the simulation unit cell, we removed 102 carbon atoms from pristine graphene of 364 carbon atoms to make a hole and edges. In Figure 4-7 (b), the blue dotted circles show the region where the triangle structure appears. The blue-coloured atom within the circle is used to identify the extra atom compared with the previous frame. Figure 4-7 (c) shows the deconstruction of the triangle structure by breaking one of the bonds connected to the hexagon, and its transformation into a Klein edge on the armchair configuration. These TBMD simulations were conducted without the presence of hydrogen, and Figure 4-7 (b) shows that the seven atoms within the blue circle prefer to adopt a hexagon–triangle structure instead of opening up to form a heptagon structure under these hydrogen-deprived conditions. Multi-slice image simulations utilising different microscope conditions reveal that the triangular edge structure can only be resolved with near sub-Angstrom spatial resolution (see Figure 4-8), which is achievable with our monochromated AC-TEM system. While observing the electron beam-induced sputtering of holes in graphene I have recorded the unique triangular edge structure predicted from the TBMD simulation. Figure 4-7 (g–i) shows a time-series of TEM images with ~ 20 s between frames: they depict the emergence of the triangular edge structure, with the respective

models below them. The triangular structure observed in Figure 4-7 (h) is rare and only lasted one frame (~ 2 s) before being lost. However, since the triangle structure must exist for an appreciable portion of the image exposure time of 2 s it must at least be meta-stable and must occupy a local minimum in edge energy.

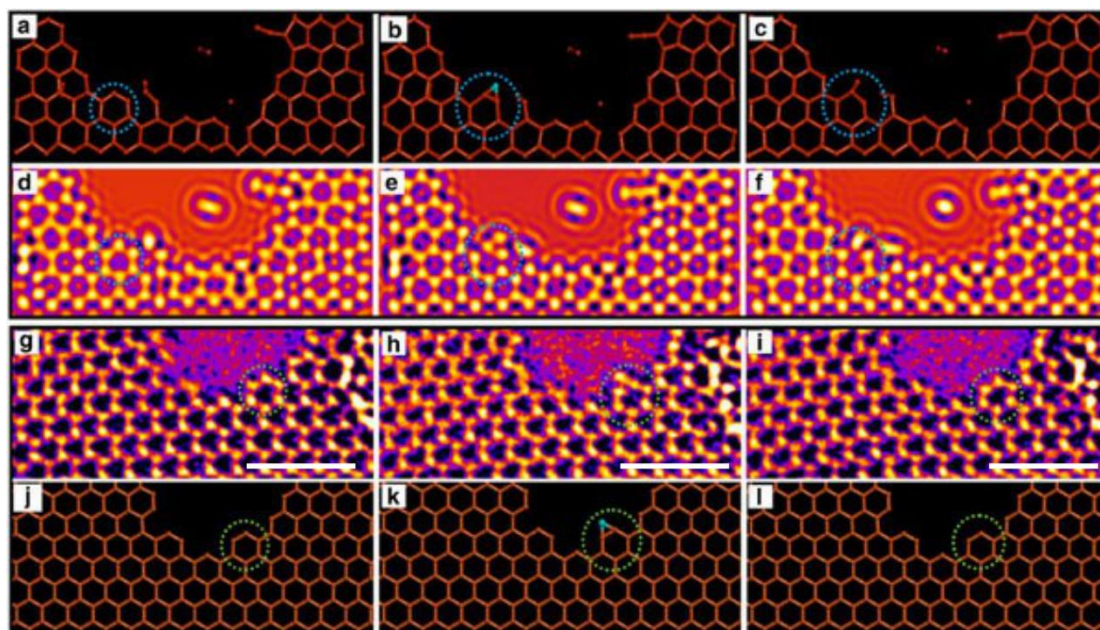


Figure 4-7. Time-dependent functionalisation of graphene edges. (a) and (c) are the frames seen in the molecular dynamic simulation, before and after the occurrence of the triangle edge structure that can be seen in (b). (d–f) are multi-slice image simulations based on the atomic models in (a–c) respectively. (g–i) are three consecutive TEM images (20 s between each image) showing the occurrence of the triangle edge structure. (j–l) are atomic models based on the respective TEM images above. Scale bar = 1 nm

Figure 4-8 shows the multi-slice image simulations of a DFT relaxed atomistic model, seen in Figure 4-8 (a), under different defocus spread values while keeping other parameters constant. The defocus spread value changes from 3, 5, 7, to 9 nm progressively. The value of 3nm is equal to the microscope setting when the monochromator is turned on and a value of 9nm is similar to the normal aberration corrected conditions. The values of 5nm and 7nm represent the evolution of the image

simulation in regard to the change of defocus spread. With a value of 3nm setting, as can be seen from Figure 4-8 (b,f), all the atoms could be fully resolved including the extra atom on top of the hexagon which makes up the triangle structure. With a value of 9nm, as shown in Figure 4-8 (e,i), the resolution has degraded comparing to the monochromated image, thus the triangle-hexagon structure might appear like a five-membered ring with the outer-most atom appearing brighter than the rest. This effect will cause difficulties when attempting to resolve this triangle structure under this microscope setting. Most studies that have characterised graphene using AC-HRTEM have had a resolution similar to that shown in Figure 4-8 (e), which is a typical resolution, and therefore is difficult to resolve the triangle structure. According to the above evidence, this novel structure could occur more often than we may think. However, this conclusion is subject to further studies using monochromated AC-HRTEM.

Figure 4-9 shows a time-series of AC-TEM images from Figure 4-7 (g–i) in greater detail, along with their bond length measurements. The triangle–hexagon structure could be interpreted as an armchair edge structure being functionalised with an extra atom. Figure 4-9 (a–c) show three frames for (a) before, (b) functionalised, and (c) after the attachment of the single atom. Box line profiles were taken from the black rectangle area marked in Figure 4-9 (a–c), and are shown in Figure 4-9 (d–f). The three measured bond lengths reveal a change, with the addition of an extra atom. The bond length increased from its contracted value of 1.31 Å (Figure 4-9 (a,d)) to an expanded value of 1.51 Å when the edge was functionalised with a single atom (Figure 4-9 (b,e)), then returned to its original contracted length when the extra atom was detached (Figure 4-9 (c,f)). These results confirm that I am able to detect variations in the distance between

the same two carbon atoms in real-time and demonstrate that local bonding variations at the edge are disturbed by atomic functionalisation.

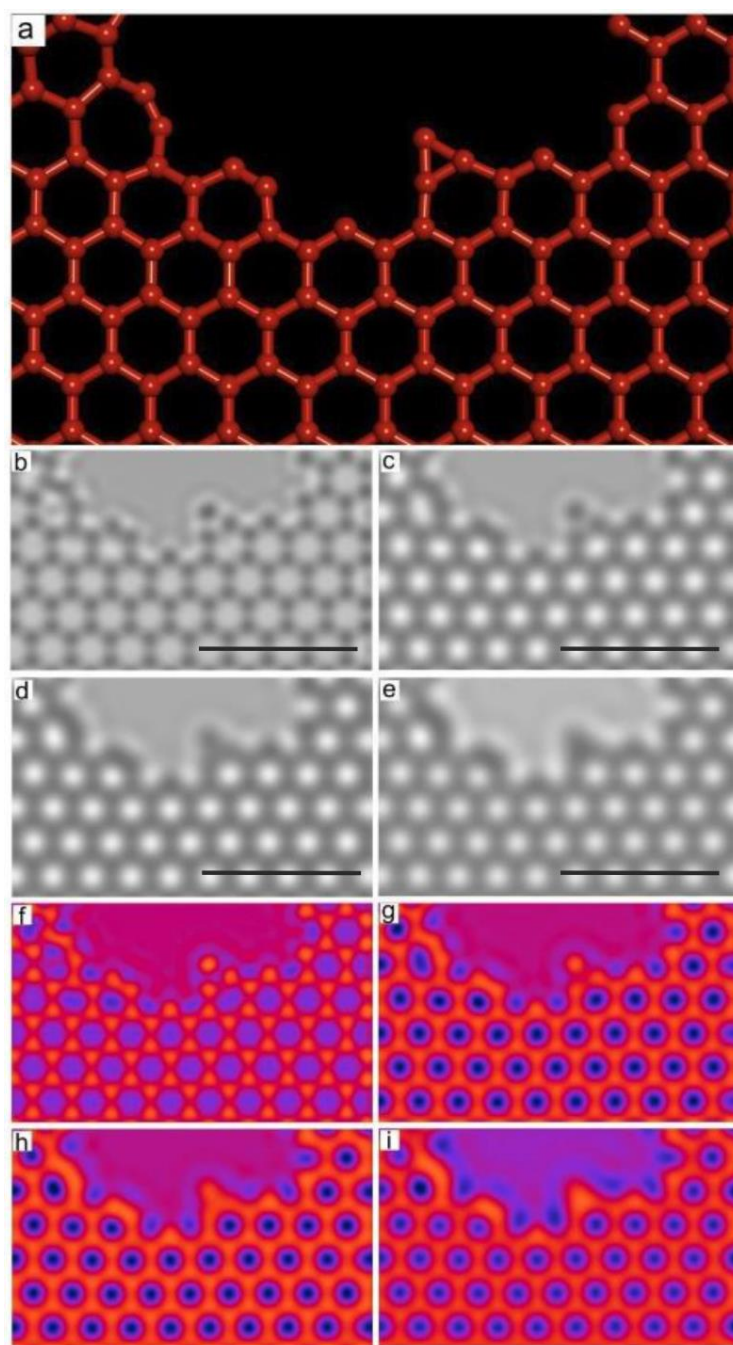


Figure 4-8. (a) DFT-relaxed graphene edge structure, including the triangle structure. (b–e) Multi-slice image simulation of the atomistic structure shown in panel (a) with defocus spread values of (b) 3nm, (c) 5nm, (d) 7nm, and (e) 9nm respectively. (f)–(i) Lookup table colour coded images of (b–e). Scale bar = 1 nm

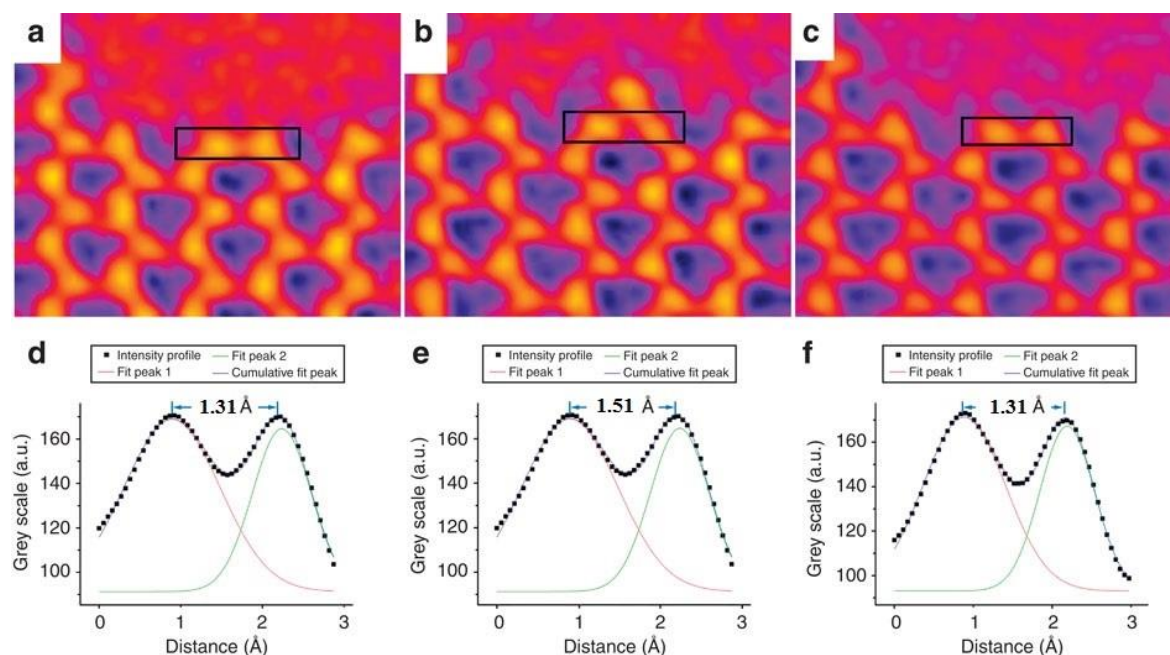


Figure 4-9. Triangle structure analysis. (a–c) Smoothed and false coloured AC-TEM image sequence depicting the occurrence of the triangle structure (20 s between images, 2 s acquisition time). (d–f) Boxed line profiles from the regions marked in (a–c), with fitted Gaussian profiles for bond length measurements. The bond lengths of the frames before, at the time of, and after the occurrence of the triangle are marked above the curves.

4.5 Discussion

TEM can reveal the location of atoms with the lattice structure of graphene, which in turn can be used to determine the distance between atoms and the C–C bond lengths in graphene. Bond lengths in graphene are dependent upon the electronic charge density within the C–C bonds and therefore large changes in the charge density within graphene C–C bonds can lead to changes in the position of atoms that can be detected using AC-TEM with high spatial resolution. I use this property to show that hydrogen is not attached to the outermost bond of the armchair edge, indicating the formation of a triple bond, rather than the saturation of free edge states by hydrogen passivation. This was further confirmed by real-time tracking of the bond lengths, where elongation occurred

from functionalisation by an additional atom to form a triangular edge state, followed by the contraction of the same C–C bond when the additional carbon was removed. These observations provide strong evidence that the edges of graphene are not always hydrogenated, which is important information for the design of future graphene electronic devices.

4.6 Conclusion

Graphene edges and their functionalisation influence the electronic and magnetic properties of graphene nanoribbons. Theoretical calculations predict that saturating graphene edges with hydrogen lowers their energy and form a more stable structure. Despite the importance of this subject, there have been only limited experimental investigations of whether graphene edges are always hydrogen-terminated. Here I have studied graphene edges produced by sputtering in vacuum; direct measurements of the C–C bond lengths at the edge show ~86% contraction relative to the bulk. DFT reveals the contraction is attributed to the formation of a triple bond and the absence of hydrogen functionalisation. Time-dependent images reveal temporary attachment of a single atom to the armchair C–C bond in a triangular configuration, causing expansion of the bond length, which then returns to the contracted value once the extra atom moves on and the armchair edge is restored. Our results provide confirmation that non-functionalised graphene edges can exist in vacuum.

4.7 References

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Chapter 5

Extended Klein (EK) Edges in Graphene

5.1 Introduction

The properties of graphene, especially nanoribbons, are influenced by the edge's atomic structure.^{1–9} So far, three classifications of periodic graphene edge terminations have been experimentally confirmed: the zig-zag, reconstructed zig-zag (rec5–7), and armchair edges.^{10–19} However, a fourth type of periodic edge structure has been theoretically predicted, consisting of an array of single carbon atoms extending from a zig-zag edge, which can be described as an EK edge.^{20,21} This has never been experimentally observed or verified beyond the single Klein edge level. It has been assumed that arrays of dangling carbon atoms at the edges of graphene would be unstable, limiting previous studies to artificial “photonic graphene”.²² To experimentally confirm the predicted EK edge with convincing evidence, it is important to directly image the atomic structure.

AC-TEM has again proven to be an excellent method for studying the dynamics of the atomic structure of graphene.^{23,24} Using low accelerating voltages (80 kV and below) in AC-TEM has permitted the study of defects, dopants, edges and layer stacking sequences at the atomic level.^{15,25,26} Studies of graphene edges show that zig-zag, armchair, and rec5–7 form long-range periodic terminations,^{14,16} while at the shorter scale, other unusual structures can form, such as carbon chains and the single atom Klein edge.^{11,27} Real-time AC-TEM image sequences of graphene edges have shown

interesting atomic scale dynamics, such as migration of C atoms along the edges, single atom sputtering from graphene edges, bond rotations, and the rapid switching from zig-zag edges to rec5–7 edges.¹³ Scanning AC-TEM (AC-STEM) combined with atomic resolution EELS has confirmed that energy states of carbon atoms at the edge of graphene are different to those in bulk graphene.^{11,28}

5.2 Nanoribbon and EK edge fabrication

In our experiment, nanoribbons in graphene were fabricated *in situ* in a TEM. As schematically illustrated in Figure 5-1 (a-d), a pristine area of graphene was initially located, and a focussed probe with a high current density ($\sim 10^8 \text{ e}^{-1}\text{nm}^{-2}\text{s}^{-1}$) was used to form the first hole, and then sputter a second hole in the vicinity of the first hole (Figure 5-1 (a,b)). The beam was then allowed to spread, with a typical beam current density of $\sim 10^5 \text{ e}^{-1}\text{nm}^{-2}\text{s}^{-1}$: this allowed the carbon atoms on the edge of the two holes to be slowly sputtered by the electron beam flux (Figure 5-1 (c,d)). The desired width of GNR could be fabricated by exposing the nanoribbon to an electron beam for different lengths of time. A typical experimental result from a hole making process is shown in Figure 5-1 (e).

Multiple sets of results were obtained by using the above-mentioned GNR fabrication method. Among the results, there was a set of time series AC-TEM images that demonstrated a previously unreported peculiar edge structure on a nanoribbon. The unprocessed AC-TEM frames are shown in Figure 5-2: panel (b) shows the regular periodic ordering of EK edges on both side of the ribbon. One single occurrence of Klein edges has been reported before, but this was considered to be unstable under the electron beam irradiation and was treated to be a rare observation of a rare phenomenon.^{11,12} The unprocessed images are shown in this occasion, as these images

were later subjected to multiple steps of image processing to enhance what was quite a weak level of contrast, especially on EK edges, to allow a more direct observation by the naked eye and also to ensure no artefacts were caused by the image processing.

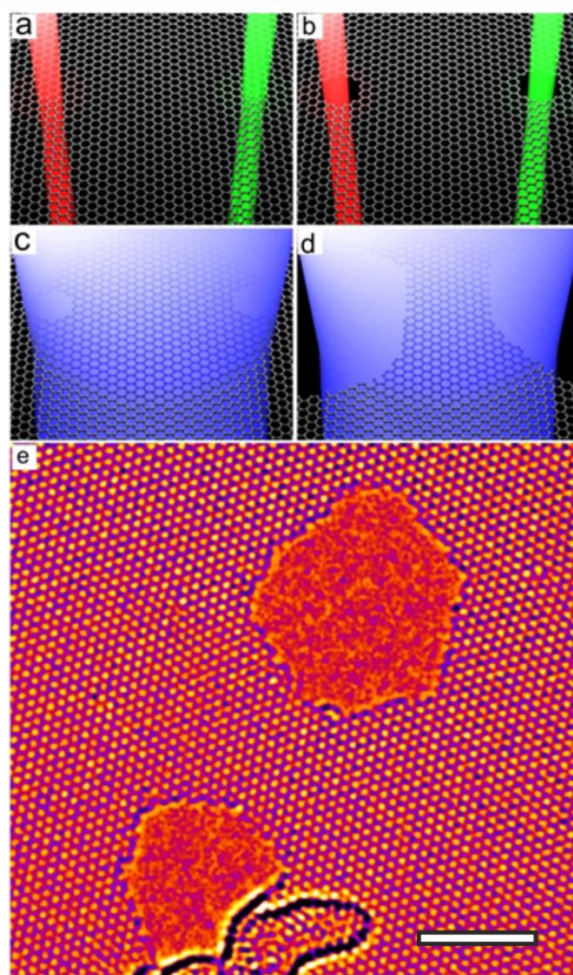


Figure 5-1. TEM *in situ* nanoribbon fabrication. (a – d) Schematic illustration of the fabrication process. (a) A focused electron beam has been applied sequentially to two different regions on a pristine graphene sheet: two small holes are formed after five minutes, as shown in (b). The electron beam was then spread, so as to expose a larger area and allow edge atoms to be ejected. As a consequence, the size of the holes increased and the nanoribbon formed between the two holes as they narrowed down to a thinner strip, as shown in (d). (e) Experimental AC-TEM image obtained from the above-mentioned process. Scale bar = 2 nm

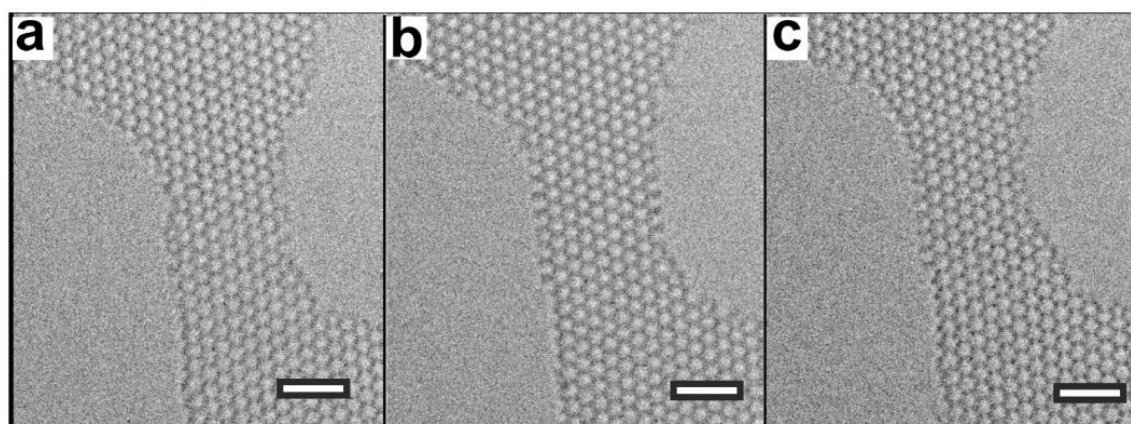


Figure 5-2. Time series of unprocessed TEM images of EK edges occurrence on a GNR; each frame is 10s apart at 3s exposure time. The EK edge is seen on both side of the ribbon in (b). Scale bars = 1nm.

5.3 Dynamics of EK edges

The dynamics of EK edges were then further analysed. The GNR runs parallel to the zig-zag lattice direction shown in Figure 5-3 (a): the edges generally appear in zig-zag form, with distortions from pentagons, heptagons and the occasional single Klein edge atom. Seconds later (Figure 5-3 (d)), the edge has transformed to form EK edges on both sides of the GNR. This double GNR EK edge was stable for 2 s during image acquisition before undergoing further structural transformations (Figure 5-3 (g)). The structural transformations, Figure 5-3 (c,f), occur through a combination of atom loss, bond breakage and reformation, and Stone–Wales bond rotation.²⁹ To my knowledge, this is the first experimental observation of an EK edge in graphene as well as a double-sided EK edge structure in a GNR. Prior work on imaging EK edge structures has been limited to two to three atom sequences.^{11,12}

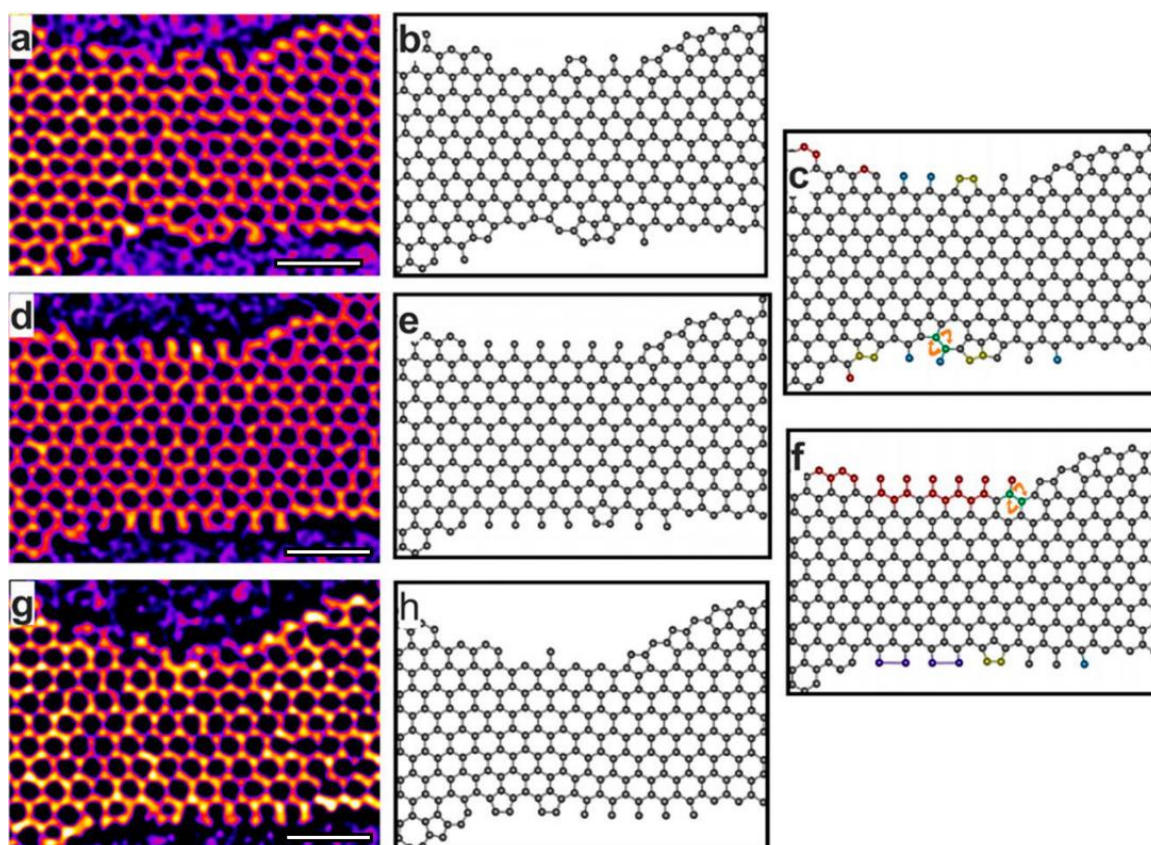


Figure 5-3. Dynamics of EK edges in a GNR. (a, d, and g) Three consecutive AC-TEM frames showing the appearance of double-sided multiple Klein edges and the frames prior to and after this appearance. The raw AC-TEM images are shown in Figure 5-2 and the image processing techniques are shown in the methodology chapter (Chapter 3). (b, e, and h) are the three corresponding atomistic models of (a, d, g). Panels c and f depict the transition from (b) to (e) and (e) to (h), respectively. The atoms on the edge are highlighted using different colours, to make clear the transition different atoms underwent: red indicates atom loss, blue indicates atom addition, green indicates near edge Stone-Wales rotation, the arrows around the green atoms indicate the direction of Stone-Wales rotation, and yellow indicates bond breakage and purple indicates bond reconstruction. Scale bars = 1 nm.

A double EK edge in a GNR can have EK edges on either side, either symmetrically or offset by one atomic row (Figure 5-5). A detailed analysis of the double EK edge

structure shown in Figure 5-3 (e) and Figure 5-4 (a,b) show a symmetric EK edge for the GNR. After the GNR undergoes structural transformation, as shown in Figure 5-3 (g), a row of EK edge atoms is lost and this results in the breaking of the symmetry and the resultant offset between the top and bottom EK edges, shown in Figure 5-4 (c,d). Occasionally, pairs of atoms within an EK edge rebond to form five-membered rings at the edge, Figure 5-4 (e–h). The reverse process also occurs, where the bond breaks between the two outermost atoms in a five-membered ring at the edge to form two single Klein edges. The reconstruction and dereconstruction of bonding took place over the time period of 1 frame (~ 15 s), and was driven by energy supplied from the electron beam. These sequences not only demonstrate the dynamic loss and addition of atoms at the edges, but also the occurrence of frequent bond breakage and reconstruction. Careful examination of the two sides of the EK edge in the GNR shown in Figure 5-3 (d) and Figure 5-4 (m,n) reveals that some atoms along the EK edge deviate in angle from the 120° sp^2 bonding. We carried out a DFT study to further investigate the nature of bond bending.

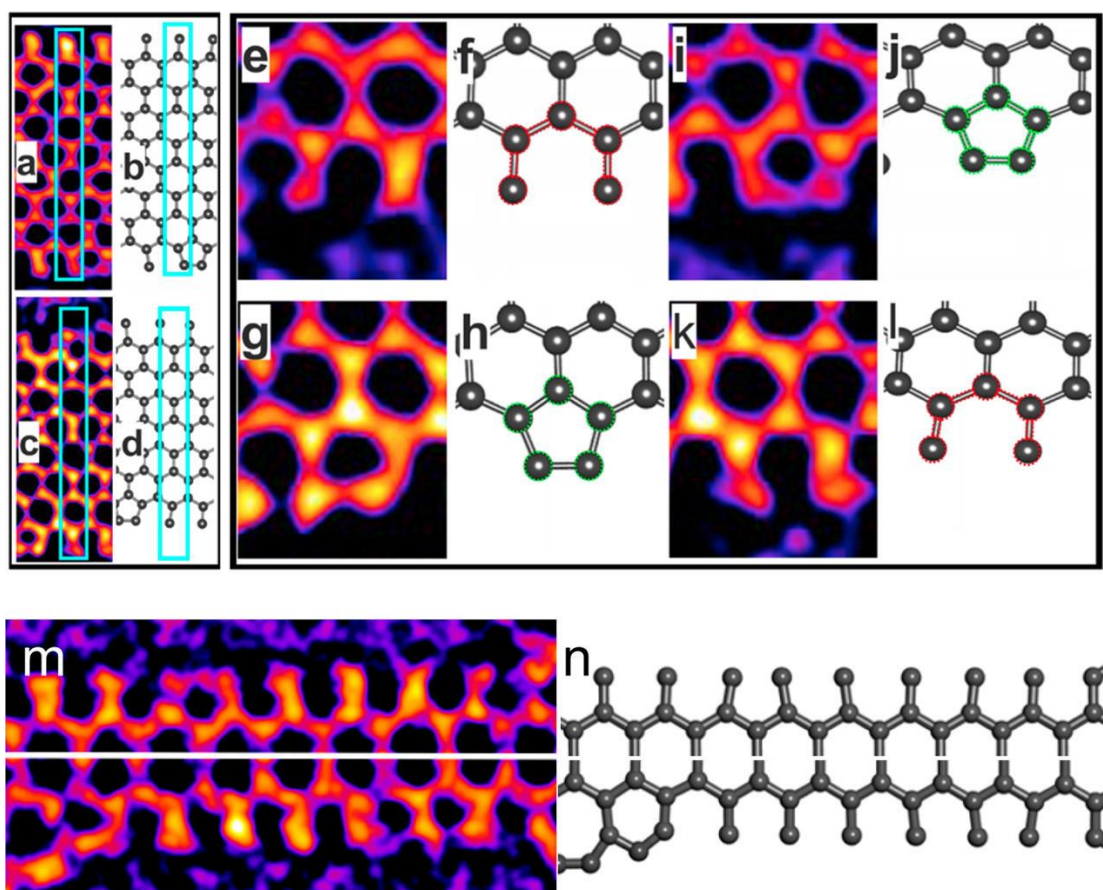


Figure 5-4. Detailed analysis of EK edge symmetry in a GNR. (a and b) AC-TEM and atomistic model of a symmetric EK edge. (c and d) AC-TEM and atomistic model of an offset EK edge. Panels e–h illustrate the mechanism of the reconstruction of multiple Klein edges; panels e and f show the AC-TEM image and atomistic model of multiple Klein edges in their unreconstructed states; and panels g and h illustrate the reconstructed structure. Panels i–l demonstrate the de-reconstructing procedure, with (i) and (j) being the initial structure, and (k) and (l) being the subsequent structure. (m) AC-TEM image of the two sides of the EK GNR with corresponding atomic models in (n).

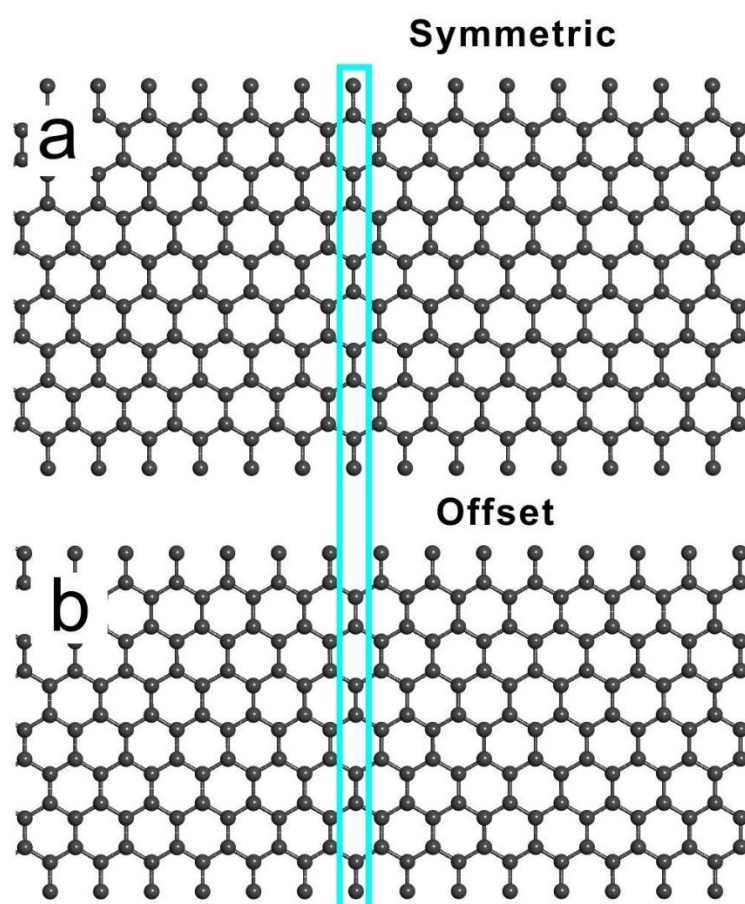


Figure 5-5. EK edges on two side of the GNR. (a) The atomistic structure of periodic EK edges on two sides of the nanoribbon show symmetric behaviour. (b) The atomistic structure of periodicity of EK edge on the top row is offset by one atomic row compare to the bottom row.

5.4 DFT calculations of EK edges

To understand the reconstruction processes of the EK edges, we carried out a DFT calculation in respect of both symmetric and offset EK edges. The basis set contained plane waves up to an energy cut-off of 400 eV. The supercells in our simulations contained 252 atoms for the symmetric EK edge GNR, and 280 atoms for the offset EK edge GNR, and 20 atoms for the calculation of the bending edges shown in Figure 5-9 (a,e,i). In constructing the super cell for simulation, we contained a vacuum region

of 30 Å in the y and z direction. The Brillouin zone was sampled using a $(2 \times 2 \times 1)$ Γ -centred mesh for the symmetric and offset EK edge GNR and a $(12 \times 2 \times 1)$ Γ -centred mesh for the calculation of the bending edges. In the structural relaxations, the structures were fully relaxed until the force was smaller than 0.02 eV/Å, except in the case of the calculation of bending edges, in which the structures were relaxed under the constraints keeping the bending. In Figure 5-6 (a), two single Klein edges are initially bonded to form a five-membered ring (pentagon) on both sides of a symmetric EK edge; Figure 5-6 (b) shows the AC-TEM image simulation. When the structure is relaxed by DFT calculation, a majority of the EK edges also reconstruct to form pentagonal edge terminations, Figure 5-6 (c) – with the image simulation in Figure 5-6 (d). Not all the Klein edges have reconstructed: the green dashed circle in Figure 5-6 (c) shows a single Klein edge remaining, but with deviation from a pristine perpendicular orientation. We have observed several cases in our experimental AC-TEM images where single Klein edges next to pentagonal edge terminations have non-perpendicular orientation; an example is shown in Figure 5-6 (e,f). The structural relaxations for the offset EK edges in a GNR are shown in Figure 5-6 (g–j). The major difference observed compared to the symmetric EK edges is that a double pentagon edge termination arises, Figure 5-6 (i,j). We have also experimentally observed this double pentagon structure, shown in Figure 5-6 (k,l).

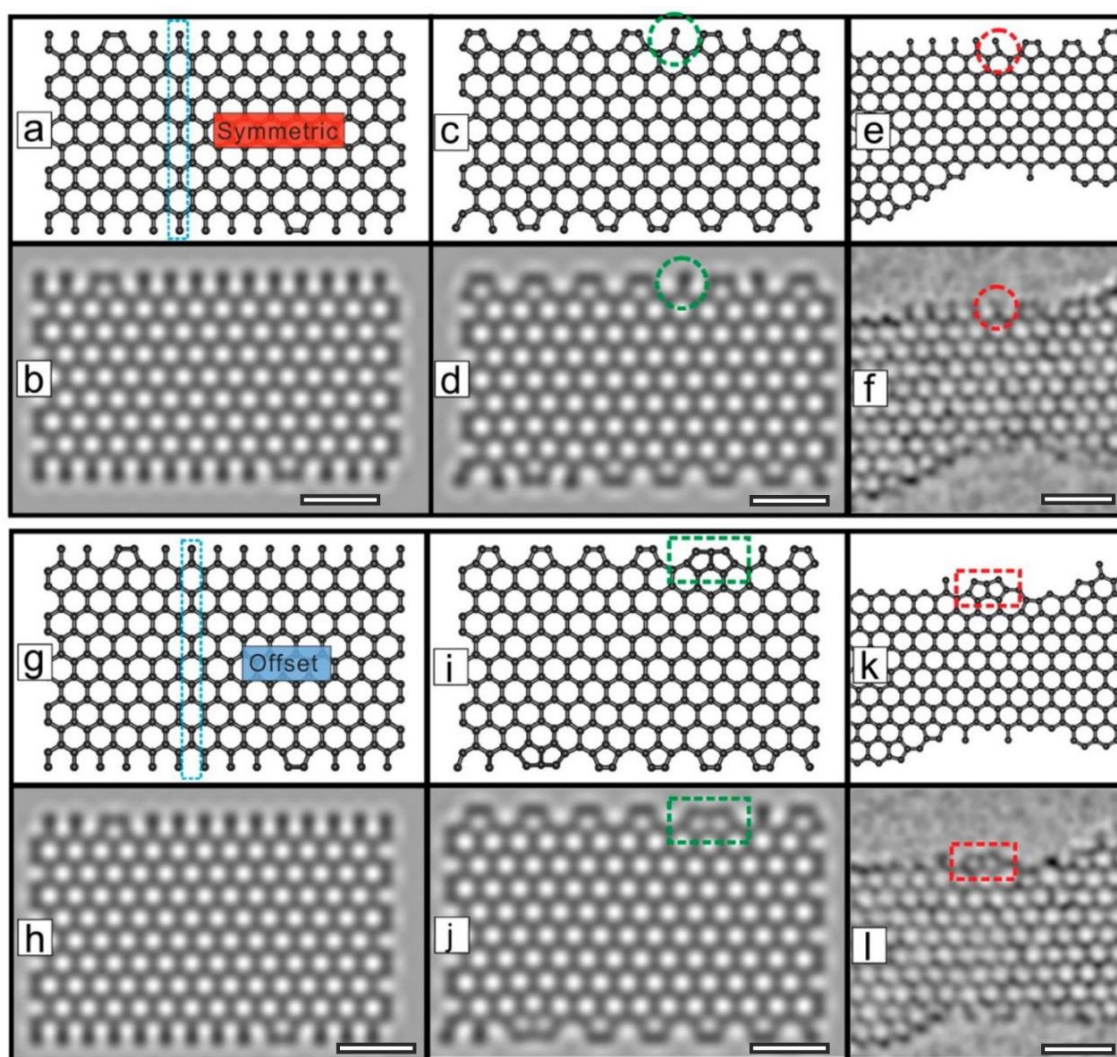


Figure 5-6. (a and c) Atomistic models of the initial and fully relaxed structures in a DFT calculation of symmetric EK edges on a GNR. (b and d) The multi-slice image simulations of the structures, respectively. TEM image shown in (f) and its model (e) illustrate the same reconstruction and Klein edge bending effect as observed in the DFT calculation. (g–l) The same analysis applied to an offset EK edge on a GNR. Scale bars = 1nm

The details of the EK edges can be further analysed by measuring changes to the bond lengths both within the ribbon and on the EK edges. In the AC-TEM image of Figure 5-7 (b), the C–C bond lengths were determined by fitting double Gaussian peaks to the intensity profiles for each pair of atoms forming a bond. A typical box profile is taken

from the yellow boxed region of Figure 5-7 (b) and is shown in Figure 5-7 (c). The distribution of bond lengths within the ribbon (marked by the red box in Figure 5-7 (b)) and on the Klein edges (marked by blue boxes) are shown in Figure 5-7, panels d and e, respectively. The distributions were then fitted with a normal distribution equation, the peak position of the “within ribbon” bond lengths was set to 1.42 Å, and as a result, the peak position of the “Klein edges” bond lengths was measured at 1.24 Å. These values represent the average C–C bond lengths within these regions.

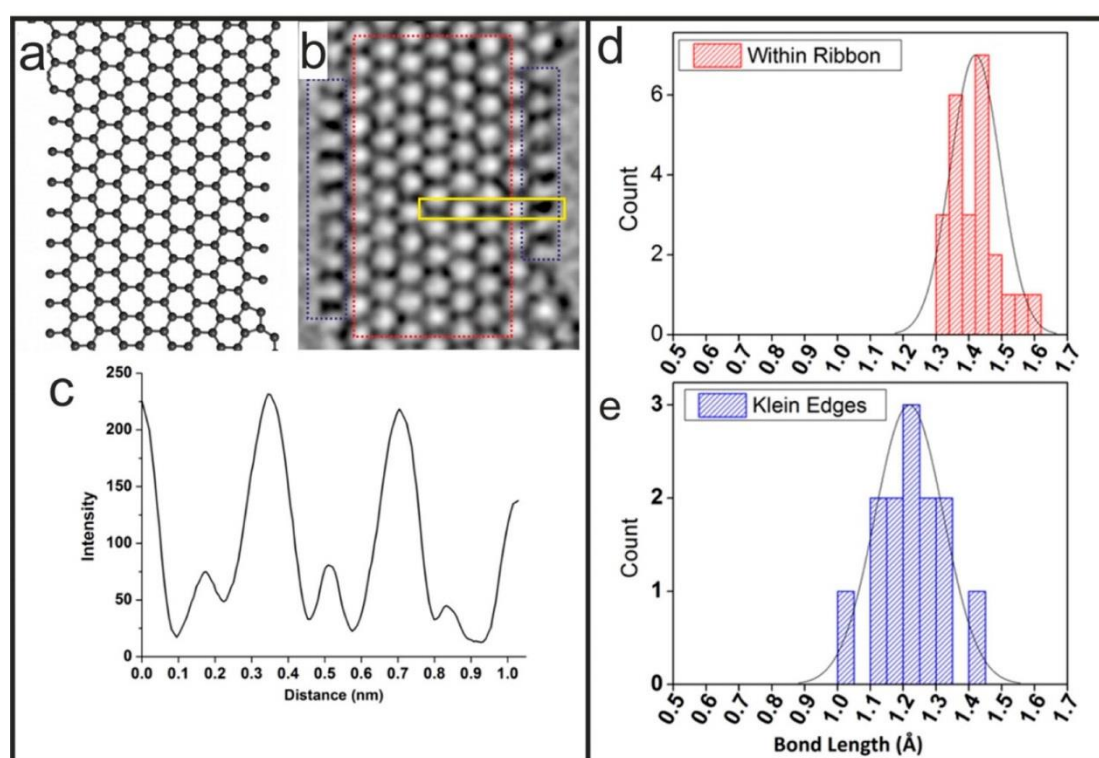


Figure 5-7. EK edge bond length analysis. (a) Atomistic model corresponding to the structure imaged in (b). (b) AC-TEM image of a double EK edge GNR. (c) A typical intensity vs. distance profile taken from the yellow box region in (b). (d) Histogram of the bond length distribution within the GNR as indicated by the red box in (b). (e) Histogram of the bond length distribution of the Klein edges, taken within the region of the blue box in (b).

We have also employed DFT to relax pristine and hydrogenated EK edge structures, as shown in Figure 5-8. The calculated bond lengths of non-functionalised EK edges and hydrogen functionalised EK edges are 1.38 and 1.36 Å, respectively. The average experimentally observed bond length for EK edges is 1.24 Å as shown in Figure 5-7 (e). This bond length value is significantly shorter than both pristine and hydrogenated EK edges. To understand this difference we have examined the possibility of out-of-plane distortions for the EK edges arising from bending of the GNRs. Each repeating unit was bent out of plane to different angles, and then relaxed by DFT. This unit structure was then laterally extended to form a nanoribbon structure, to simulate the bent EK edge scenario. As shown in Figure 5-9, three different amounts of bending distortion are explored: 16 °, 21 °, and 25 °.

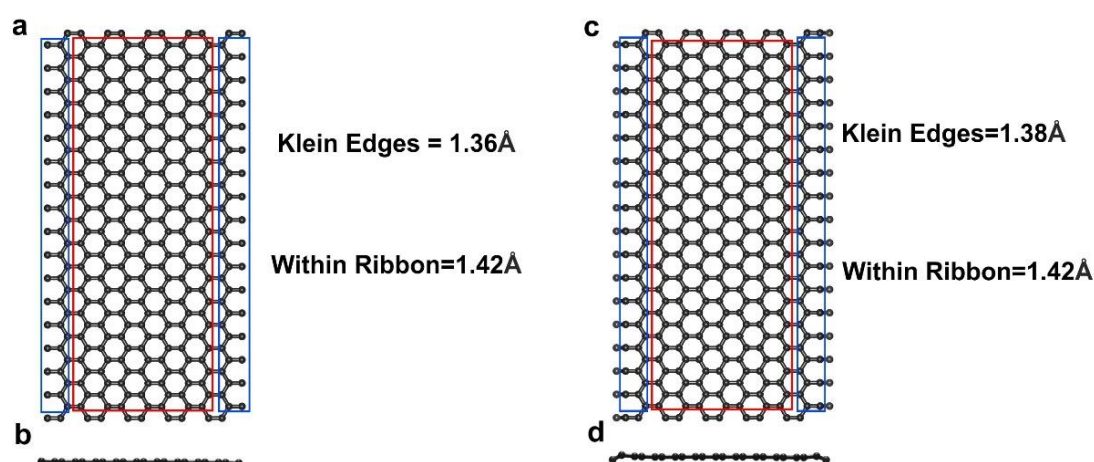


Figure 5-8. DFT calculation of pristine and hydrogenated EK edges. (a) and (b) are the front and side view of the pristine EK edge graphene ribbon, (c) and (d) are the same views for hydrogenated EK edges. The blue rectangles indicate the Klein edges region and the red boxes indicate the within the ribbon region.

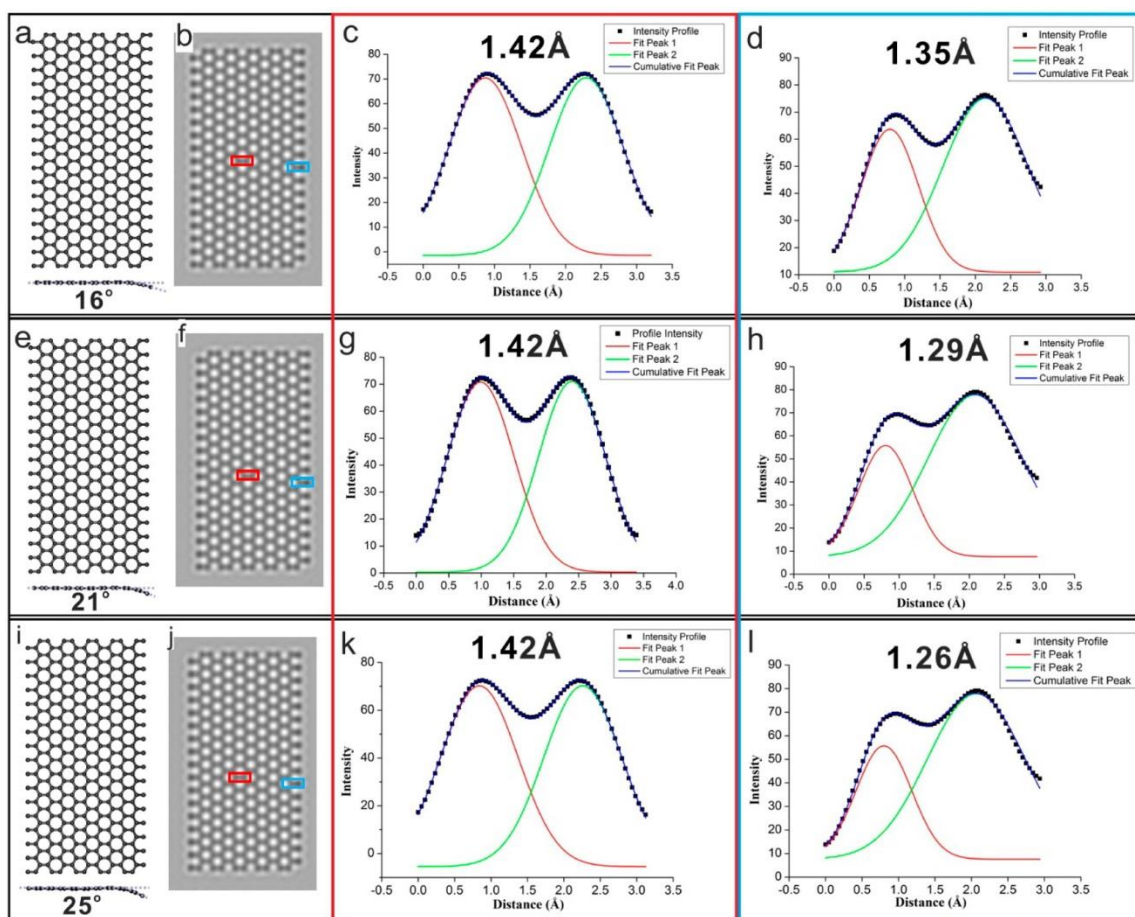


Figure 5-9. DFT calculations of bent EK edges. One side of the GNR with an EK edge is bent 16° out of plane as shown in the front and side view of the atomic model in (a), with its multislice image simulation shown in (b). The box profiles taken from the red and blue boxed region of (b) are shown in (c) and (d), respectively; the intensity profiles are fitted by two Gaussian curves to measure the bond length. (e–h) and (i–l) show the same analysis applied to 21° and 25° bent nanoribbon structures.

The intensity profiles in the centre of the ribbon (the red rectangle regions in Figure 5-9 (b,f,j)) are fitted with two Gaussian curves and the separation between the two peak positions is set to $1.42 \text{ \AA}$ from the simulated atomic model. The intensity profiles taken from the blue rectangle region of Figure 5-9 (b,f,j) are fitted by two Gaussian curves as well, to determine the bond length of the EK edges by measuring the peak separation. The results are shown in Figure 5-9 (d,h,l). The bond lengths measured from the

simulated HRTEM images are 1.35, 1.29, and 1.26 Å for the 16°, 21°, and 25° bent structures. The energy of the repeating unit for the structures in Figure 5-9 (a,e,i) is only 0.19, 0.39, and 0.53 eV higher than the pristine edge in the in-plane model shown in Figure 5-8 (a): well below the maximum energy that can be transferred by an 80 keV electron to a carbon atom.³⁰ It is therefore plausible to suggest that some EK edges might have suffered different degrees of bending to allow the bond length to appear shorter in the TEM image compared to its intrinsic bond length.

5.5 EK edges on the bulk of graphene

We also observed EK structures at the edges of bulk graphene, Figure 5-10. Time dependent imaging, Figure 5-10 (a,d,g,j), shows a section of an atomically defined zig-zag edge losing six of the outermost atoms, Figure 5-10 (c), resulting in the formation of the EK edge, Figure 5-10 (d). Further atoms are then sputtered, Figure 5-10 (d–k), leading to the reformation of the zig-zag edge. This sequence of images provide insights into the process of electron beam sputtering for zig-zag edges, whereby the edge can alternate between zig-zag and EK, as carbon atoms are sequentially lost. The process of the transition between these stable zig-zag or EK configurations involves bond breakage, atom loss, and bond reformation, as in the case of the GNR in Figure 5-3. We have also observed EK edges deviating from pure linear edge form, and extending throughout a change in the direction of the lattice, Figure 5-10 (i). A total of 10 individual Klein atoms are identified in this case, as it curves around the edge to follow the profile of the structure.

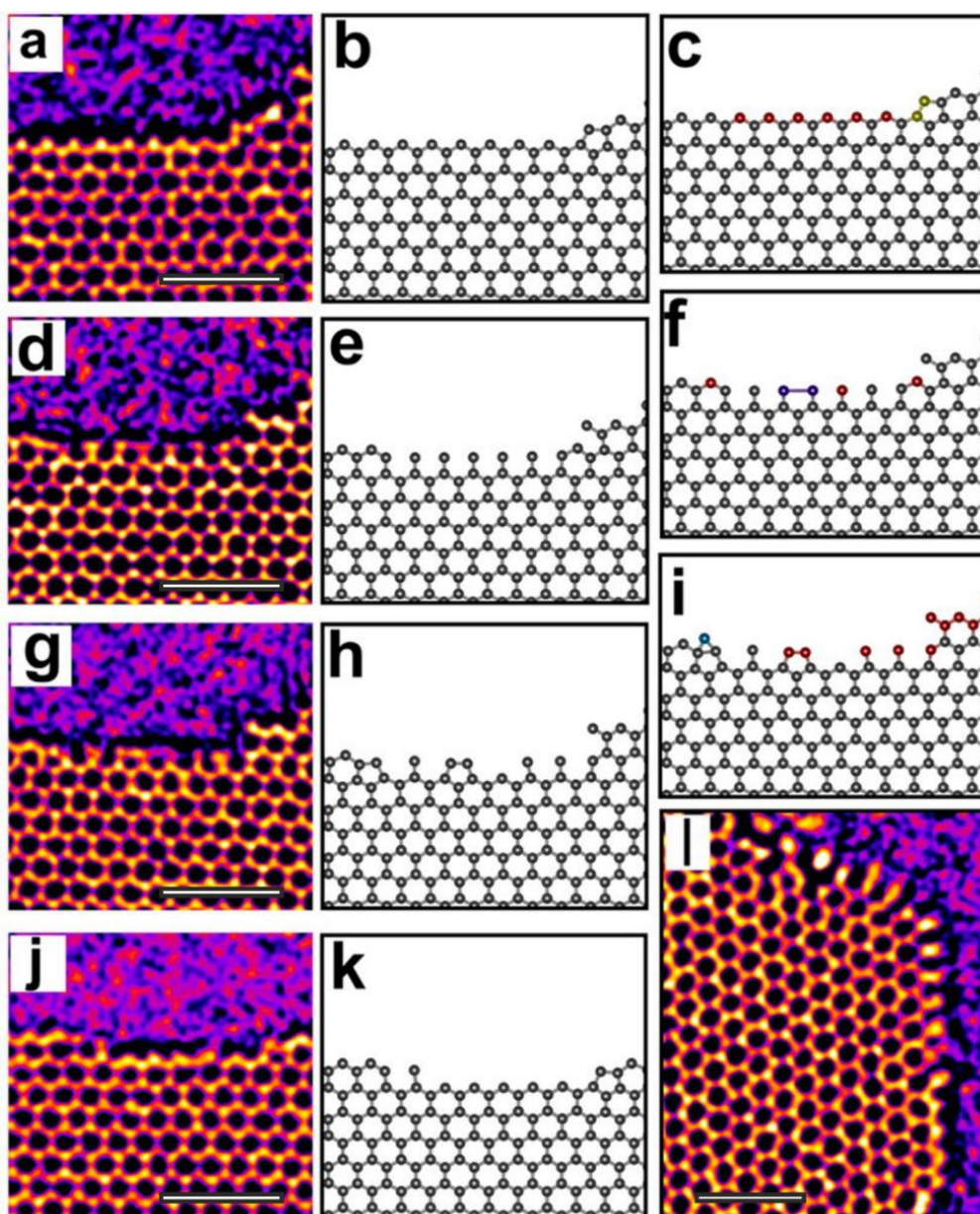


Figure 5-10. (a, d, g, and j) Formation of EK edges from zig-zag edges in graphene. Four consecutive TEM frame of the appearance and transformation of multiple Klein edges on the edge of bulk graphene. (b, e, h, k) The atomistic model, showing the crystal structure of the TEM image on its left-hand side. (c, f, and i) Atomistic model with edge atoms marked by different colours to illustrate the different transformation those edge atoms underwent: red indicates atom loss, blue indicates atom addition, yellow indicates bond breakage, and purple indicates bond reconstruction. (l) Observation of extra-long EK edge over a curved edge. Scale bars = 1 nm

Edges of graphene observed during AC-TEM are those which are stable when subjected to electron beam irradiation, and do not necessarily represent the thermodynamic stability order. Recent DFT calculations have explored the displacement thresholds for nearly all known graphene edge types.³¹ Armchair edges were calculated to have the highest displacement threshold, meaning they are the most radiation-stable edges, and this explains why they are the most abundant edge type observed in graphene.³¹ Surprisingly, the DFT calculations showed that Klein edges have a higher displacement threshold and consequently higher radiation stability, than zig-zag edges.³¹ The low radiation stability of zig-zag edges is related to the limited flexibility of its edge atoms. Given the theoretical calculations in ref .[31], it is not unexpected to see highly stable EK edges in graphene, and I believe that the reason many of these structures were not previously observed is due to the challenge of distinguishing them from zig-zag edges.

5.6 Non-monochromated AC-TEM images of EK edges

By going through my extensive data base of AC-TEM images, careful examination reveals that EK edges exist with a much higher frequency than their thermodynamic stability suggests. As shown in Figure 5-11, five examples of EK edges were identified after being subjected to image processing. The only image processing techniques applied were a band-pass filter from 100 pixels to 1 pixel and Gaussian smoothing with a 5.0 pixel radius. No reconstruction from manually selected masked FFT was applied, to minimise the effect image processing would have. After image processing the EK edges become immediately evident, confirming the earlier suggestion that the reason why they are less observed than may be expected is due to the difficulty in distinguishing between EK and zig-zag edges.

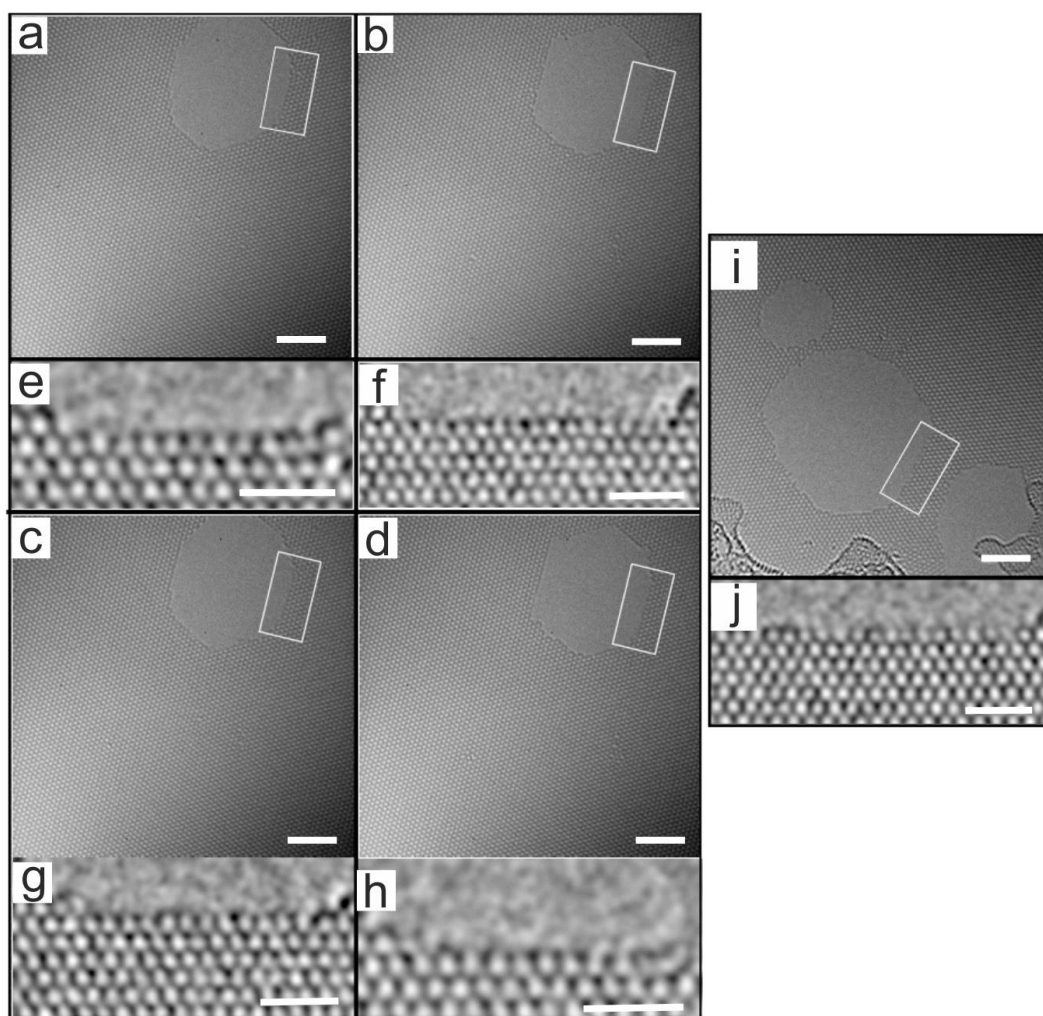


Figure 5-11. Non-monochromated AC-TEM images containing EK edges. (a, b, c, d) are four AC-TEM frames of one series, the EK edges are displayed in panels (e, f, g, h). Another EK edge was found in panel (i) and is shown in (j). The scale bars of (a,b,c,d,i) is 2 nm, and the scale bars of (e,f,g,h,j) is 1 nm.

5.7 Conclusion

My success has been helped by improvements in the spatial resolution of our AC-TEM by monochromation of the electron source to reduce the effects of chromatic aberration.²² The EK edges are difficult to identify when the spatial resolution is not improved by addressing detrimental chromatic aberration effects. Extra AC-TEM images taken without monochromation of the electron source demonstrate that EK

edges are not as easy to identify in non-monochromated AC-TEM images. The EK edges form as part of the sputtering process of zig-zag edges and remain for several seconds, before being further sputtered back to zig-zag form. Not only have we verified the existence of a fourth periodic edge structure of graphene, but we have also confirmed that symmetric double EK edges can form on GNRs.

5.8 References

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Chapter 6

Cross-Over Temperature for the Reconstruction of Zig-Zag Edges in Graphene

6.1 Introduction

The structure of edges in graphene has a great influence on graphene's mesoscopic properties.^{1–7} Nano-constrained structures in graphene such as nanoribbons,^{8,9} quantum dots¹⁰ and nano-junctions,^{11–13} are largely influenced by the configurations of edges due to the high edge/bulk ratio. Experimental studies of graphene edges typically use either STM,^{9,14–17} AC-TEM^{18–21} or micro-Raman spectroscopy.^{22,23} Despite the abundant studies, and structural characterisation carried out on the geometry of edge structures, being able to control the edge termination freely still remains a challenging topic. Most top-down production techniques such as electron and photo- lithography, unzipping of carbon nanotubes and metal particle assisted etching result in defective graphene edges.^{8,24–27} Anisotropic etching of graphene with the assistance of metal nanoparticles and hydrogen at elevated temperatures has recently been reported to produce predominately zig-zag edges,^{28,29} but characterisation of these edges at the atomic scale is lacking. Whilst graphene edges might appear regular at the micrometre scale, often closer examination at the detailed atomic level reveals more complex edge terminations

that are not fully periodic.^{30,31} Tearing graphene has been shown to be one approach for achieving long periodic edge structures.³³

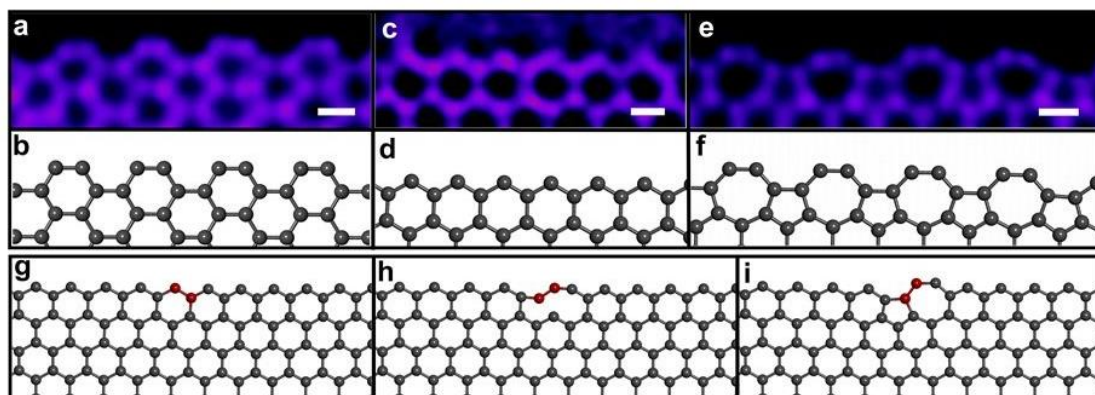


Figure 6-1. Three periodic edge terminations of graphene. (a) AC-STEM image of an armchair edge and (b) its atomic model. (c) AC-TEM image of a zig-zag edge and (d) its atomic model. (e) AC-STEM image of a Rec. 5-7 edge and (f) its atomic model. (g–i) Schematic illustration showing the reconstruction process from zig-zag to Rec. 5-7 edge: the atoms highlighted in red are the rotated atoms. All scale bars are 0.2nm.

The three main periodic edge terminations of graphene are presented in Figure 6-1. The armchair configuration shown in Figure 6-1 (a,b) and the zig-zag configuration shown in Figure 6-1 (c,d) have long been recognised as the intrinsic edges of graphene. Both types can also reconstruct into different geometries. For example, zig-zag edges are known to reconstruct into a pentagon–heptagon structure (namely Rec. 5-7 edges) through a series of bond rotations, as shown in Figure 6-1(e,f), to lower their energy.^{32,33} No atom loss is involved in this process, as can be seen from Figure 6-1(g–i): one C-C bond rotates 90° and rebonds to the nearest atom after rotation. This is similar to the Stone-Wales bond rotation in the bulk of graphene³⁴. Armchair edges have two reconstructed forms: a hexagon–heptagon–heptagon structure (namely ac(677)) and a pentagon–hexagon structure (namely ac(56)),³⁵ both of which have higher energy than

the original un-reconstructed form. For this reason, no long ordered structures of these configurations have been observed experimentally – they only appear as isolated incidents on an occasional basis.^{32,35}

Koskinen *et al.* studied the theoretical geometry and energy of graphene edges and predicted that armchair, zig-zag and Rec. 5-7 have edge energies of 2.09, 3.22, and 2.36 eV/atom, respectively.³⁵ A recent report has showed that under electron beam irradiation at an accelerating voltage of 300 kV and at high temperatures of 800 °C, armchair edges become the major edge termination of graphene.⁴⁰ A similar result was observed by Joule heating a graphene sample to even higher temperatures using an *in-situ* electrical holder inside an AC-TEM at a lower accelerating voltage of 80 kV.⁴¹ However, not much attention has been paid to the fine details of the temperature dependence of zig-zag edges: in particular, determining the cross-over temperature where the low-energy Rec. 5-7 edge dominates over the zig-zag edge. At room temperature zig-zag edges are far more prevalent than Rec. 5-7 edge when observed using AC-TEM. This has been attributed to their higher stability under electron beam irradiation.¹⁹ Even though the Rec. 5-7 edge has lower energy than the zig-zag edge, a small energy barrier must be overcome for this transition to occur, in the same way that a Stone-Wales bond rotation requires an energy barrier to be overcome. A single Stone-Wales rotation within a bulk graphene sheet has been estimated to have a formation energy of 5.08 eV, after overcoming the initial ~10 eV barrier³⁶. At the edge, this is reduced to ~1.1 eV because one of the atoms involved in the rotation is only bonded to two other atoms, therefore less bonds need to be broken.³³ At a certain temperature, the thermal energy provided to the system might be large enough to overcome this lower barrier of bond rotation at the edge and this would then result in the zig-zag edge flipping to its Rec. 5-7 form. DFTB calculations predicts that under 80 keV electron

beam sputtering, the armchair structure has the highest radiation stability, followed by Rec. 5-7 and zig-zag configuration.³⁷ Residual contamination, such as amorphous carbon or metal particles are known to remain on the surface of graphene from the synthesis and transfer process. Heating of the sample would dissipate the contamination and prevent the chemical etching effect under continuous electron beam irradiation and revealing the accurate graphene edge behaviour.

6.2 Exemplary edge behaviour at different temperatures

I have explored exemplary edge behaviour at different temperatures by adjusting the temperature of graphene in stages, from room temperature to 800 °C using an *in situ* heating holder within an AC- TEM. Atomic resolution images of the edges of holes in graphene enabled us to determine the statistical ratio of the three different edge terminations. The holes were intentionally created in graphene using a controlled focused electron beam sputtering method. This approach for hole creation is well established and has been previously reported.³⁸ I have allowed the holes to grow until they reached at least 15nm in size to ensure individual edge lengths around the hole were sufficiently long to have statistical meaning.

6.2.1 Typical edge behaviour at room temperature

Figure 6-2 shows the results at room temperature (~25 °C). Figure 6-2 (a–c) shows the three different representative holes, the edges being colour coded according to different edge terminations. The insets in Figure 6-2 (a,b) provide atomic models of the zig-zag and armchair edges observed in these regions. The room temperature statistics, Figure 6-2d, for all three time series for different holes show that ~45% are zig-zag, ~40% are armchair and ~10% are Rec. 5-7. I found that in general, the lengths of the armchair edges were shorter than the zig-zag edges at this temperature. Typical long ordered zig-

zag edges are shown in Figure 6-2 (e,f), respectively and a long ordered armchair edge in Figure 6-2 (g).

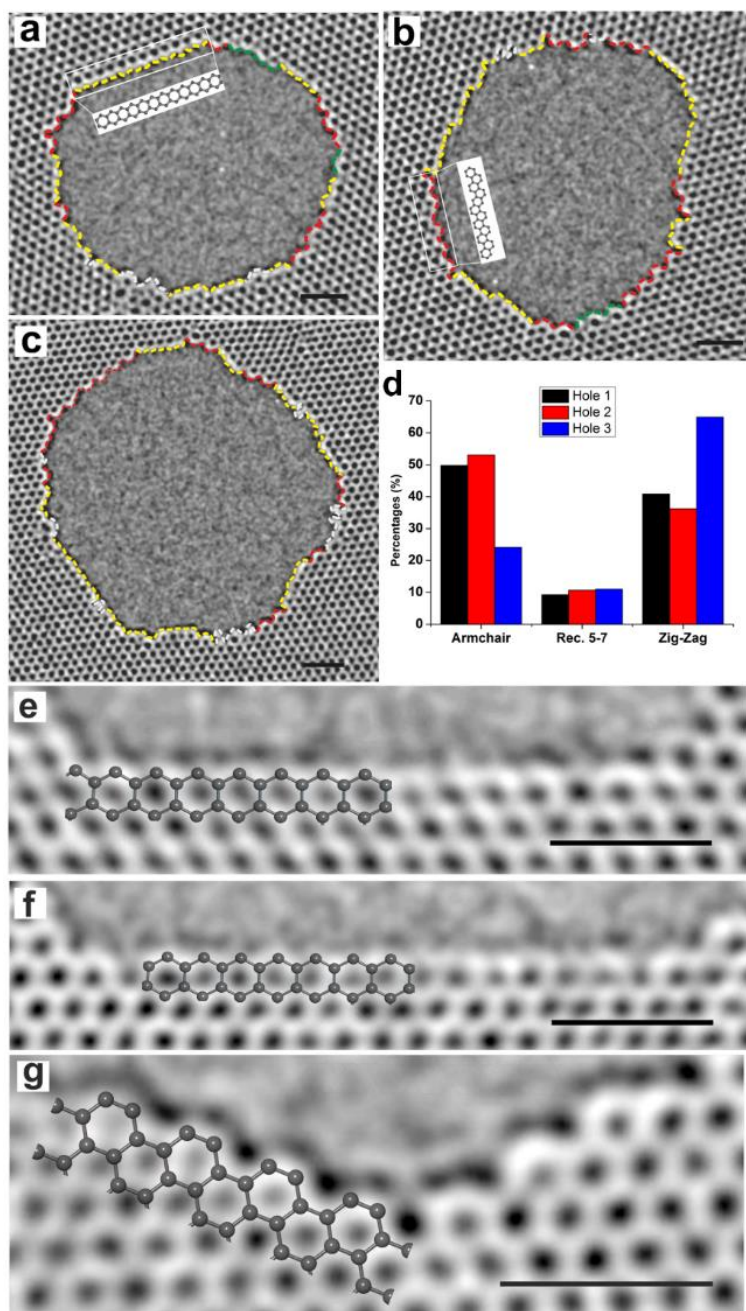


Figure 6-2. Edge behaviour at room temperature (~25°C). (a–c) show three typical HRTEM images of graphene holes at that temperature. The edges are colour coded to differentiate the types of edge configurations. Red represents armchair, yellow is zig-zag and green is reconstructed 5-7; white indicates mixed or unidentified edge types. The insets in (a) and (b)

show typical long order zig-zag and armchair configurations at this temperature. The statistics for three examples are shown in (d); the percentages of the edges occupied by different types of edges are ranked accordingly. Black columns represent panel (a), red columns panel (b) and blue columns panel (c). (e) and (f) are long ordered zig-zag edges from both bulk of graphene and the edge of a nano-ribbon, respectively. Panel (g) is a representative long ordered armchair edge found at this temperature. Scale bars = 1 nm

6.2.2 Typical edge behaviour at 400°C

Increasing the temperature to 400°C did not change the distribution of edge terminations significantly, as shown in Figure 6-3. Three typical holes are shown in Figure 6-3 (a–c), together with the statistics for three time series of different holes shown in Figure 6-3 (d). Zig-zag edges still form ~70%, armchair ~20%, and Rec. 5-7 < 5%. Figure 6-3 e shows a typical long ordered zig-zag structure and, again, is generally longer than the armchair edges shown in Figure 6-3 (f). This shows that the edge structure of graphene at 400 °C is similar to that at 25 °C.

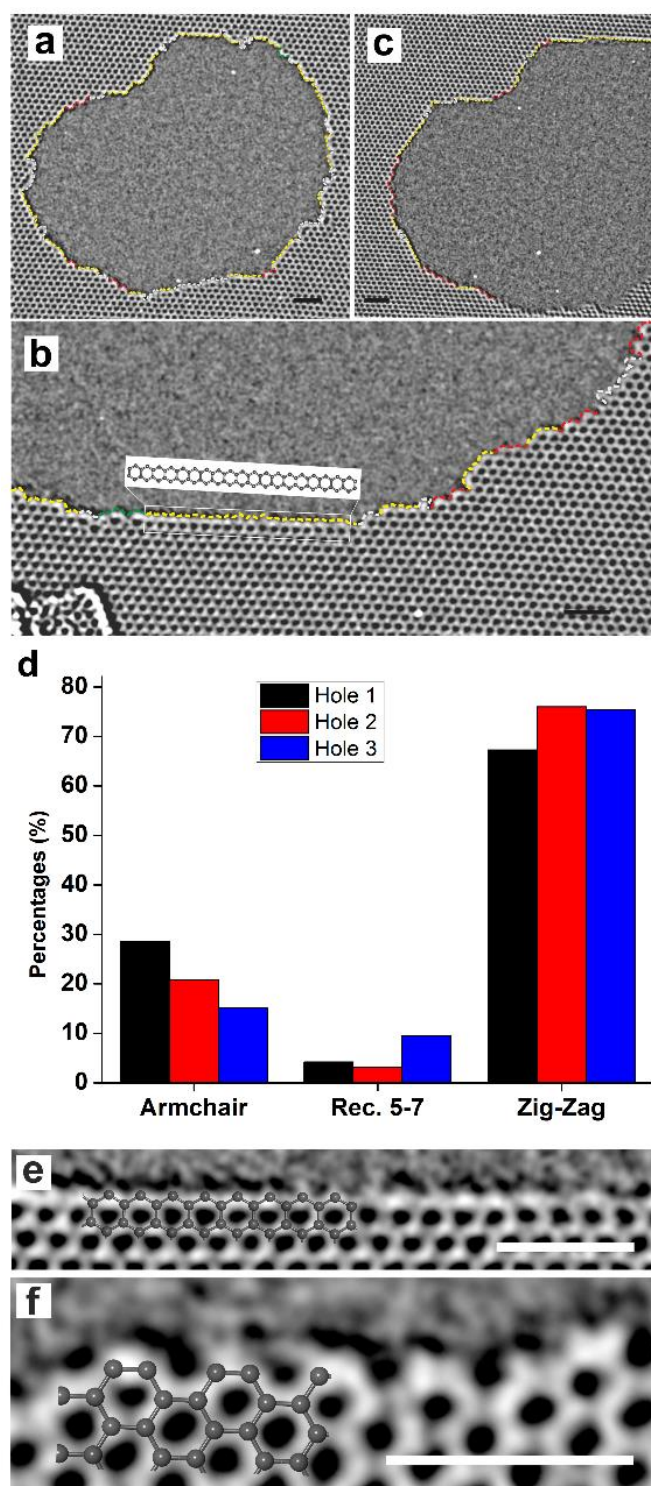


Figure 6-3. Edge behaviour at 400°C. (a–c) show three typical AC-TEM images of graphene holes at this temperature. The edges are colour coded to differentiate the types of edge configurations. Red represents armchair, yellow is zig-zag and green is Rec. 5-7, while white indicates mixed or unidentified edge types. The inset in (c) shows that a typical long order zig-

zag configuration occurred at this temperature. The statistics for three examples are shown in panel (d); the percentages of edges occupied by different types of edges are ranked accordingly. Black columns represent panel (a), red columns panel (b) and blue columns panel (c). (e) is a representative long ordered zig-zag edge cropped from panel (c) and zoomed in. (f) is an representative long ordered armchair edge cropped from Panel (b) and zoomed in. Scale bars = 1 nm.

6.2.3 Typical edge behaviour at 600 °C

Increasing the temperature to 600 °C resulted in a drastically different distribution of edge terminations, shown in Figure 6-4. Armchair edges now account for ~60%, zig-zag <5% and Rec. 5-7 30-40%. The major change is the large decrease in the percentage of zig-zag edges, at the expense of a rise in Rec. 5-7 edges. The inset of Figure 6-4 (a), shows the long ordered Rec. 5-7 edges and the inset of Figure 6-4 (c) shows the long ordered armchair edge. No long ordered zig-zag edge structure was observed. A typical long ordered armchair structure is shown at higher magnification in Figure 6-4 (e), and the length is longer than those obtained at room temperature and 400°C. Long ordered Rec. 5-7 structures, such as those seen Figure 6-4 (f), start to appear more frequently.

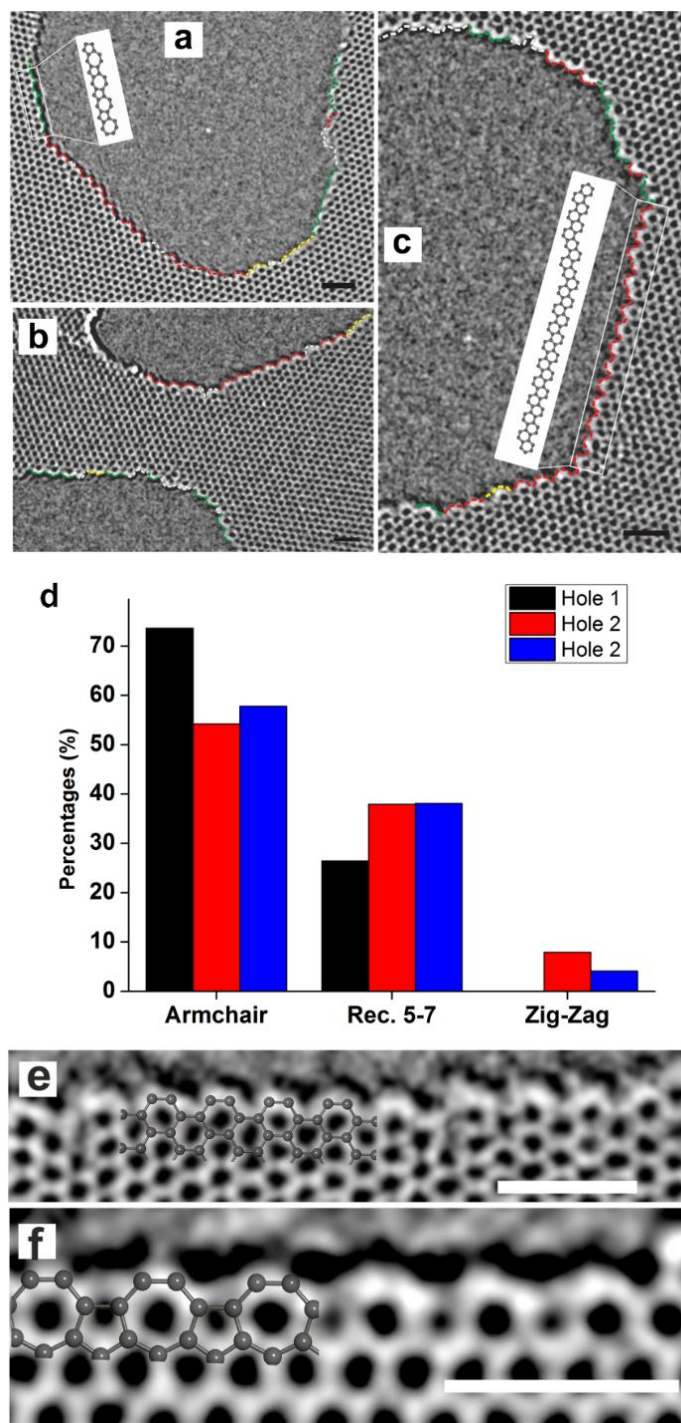


Figure 6-4. Edge behaviours at 600 °C. (a–c) are three typical HRTEM images of graphene holes at this temperature. The edges are colour coded to differentiate the types of edge configurations. Red represents armchair, yellow is zig-zag and green is Rec. 5-7; while white indicates mixed or unidentified edge types. The insets in (a) and (c) show that typical long order reconstructed 5-7 and armchair configurations at this temperature. The statistics for three

examples are shown in (d); the percentages of edges occupied by different types of edges are ranked accordingly. Black columns represent panel (a), red columns panel (b) and blue columns panel (c). (e) is a representative long ordered armchair edge cropped from panel (c) and zoomed in. (f) is a representative long ordered Rec. 5-7 edge cropped from panel (a) and zoomed in. Scale bars = 1 nm

6.2.4 Typical edge behaviour at 800°C

Finally I increased the temperature to 800°C to identify if any further changes occurred to the distribution of edge types, shown in Figure 6-5. The statistics given in Figure 6-5e show that armchair remains the most predominate edge, at ~70%, followed by Rec. 5-7 edge (20%–30%), with zig-zag edge being the least frequently observed edge type (<5%), similar to the case at 600 °C. Figure 6-5 (f,g) are typical examples of armchair and Rec. 5-7 edges at this temperature. The absence of any further changes in the edge distributions indicates that the region between 400 °C – 600 °C is the major point of interest.

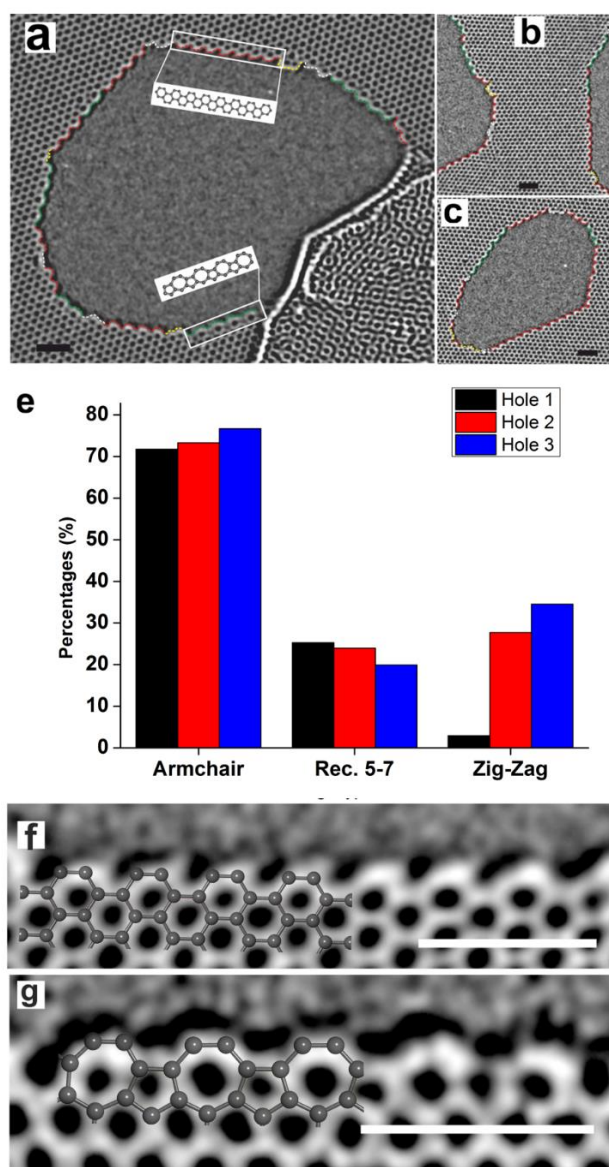


Figure 6-5. Edge behaviours at 800°C. (a–c) are three typical HRTEM images of graphene holes at this temperature. The edges are colour coded to differentiate the types of edge configurations. Red represents armchair, yellow is zig-zag and green is Rec. 5-7; white indicates mixed or unidentified edge types. The inset in (a) shows typical long ordered Rec. 5-7 and armchair configurations at this temperature. The statistics for three examples are shown in panel (d), the percentages of different types of edges are ranked accordingly. Black columns represent panel (a), red columns panel (b) and blue columns panel (c). (f) is a representative long ordered armchair edge cropped from panel (c) and zoomed in. (g) is a representative long ordered Rec. 5-7 edge cropped from panel (a) and zoomed in. Scale bars = 1 nm.

6.3 Understanding the statistics and the mechanism for edge behaviour

6.3.1 Statistical analysis of edges at all four temperatures

More than 350 frames like those shown above at each temperature were taken over multiple numbers of holes and were then used in the statistical analysis of edge types. The results are shown in Figure 6-8(a–d) for room temperature, 400 °C, 600 °C and 800 °C respectively. Only holes with diameters larger than ~15 nm were included in the counting process, to keep the edge strain effect to a minimum. Also, only edges that have four rings or longer were considered. The maximum counts occur for edge lengths of ~six rings for all four temperatures, with the counts tailing off for longer edge lengths. The most perceptible difference between room temperature, 400 °C (a,b) and, 600 °C, 800 °C (c,d) is the decrease in the number of zig-zag edges and the increase in the number of armchair and Rec. 5-7 edges. This is summarised in Figure 6-8 (a), where the temperature dependence of the average population distribution of the three edge types is plotted. Thus shows the major change lies between 400 °C and 600 °C, where the edges undergo abrupt transformations: zig-zag edges experienced a reduction from ~60% to ~5%, armchair edges increased from ~30% to ~60%, and Rec.5-7 edges increased from ~5% to ~30%. This shows that the temperature between 400 °C and 600 °C is the cross over point for zig-zag edges to be converted into Rec.5-7 edges.

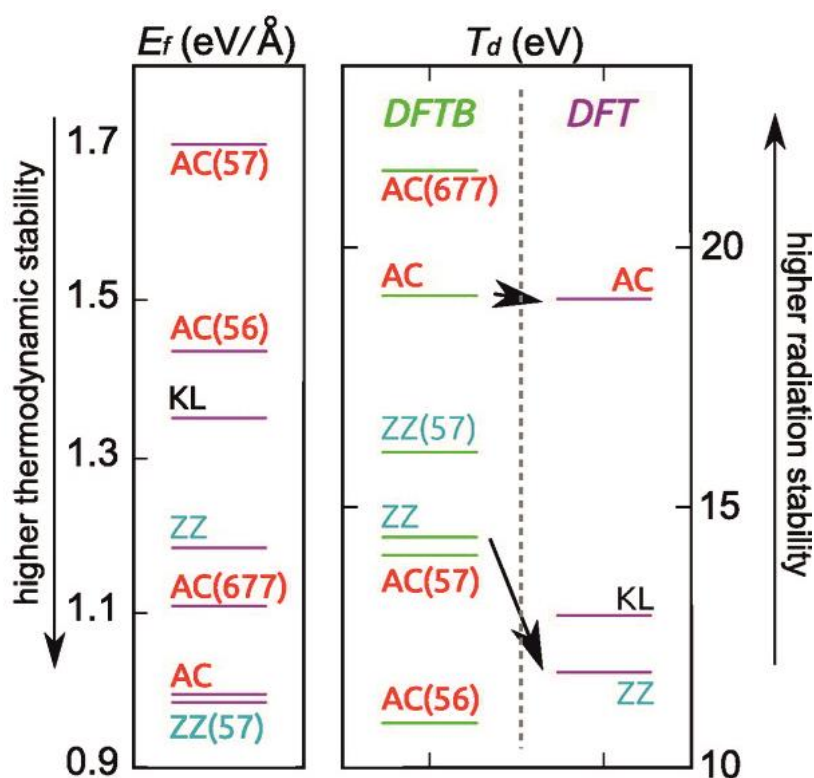


Figure 6-6. The formation energy E_f and displacement threshold T_d calculated for different edge structures. The formation energy is calculated for DFT and the displacement energy is calculated with both DFT and DFTB. (Reprinted with permission from (37), Copyright (2012) American Chemical Society)

The theoretical formation energy for graphene edge types decreases from zig-zag, armchair to Rec. 5-7 as seen in Figure 6-6.^{32,35,39,40} This means the thermodynamic stability should increase from zig-zag, armchair to Rec. 5-7. However, within the TEM, edges are irradiated by the electron beam and the radiation stability of the edge is extremely important. DFTB calculations results shown in Figure 6-6 indicate that the radiation stability of edges is reduced from armchair, Rec. 5-7 to zig-zag: this is different to the formation energy.³⁷ Both armchair and Rec. 5-7 edges have two atoms at the edge that are only bonded to two other atoms, the neighbouring two atoms form a dimer, the kinetic energy provided by the electron collision is distributed between the dimer and occasionally results in a 180 °rotation (flipping).³⁷ The zig-zag edge, on the

other hand does not allow this kind of rotational reconstruction due to the geometrical restrictions, and is therefore the least stable structure out of the three under electron beam irradiation. Calculations of the sputtering threshold of graphene edges indicate that the edges should be much more stable than current observations reveal.³⁷ It is therefore suggested that the rapid sputtering rate of graphene holes at room temperature is due to a chemical etching process, which essentially lowers the energy threshold of atom removal.

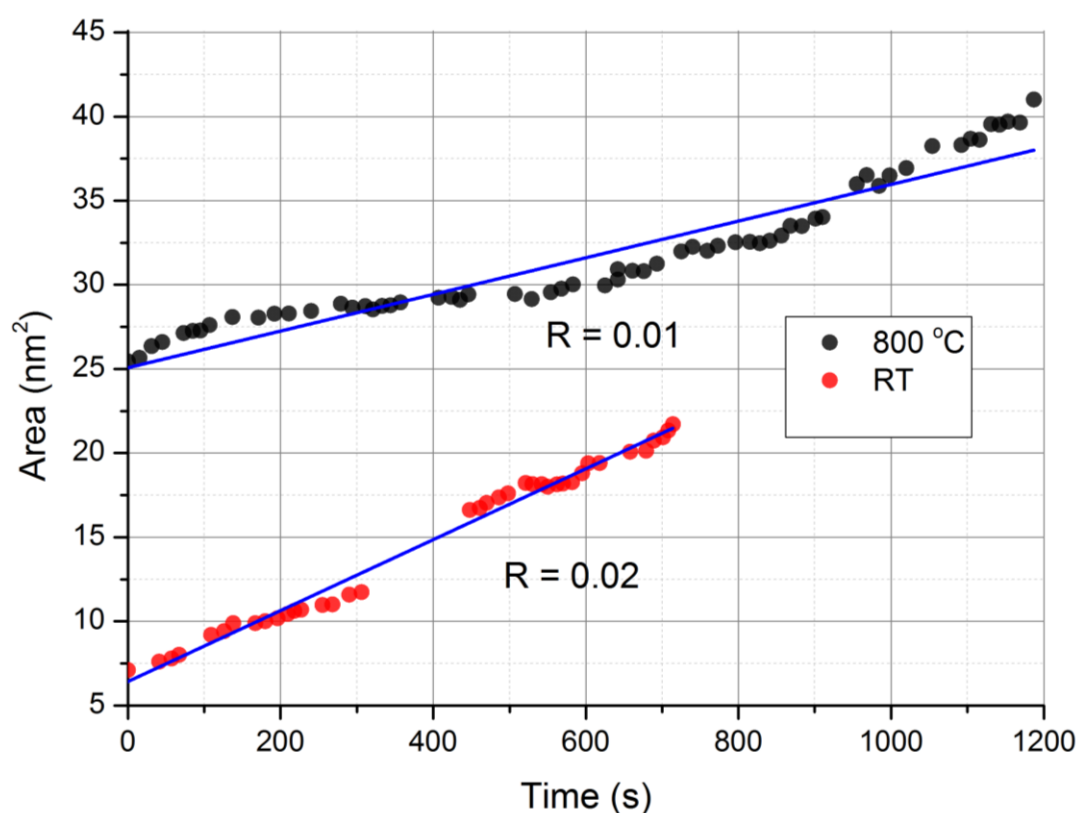


Figure 6-7. The size of the nanopore plotted against time at both room temperature and 800 °C and then fitted with a linear equation.

The large change between the low temperature (room temperature and 400 °C) and high temperature (600 °C and 800 °C) results is related to both electron beam induced sputtering effects and the thermodynamic low-energy structure. Graphene is typically covered with surface adsorbates that remain attached until they are heated to

approximately 500°C inside the TEM, when they evaporate off and leave a pristinely clean graphene surface. This also influences the concentration of surface chemical species, which that dictates the chemical etching process of graphene edges. The growth rate of holes in graphene at both room temperature and 800 °C is shown in Figure 6-8. Holes grow twice as fast at room temperature compared to 800 °C in our experiment, indicating a decrease in the chemical etching effect at high temperature due to the reduced adsorbate concentration on the surface. During the hole fabrication process, the electron beam is contracted to a 10nm spot to maximise the beam current density, and it takes noticeably longer to create a hole using this method at 800 °C (10 min.) compare to room temperature (3 min.). This supports the notion that the hole fabrication/growth process at low temperature (below 400 °C) is dominated by chemical etching, activated by large concentration of surface contamination, which might include metal particles, hydrocarbons, and amorphous carbon. The chemical etching effect diminishes as the contamination evaporates off with increasing temperature. The 600°C and 800°C statistics are least affected by chemical etching and reflect theoretical predictions in regard to edge stability. Long edges are more stable at these high temperatures, illustrated by the larger number of edges with 9–16 rings. Zig-zag edge has previously been reported to be the predominant edges at room temperature during TEM studies.^{19,41} Armchair edges are reported to be more abundant during current annealing with an effective temperature of 2000K inside the TEM.^{42,43} However, these data are based on only a couple of frames and a small number of statistics. My study tries to address this issue specifically by studying an extensive data base (~1400 frames) that covers a full range of temperatures up to 800 °C.

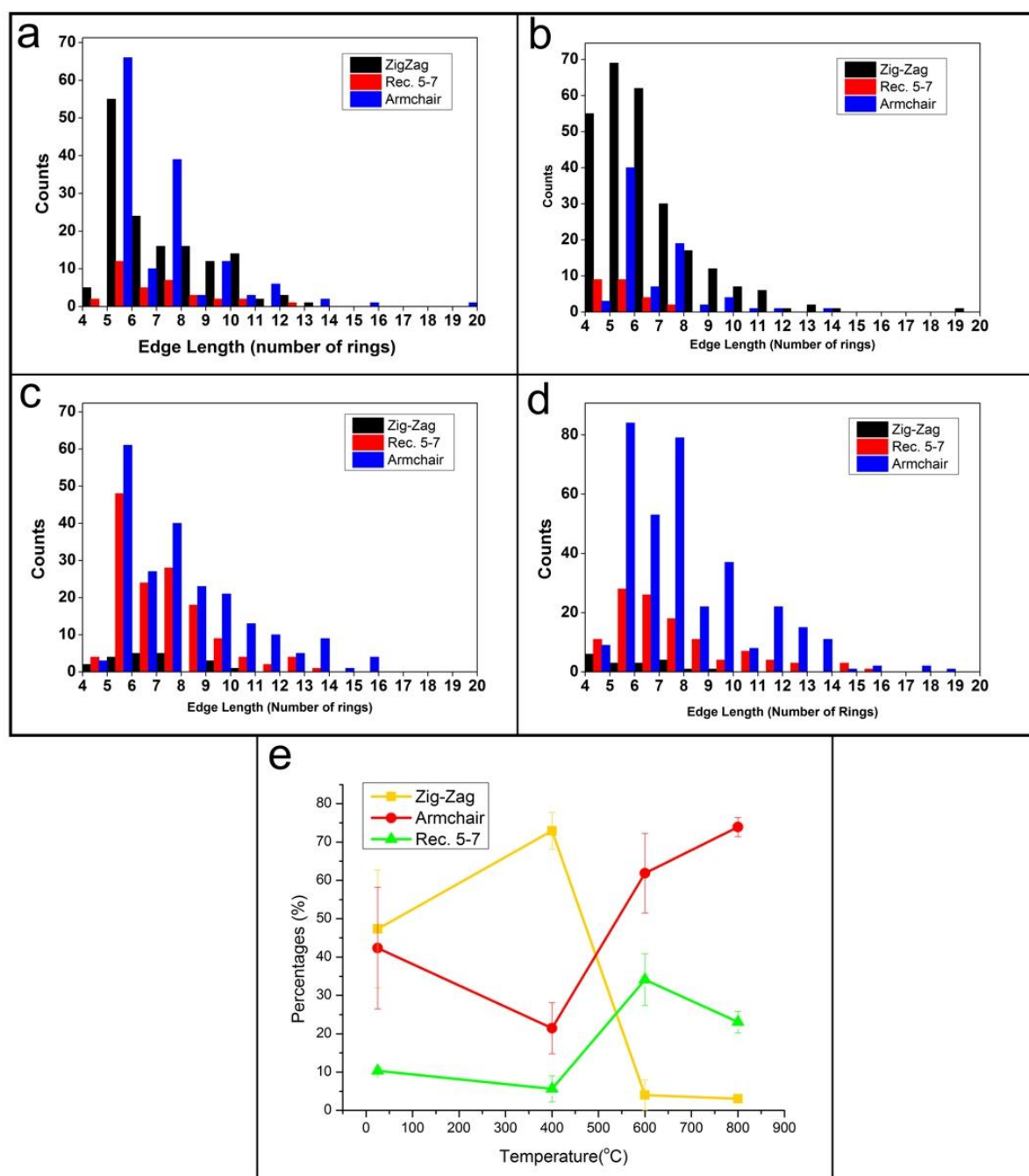


Figure 6-8. Statistics of edge configurations at various temperatures. (a–d) Statistics of edge configuration at room temperature, 400 °C, 600 °C, and 800 °C respectively. The number of occurrences is plotted against the edge length (the number of rings that makes up the edge). (e) The three trend lines represent the temperature dependency of different edge configurations: yellow for zig-zag, red for armchair, and green for reconstructed 5-7. The percentage of each edge type is calculated by dividing the sum of the edge lengths of this type by the total number of edges counted.

6.3.2 Temperature dependent edge etching effect

Fully understanding the statistics of edge types at different temperatures requires consideration of the dynamics and lifetime of the edge. It is reported that zig-zag edges reconstruct into Rec. 5-7 via a series of bond rotations driven by electron beam impacts.³³ Prior work has showed that graphene torn along the zig-zag direction has an edge termination that is stable against electron beam sputtering for about ~50 frames (65s) and enables flipping rates as follows: zig-zag $\rightarrow$ Rec. 5-7 of 0.26s^{-1} and Rec. 5-7 $\rightarrow$ zig-zag of 0.12s^{-1} .³³ In my experiments at low temperature (room temperature and 400 °C), the edge configuration changes on a frame-by-frame basis due to the enhanced sputtering from chemical etching, illustrated in Figure 6-9 (a,b): the blue dashed lines indicate the number of atoms being etched away, by 95s at room temperature and 70s at 400 °C; one row of zig-zag atoms has been removed. Most of the zig-zag edges are being etched away without having time to reconstruct, with only a small proportion remaining long enough to reconstruct into Rec. 5-7 configuration. Furthermore, the sputtering of atoms from a Rec.5-7 is found to often lead to the transformation back into a zig-zag edge, and reduces its contribution to the edge distribution statistics.

At high temperature (600 °C and 800 °C), shown in Figure 6-9 (c,d), the outer most row of atoms remained stable for 557s and 173s under electron beam, respectively and the observation of the zig-zag edge was only for one frame, making its lifetime extremely short compared to that of the Rec.5-7. Whereas for the low-temperature measurements <400°C, both edge states can be imaged for multiple frames, indicating much longer lifetimes. This can be understood by reference to the mechanisms behind the flipping process. Below 400°C, the edges are flipped back and forth by electron impacts from the beam causing bond rotations. This is a stochastic process and would occur equally for both low temperature and high temperature measurements, but for the case of

temperatures above 600°C, any time that the electron impacts flip the edge from Rec.5-7 to zig-zag, the thermal energy in the system rapidly flips it back to Rec.5-7, giving rise to the short lifetime of zig-zag edges. It is likely that the edge flipping process happens many times for the high temperature measurements: it is simply the case that it does not remain long enough in that state to image and therefore I cannot capture it. The edge flipping process happens on a much faster time-scale than my image acquisition time.

As the temperature increase to 600 °C and 800 °C, the chemical etching effect weakens dramatically and the edge structure is much more stable. Combined with the effect temperature has on the flipping rate explained above, the zig-zag edges therefore have enough time to reconstruct themselves into a more stable configuration at these two higher temperatures, and this results in a higher relative Rec. 5-7 ratio in the statistics. Ref 33 reports a very special circumstance at room temperature: the graphene is extremely clean around the edge area and no sputtering (atom loss) occurred during the entire reconstruction process, essentially emulating the high temperature behaviour in my experiment. My experiment attempted to generalise the statistics to reflect the edge behaviour under all conditions, including the sputtering effect. Therefore, more than 1400 frames were used in the statistics.

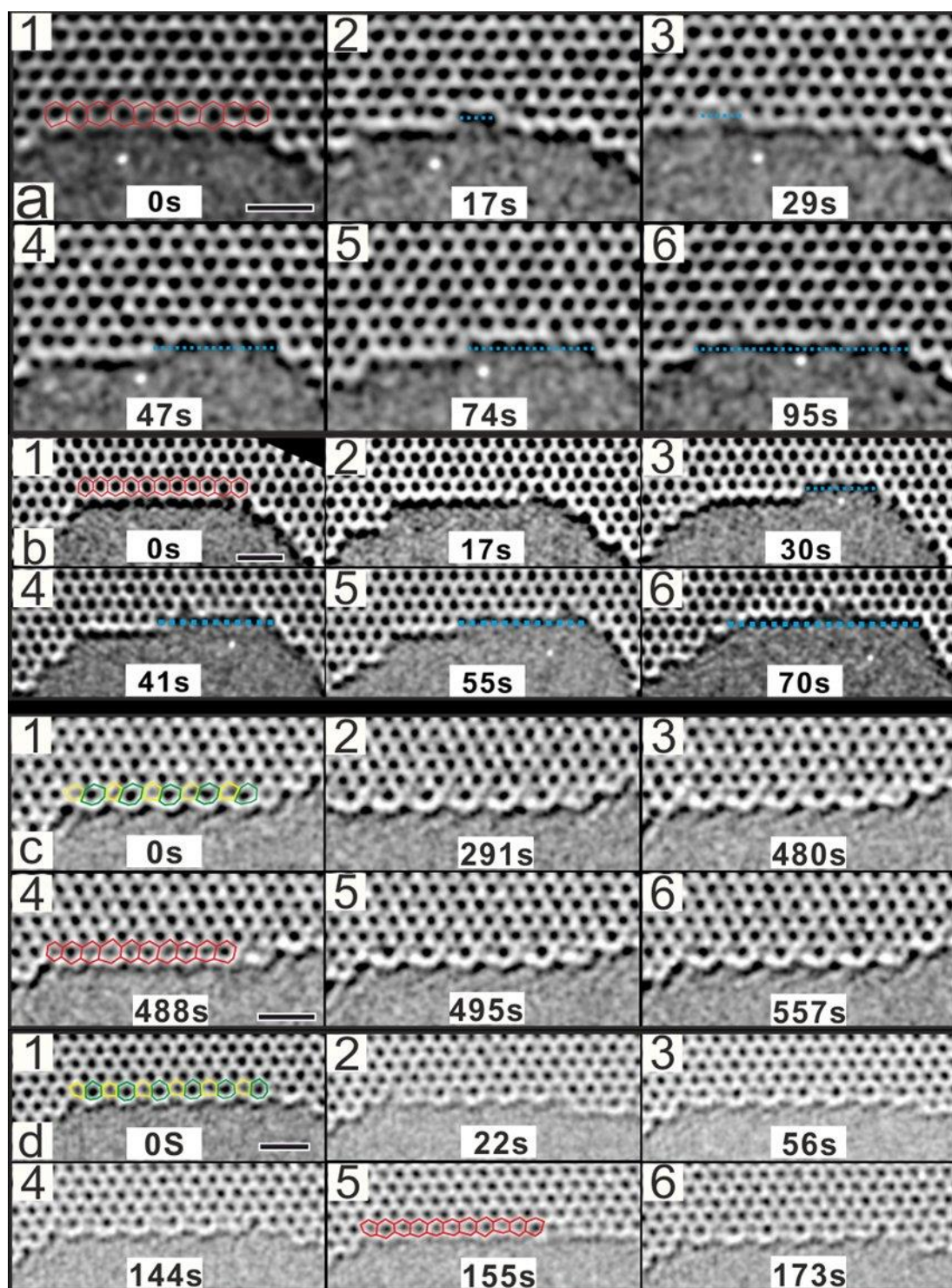


Figure 6-9. Temperature dependent edge etching effect. Red, yellow and green solid lines represent hexagon, pentagon and heptagon, respectively. The blue dashed lines indicate the row of carbons being lost due to electron sputtering. (a–d) are six time series frames of the same region of the graphene edge at RT, 400 °C , 600 °C , and 800 °C respectively. Scale bars = 1 nm

6.4 Dynamics of edge atom movement

6.4.1 STEM study of zig-zag to Rec. 5-7 switching at 550 °C

Probing graphene edges at high temperature using AC-STEM may provide further insights, because the STEM probe slowly raster-scans across the sample, rather than illuminating the entire edge (as is done in phase-contrast HRTEM) (Figures 2-7). Flipping an entire long edge from Rec.5-7 to zig-zag at high temperature requires multiple bond rotations, likely induced by multiple sequential electron scattering events. I would expect that any local bond rotation randomly induced by the STEM beam will quickly relax back by the time the STEM probe reaches the next section of the edge and therefore the edges should be stable Rec.5-7 structures. Figure 6-10 shows an example, at 550 °C, in which I have seen transitions between Rec.5-7 and zig-zag, initiated by atom sputtering at the edge, Figure 6-10 (b–c). However it quickly relaxes back to Rec.5-7 as expected and remains stable in this configuration, Figure 6-10 (c–d). Atomic models in Figure 6-10 (e–p) schematically illustrate the structural transitions that occur between the STEM images.

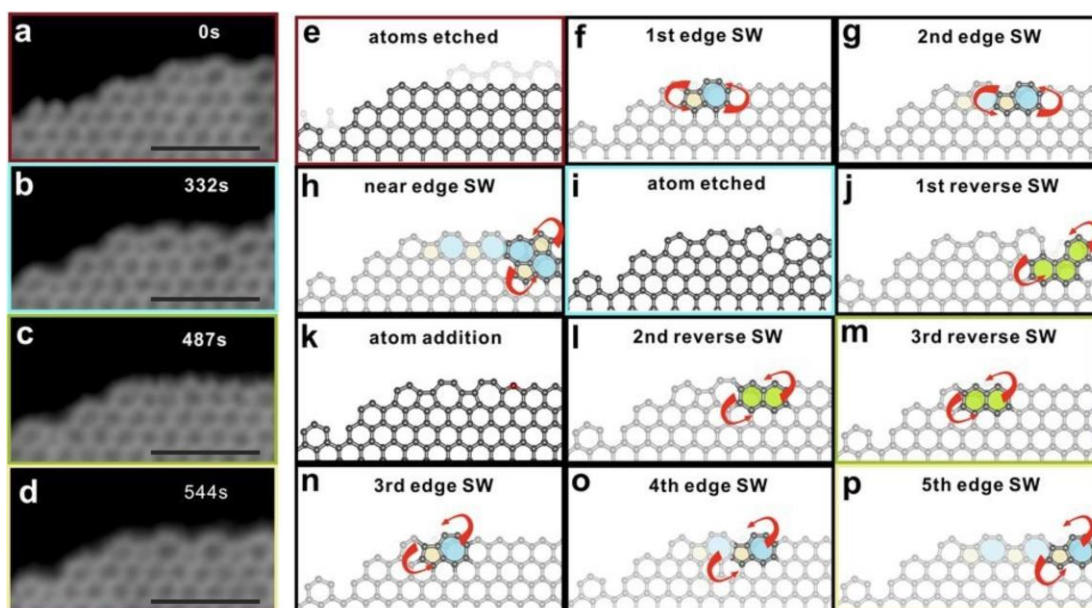


Figure 6-10. STEM study of zig-zag and Rec. 5-7 switching at 550°C. (a)-(d) a time sequencing STEM images of graphene edges firstly being etched and then transformed into Rec. 5-7 configuration. (e-p) Atomic models illustrating the reconstruction process shown in the STEM images. Carbon rings are highlighted in different colours in order to differentiate six-membered rings (green), five-membered rings (yellow) and seven-membered rings (blue). The red arrows demonstrate the direction of Stone-Wales rotation. The atomistic model that is outlined by different colours corresponds to the same atomic structure as shown in the STEM image that is outlined in the same colour. Scale bar = 1 nm

6.5 Conclusion

AC-TEM imaging of graphene edges has been carried out at four different temperatures (room temperature, 400°C, 600°C and 800°C). The statistical results show a dramatic transformation of edges between 400°C and 600°C: armchair became the predominant termination structure rather than zig-zag, and the Rec. 5-7 edge type also increased. This is caused by the combined effect of the reduction in chemical etching and an

increase in the flipping rate. The statistics of edge configuration at high temperature (600 °C and 800°C) therefore represent the true radiation stability order and are consistent with theoretical calculations in the literature. I have also carried out a STEM study of the detailed atom movements involved in this reconstruction process. This temperature dependent study of graphene edges provides insight into graphene edges on atomic scale and will provide useful evidence for the future study of graphene nanostructures, since edges have a major influence in regard to graphene's physical properties.

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Chapter 7

In situ Second-Layer Graphene Growth in a TEM

7.1 Introduction

Since the discovery of a mechanical exfoliation method to isolate a single layer of graphene and to demonstrate graphene's physical properties,¹ many researchers have attempted to synthesise graphene on a large scale in a reproducible fashion using chemical exfoliation,²⁻⁴ CVD on various metal catalysts,⁵⁻⁹ reduced graphene oxide,¹⁰ and thermal decomposition of SiC.^{11,12} Understanding the growth mechanism affects our ability to control the synthesis parameters. Direct visualisation of the growing front and how the lattice structure evolves is therefore desirable. Graphene grows at a rate of a micrometre per minute during CVD growth. Together with the physical limitations with regard to the instrumental setup, this makes atomic resolution analysis during the growth inconceivable. CVD is a process whereby, under high temperature, the volatile precursors, which are usually methane for graphene growth, decompose on the surface of a metal catalyst. In this experiment, I have attempted to grow second layer graphene on an existing layer in a high temperature environment by activating surface adsorbates using electron beam irradiation together with the residual hydrocarbon gas in the sample chamber.

It is well known that the structures of edges greatly affect the mesoscopic properties of graphene nanostructures.^{13–18} Geometries with a high edge/bulk ratio such as nanoribbons,^{19,20} quantum dots²¹ and nano-junctions^{22–24} are particularly affected by the edge morphology. STM,^{20,25–28} AC-TEM^{29–31}, STEM,³² and micro-Raman spectroscopy^{33,34} are among the most popular techniques to characterise the structure and properties of graphene edges at atomic precision. The use of an electron beam within a TEM environment is widely used to manipulate graphene nanostructures: it has been reportedly used to introduce defects and dislocations in a controlled way,³⁵ strip graphene layer by layer,³⁶ sculpt nanoribbons³⁷ and carbon chains,³⁸ grow a second layer,³² and reknit graphene nanopores.³⁹

Second-layer graphene is known to grow *in situ* in a STEM from the step edge of an existing domain.³² The crystallography and growing rates have also been shown to be temperature dependent. This technique could therefore be used to precisely design the orientation of graphene or other heterobilayer materials. The growth front of the second layer graphene is therefore an important subject of study, especially if an extensive area of graphene needs to be grown using this method. This will also facilitate further understanding of the CVD growth mechanism of graphene, to understand how atoms are attached to an existing graphene lattice. Graphene edges are also reported to fold back, forming a closed edge to increase stability. Liu et al. reported in Ref.[31] the transformation from open to closed edge, and from wavy to straight after 2000°C heat treatment.³¹ Jia et al. reported in Ref.[40] the change of edge structure from a mixed configuration and patchy frontier to a smooth and predominately zig-zag or armchair configuration. Gass et al. have also reported in Ref.[41] on the higher contrast edge effect: three possible edge structures are discussed: an openly staggered edge, a double layer back-folded edge, and a scrolled edge. These structures are distinguished based

on the comparison between an image simulation and a single frame of AC-TEM data. Here, we explore this in regard to the *in situ* grown second layer graphene by adjusting the temperature of graphene up to 800°C using a heating holder. At this temperature, edges have a tendency to fold back and give rise to higher. In this study we focused on the study of the dynamics of the edge movement by investigating the time series imaging results. Atomic resolution contrast images that trace the movement of edge front allows us to understand the nature of the growth front of second-layer graphene with more confidence. Together with multi-slice image simulation this enables a thorough understanding of the 3D morphology of the graphene film. This will help to explain the back-folding phenomenon that I have observed with CVD-grown graphene under TEM.

7.2 Heterogeneous nucleation

I have been inspired by the step-edge second layer graphene growth experiment carried out by Liu et al.³²: in their experiment the Au nanoparticles which had formed during the synthesis and transfer process to facilitate the *in situ* growth of graphene were developed. As shown in Figure 7-1, the initial layer of graphene was heated up to 800°C by utilising the *in situ* heating holder. This allows the amorphous carbon surface adsorbates to evaporate (Figure 7-1 (a,d)), revealing the lattice structure of graphene. This process has also been described in previous experiments.^{42,43} We then selected an area where there was a congregation of heavier contrasted atoms. This was likely to be residuals from the synthesis and transfer process, Several elements are likely to constitute these nanoparticles, such as Cu from the CVD substrate and the electrochemical transfer method, Fe from iron chloride contamination, Si from the silicon wafer substrate which came into contact with graphene during the transfer

process, platinum (Pt) from the heating wires on the *in situ* heating chip, and also gold (Au) from the contacts and alignment marks embedded in the heating chip. I have employed energy-dispersive X-ray spectroscopy (EDS) to try to understand the elemental composition of these nanoparticles as it is obviously important to understand the subsequent *in situ* graphene growth experiment. As shown in Figure 7-2, the nanoparticles are Au, based on the EELS acquired while the electron beam are precisely focused on the nanoparticle. This result is also backed up by a control experiment where another spectrum was taken on the plain graphene area, and no EDS signal of Au was detected. The Au atoms have a tendency to form clusters on the surface even though they do not constitute a crystallographic structure at high temperatures (600 and 800°C). The clusters adhere to the surface while other hydrocarbon and silicon adsorbates evaporate at 800°C, leaving a pristine graphene lattice with Au particles sitting on the surface, as shown in Figure 7-1 (d). The structure of the Au particles is contained *via* a small amount of the crystallised carbon structure that is immediately next to it. As has been discussed by Liu et al. in ref.[32], they have studied the TEM chamber pressure dependence of the graphene growth speed to understand the effect hydrocarbon concentration can have on the second-layer growth rate. Similarly, it was found in my experiment in which I have aimed to grow graphene around a metal particle instead of an already existing graphene step edge. At 600°C it was found there is an abundant hydrocarbon source from which to grow graphene, and not overly saturated to form amorphous carbon immediately, this temperature is therefore chosen as the growth temperature.

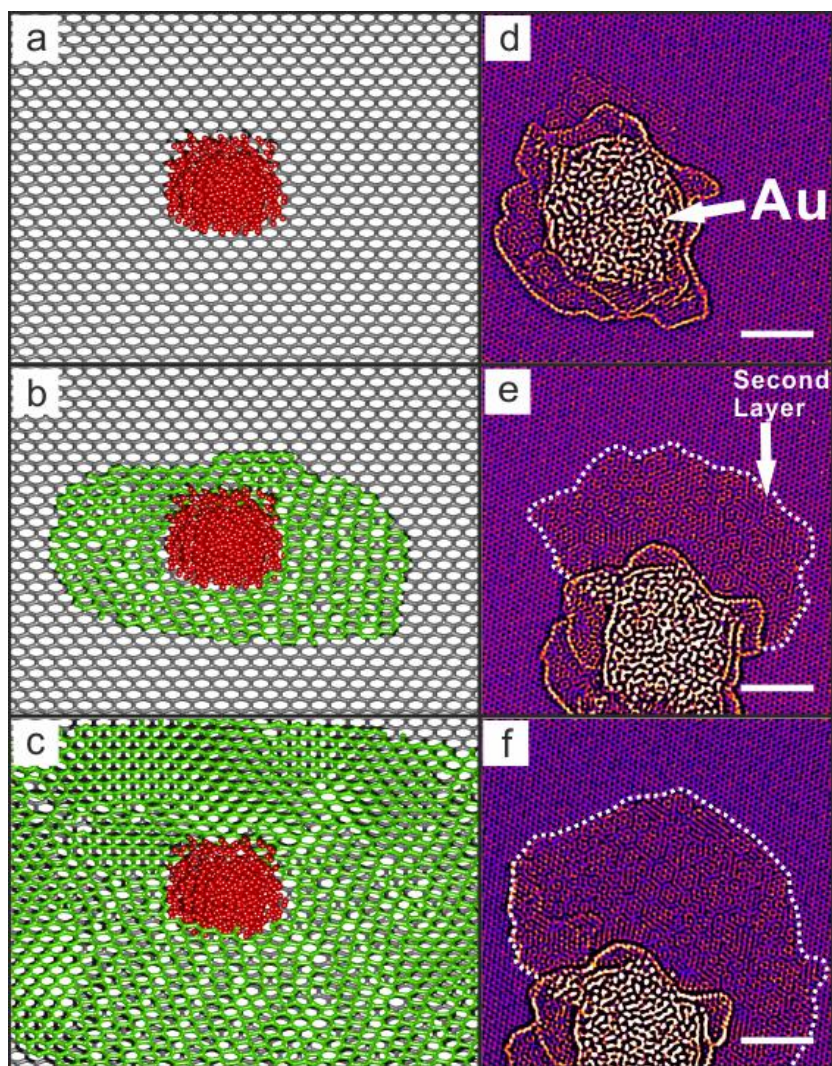


Figure 7-1. *In situ* growth of second layer graphene in a TEM (a) Atomistic model illustrating a gold nanoparticle residing on the surface of a clean graphene. The corresponding AC-TEM result is shown in (d). (b) Atomistic model showing second-layer graphene starting to nucleate around the gold nanoparticle, with the corresponding AC-TEM frame shown in (e). (c) Atomistic model illustrating the extensive growth of graphene with a continuous supply of carbon source, corresponding to the AC-TEM frame shown in (f). In (a–c), the red cluster of atoms in the middle represents the gold nanoparticle, shown as the higher contrast region in (d–f); the grey hexagonal lattice represent the initial graphene layer; the green hexagonal lattice shows the as-grown second layer region that is highlighted with white dashed lines in (e,f) Scale bars = 3nm.

A Previous report indicates second layer graphene grows at the step edge catalysed with silicon atoms attaching on the edge.³² The graphene used in this experiment, having been prepared differently, was observed to have abundant metal particles on the graphene surface, as shown in Figure 7-4 and Figure 7-2 (b). Various metal elements that have come into contact with the graphene surface during the synthesis and transfer process are potential elements that constitute the nanoparticle; EDS in the TEM was used to determine the element of those metal particles. This experiment could only be carried out at room temperature, as when the temperature is elevated, the amount of X-ray emission escalates dramatically and soon exceeds the safety threshold. At RT with electron beam sputtering, contamination aggregates at a rapid speed and covers graphene lattice, which becomes a problem for EDS experiment to unambiguously identify the elements that constitute the nanoparticle which sits on the surface of graphene. Therefore a control experiment was designed to eliminate the contamination effect. By controlling beam size at high magnification (2 MX) it is possible to selectively focus the beam on either pure graphene or the metal particle. As seen in the spectra in Figure 7-2 (c,d), signals indicating the presence of Au gold element came into existence after the electron beam started to focus on the metal particles. Si also exist, but a similar amount (weight percentage) had already existed when the beam was focused on areas far away from the particle. The amorphous agglomerates are believed to contain Si element. To further demonstrate that the metal particle was gold, during an *in situ* experiment, the beam was focused down to the smallest point possible and then placed on the graphene region. No Au signal was detected at that point, and as soon as the beam was shifted to the metal particles, the Au signal started to rise rapidly. Following the beam moving back to the graphene area, the weight percentage of Au

was again reduced. Graphene second-layer growth in our experiment was therefore catalysed with transition metal Au.

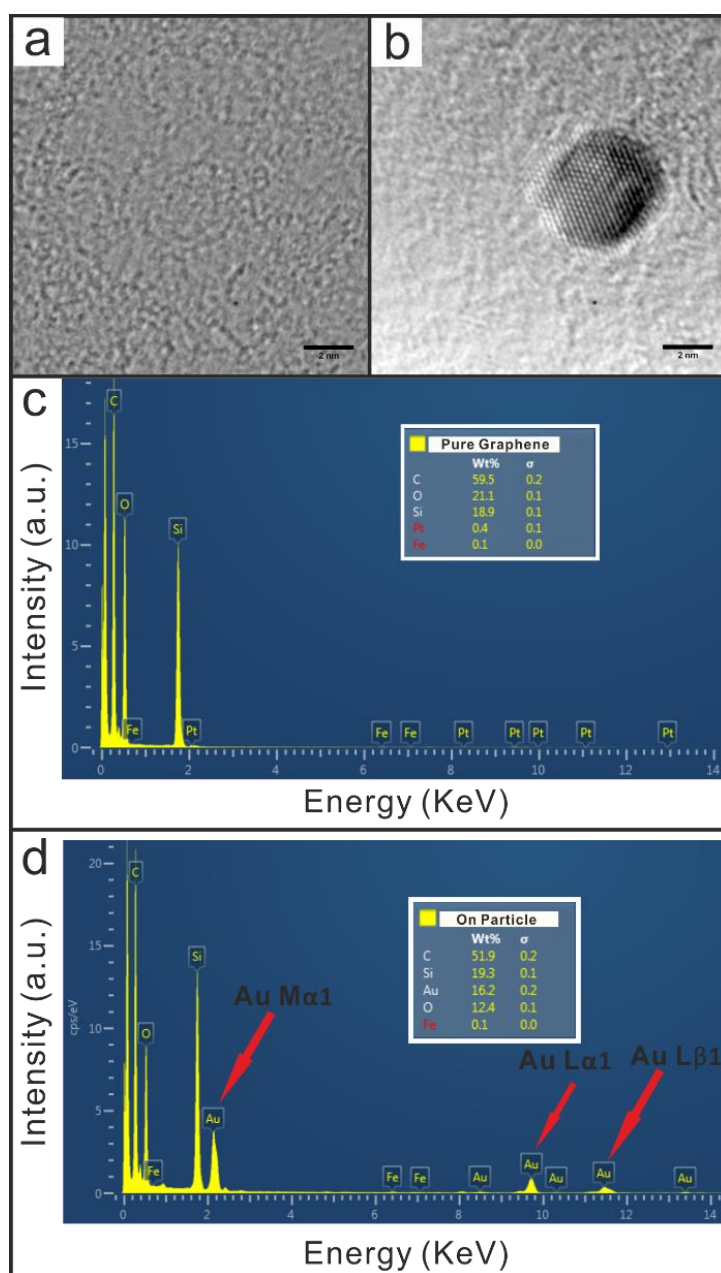


Figure 7-2. EDS characterisation of metal particles at room temperature. (a) An AC-TEM frame of graphene lattice covered with contamination. The EDS taken on this part of the sample is shown in (c). (b) is an AC-TEM frame of a metal particle sitting on top of graphene lattice also covered with contamination, with the EDS result shown in (d). The weight percentage value and the standard deviation are all listed in the insets of the two spectra. Scale bars = 2 nm.

7.3 As-grown second-layer analysis

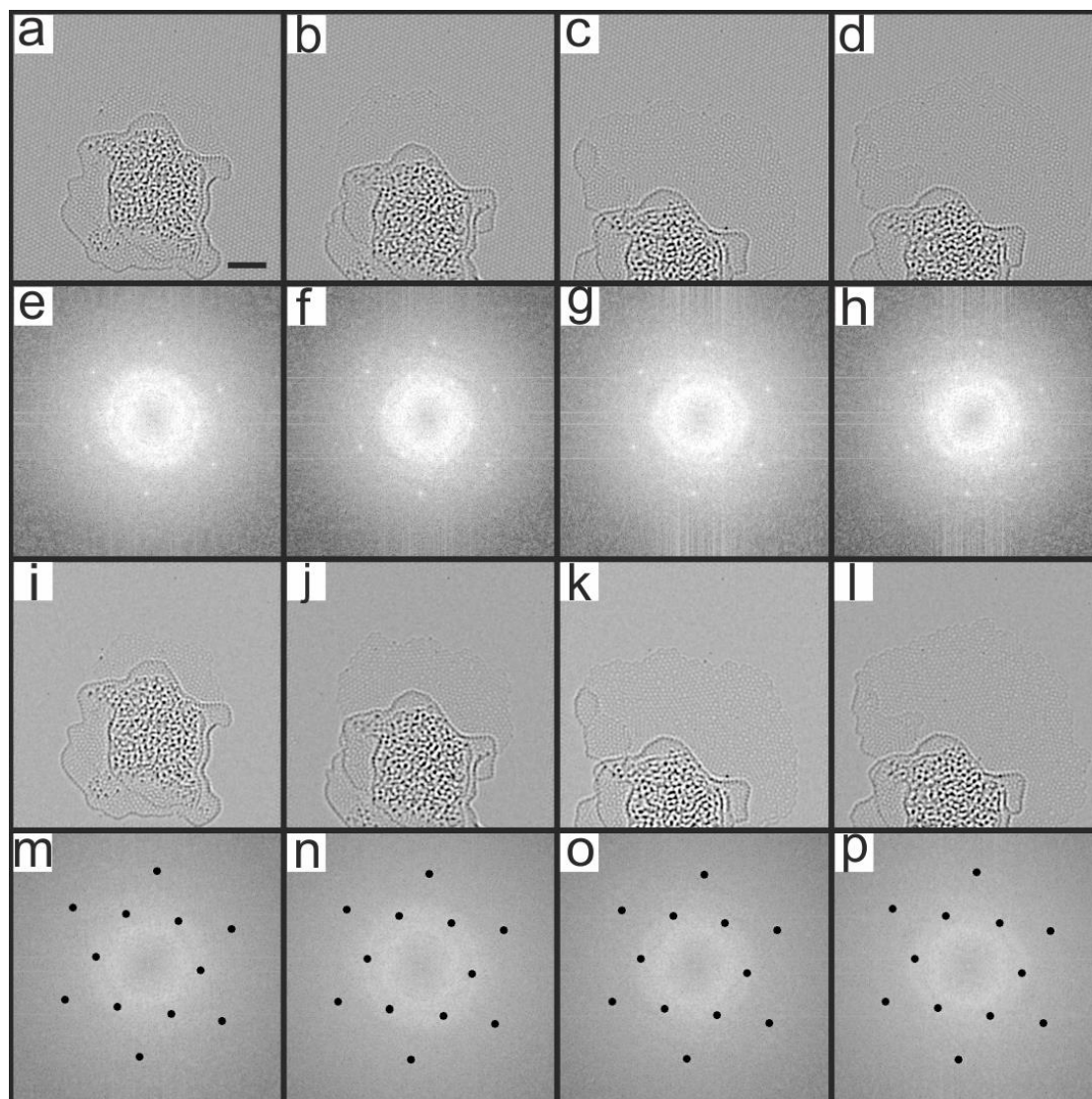


Figure 7-3. Second layer graphene growth. (a–d) are four time series TEM frames revealing the second layer graphene growth with its respective FFT shown in (e–h). (i–l) are reconstructed images from the masked FFT shown in (m–p), respectively. Scale bar = 2 nm.

Analogue to classical nucleation theory, where heterogeneous nucleation is much more commonly observed, as oppose to homogeneous nucleation. Heterogeneous nucleation is also a much faster reaction process due to the lower energy barrier for nucleation. No graphene nucleation and growth process are observed on the surface of a pristine graphene lattice. When the beam is brought close to the Au particles, second-layer

graphene nucleates swiftly and continues to grow. Figure 7-4 (a–d) show a time series of second layer growth, with the images being reconstructed from a masked FFT to allow better visualisation of the lattice structure and growth front of the second layer only. The details of the processing and the mask that was chosen are given in Figure 7-3. The original AC-TEM frames are shown in Figure 7-3 (a–d) with their respective FFT power spectrum shown in Figure 7-3 (e–h). The reconstructed images are shown in Figure 7-3 (i–l), with the negative mask shown in Figure 7-3 (m–p). The growth rate is plotted as a form of the area of second layer against time for all 39 frames, Figure 7-4 (e). Except in the case of the odd first point, the rest of the results show a linear relationship: the growth rate obtained from the slope of the linear equation is $0.14 \text{ nm}^2/\text{s}$. This relatively slow growth rate allow us to study the dynamics of the growth frontier.

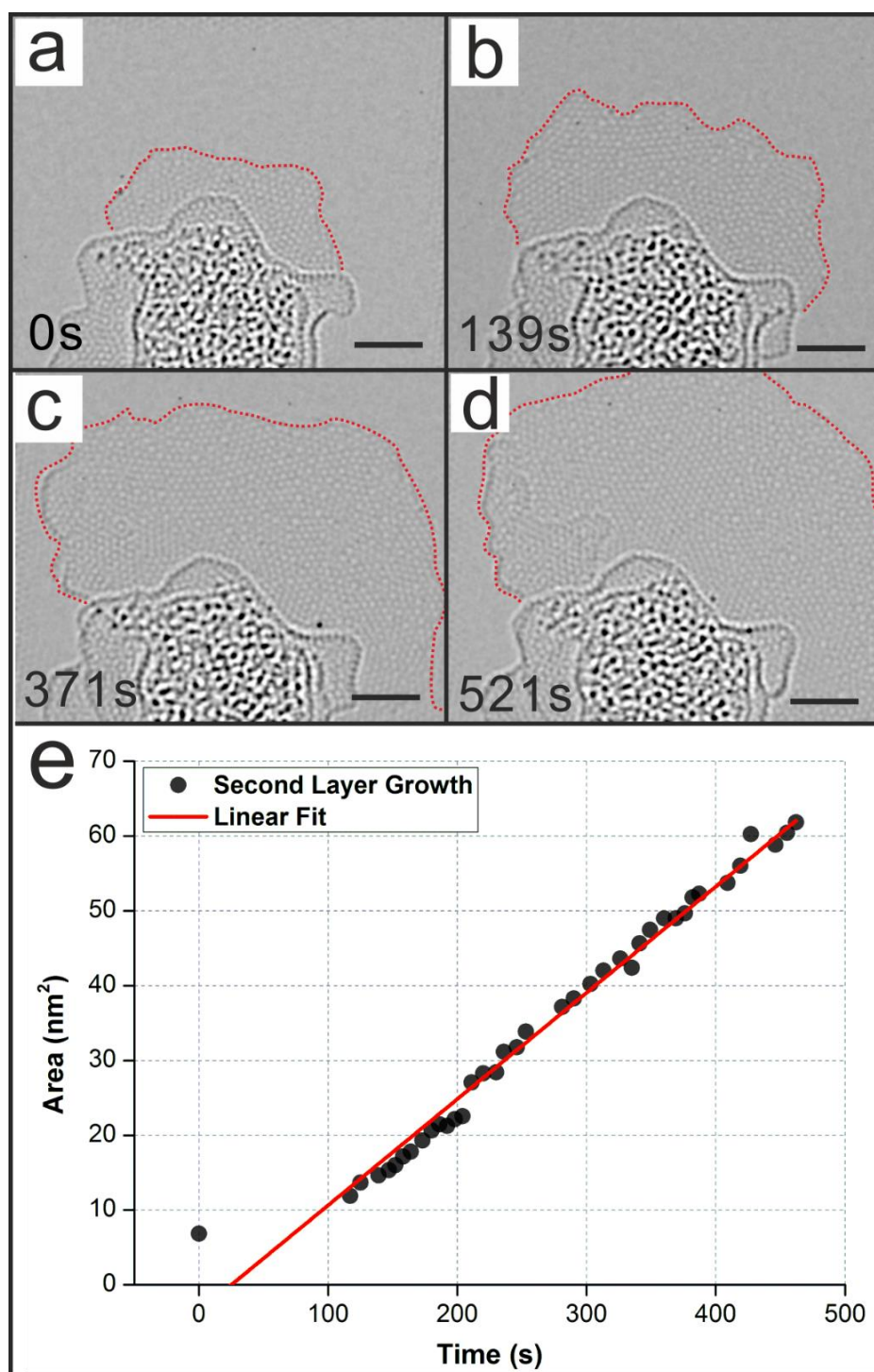


Figure 7-4. Time series FFT reconstructed images showing second layer graphene growth from surface adsorbates. The frontier for the second layer is highlighted by red dashed lines in (a-d). The reconstruction process is shown in Figure 7-3; the negative mask that is used to block the signal arising from the base graphene layer is covered. The area for the as-grown second layer is plotted against time in (e), and fitted with a linear equation. Scale bars, 3nm.

7.4 Growth mechanism

The growth front was carefully studied, in order to provide insights into the nucleation and growth mechanism for two-dimensional materials. As shown in Figure 7-5, the perimeters have a tendency to adopt a smooth rather than a rough structure. For example, in part I of Figure 7-5, where a time series of AC-TEM images are shown, a cluster of atoms is deposited onto the pre-existing graphene to initiate the growth process. This is indicated by the arrow in Figure 7-5 (b). This causes edges to be serrated, and increases edge roughness. The Valley position created by the atom cluster deposition is most likely to be filled in the subsequent frames. This process is named ‘indentation filling’ and is highlighted where it occurs in Figure 7-5 (d,f). The rough edge structure is higher in energy, because the extruded structure will increase the length of perimeter compared to a smooth edge. This echoes classical nucleation theory, according to which at a newly-formed structure that has a higher surface area will be the higher energy structure, and is therefore less favourable. The structure soon readjust itself by gradually filling the indentation sites. This carbon atom cluster deposition followed by an indentation filling process is regularly observed during second layer growth. A second case is shown in part II of Figure 7-5, where the atom cluster deposition and indentation filling process are also highlighted. This suggests that the growth mechanism, instead of taking place *via* single atom attachment, where a smooth and uniform edge structure should constantly been maintained, instead, the graphene growth mechanism involves a lump of carbon atoms being attached, and the system then having a preferential site, the indentation location, for the addition of future atoms, in order to reduce the energy of the system. The growth of graphene is therefore achieved by the continuous switching between these two processes.

It is possible that with the combinational effect of high temperature and electron beam sputtering, the gold cluster on the surface of graphene become partially amorphous. This could be seen in Figure 7-4, where the gold cluster adopt an amorphous morphology at 600°C. Whereas for the case of RT shown in Figure 7-2 (b), the gold cluster has a crystalline structure. With the gold cluster being amorphous, the diffusion rate of gold atoms increases dramatically, those atoms then diffuses to the edge of second layer graphene (Au atoms are highlighted in Figure 7-5 (a)) and act as catalytic reaction sites for the attachment of graphene clusters. The growth rate is therefore limited by two steps: the diffusion rate of Au atoms and the amount of hydrocarbons in the TEM chamber. If the temperature is low, the concentration of Au atoms at the edge is low and the concentration of hydrocarbons in the chamber is high. There is not enough catalysts to decompose the hydrocarbons, therefore amorphous carbon forms. At high temperature, there is abundant Au atoms (reactive sites) at the edge, but the hydrocarbon concentration is low, resulting in low growth rate. A temperature of 600°C is found to be the optimum temperature for second layer graphene growth under our TEM settings. The growth rate balanced by two limiting steps result in a linear growth rate as shown in Figure 7-4 (e).

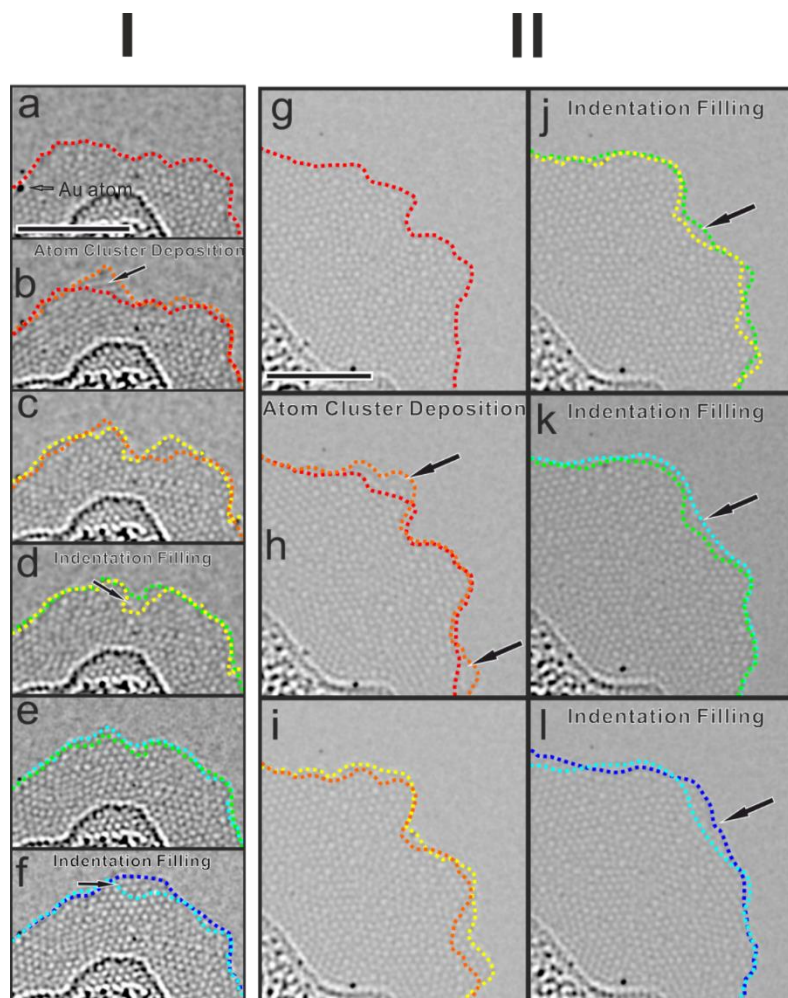


Figure 7-5. Two cases of second layer growth frontie. (a–f) and (g–l) are reconstructed images for masked FFT of six consecutive AC-TEM frames, each at 10s apart. The perimeters are colour coded differently to allow visual comparison between the two consecutive frames. The trace of the perimeter from the last frame is superimposed on the next one to compare the atom lost or added. The arrows indicates either ‘Atom cluster deposition’ or ‘Indentation filling’, both of which are highlighted in the panel where they have occurred. Scale bars = 3 nm.

7.5 Back-folding

The bonding of the second layer graphene edge to the underneath base layer produces the same enhanced contrast at the edge as does back folding, thus obscuring the true origin of this effect. Figure 7-6 (a) shows an atomic model of back-folded second-layer

graphene on top of another layer of graphene that I have used in this analysis. Isolating second layer graphene for the ease of practical analysis, Figure 7-6 (b,e,h) are three atomic models that demonstrate the folded graphene forming AA, AB and slightly offset AA, with the underneath original base layer graphene. The respective insets show the magnified images of the folded region. Box profiles are taken from the red box highlighted region along the arrow direction shown in Figure 7-6 (d,g,j); the enhanced contrast effect is again observed from all three simulation results. However, another region of the graphene sheet gives different contrast levels, depending on the stacking. Blue dashed lines indicate contrast from two layers of graphene, red dashed lines indicate contrast from the folded region (effectively three layers of graphene). It is evident from this comparison that a greater number of layers does not necessarily result in enhanced contrast. For AA stacking (Figure 7-6 (d)), the three layered region has a stronger contrast compare to two layer region. For AB stacking (Figure 7-6 (g)), the contrast in the three-layer region diminishes: it is even weaker than the two layered region. If the folded graphene retains the AA stacking order, but the lattice of the folded graphene is diaplaced for a short distance along the armchair direction, the box profile in Figure 7-6 (j) indicates the two-layer and three-layer region now have a similar contrast level.

Instead of having a folded edge, if the second layer bonds with the original graphene layer, it results in a lattice with the structure shown in Figure 7-6 (k). The lattice of second-layer graphene that is close to the edge adopt an out of plane morphology as seen in the side view illustration in the inset of Figure 7-6 (k). Shown in Figure 7-6 (i), at the pleat along the bonded region there is an increase in contrast, the area that is immediately next to it shows a reduced intensity, outlined by the red dashed line in Figure 7-6 (m). As seen from the above analysis, both the bonded and folded models

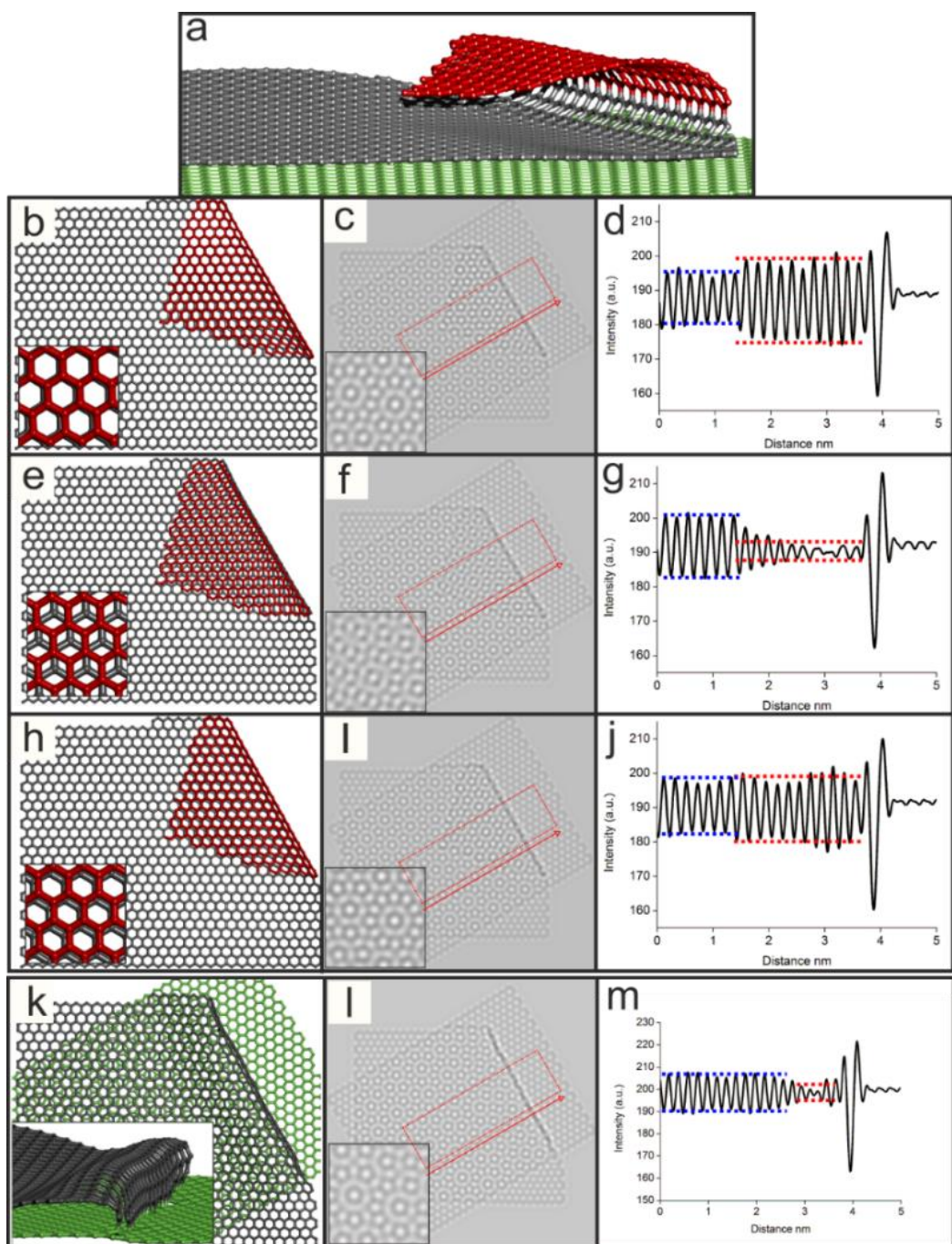


Figure 7-6. Simulation of folded and bonded second layer. (a) A side view of the folded graphene second layer atomistic model. (b,c) are the atomistic model and the multi-slice image simulation of the AA stacked folded layer. The detailed atomic structure of the stacking is shown in the inset of (b) with the corresponding image simulation shown in the inset of (c). A box profile has been taken along the red boxed region in (c) along the arrowed direction, with the results shown in (d). (e–g), (h–j), and (k–m) are the same analyses method applied to AB-stacked, offset AA-stacked folded layer and bonded second layer graphene.

give rise to an increase in contrast at the edge, and, different stacking order of the folded layer could give very similar results. A single frame of AC-TEM image is therefore not sufficient to determine the step-edge structure.

As discussed in previous text, back-folded edges are easily confused with other two-layered structures that also give rise to higher edge contrast. Figure 7-7 (a) shows an atomic model and its side views that includes a second layer graphene folding back. The multislice image simulation of this atomic structure is shown in panel (b). The area surrounded by the red dashed line indicates the back-folded region: it is apparent that the contrast along the folding pleat increases dramatically. In order to quantify this, an image is reconstructed from the FFT covered with negative mask as shown in Figure 7-7 (c), to exclude the contrast contributed by the base layer. A box profile is taken from the black box highlighted the region along the arrowed direction, shown in Figure 7-7 (f). The red dashed box highlights the apparent contrast enhanced region. Figure 7-7 (d) is an AC-TEM frame that shows a region of second layer graphene grown *in situ* on top of an already existing layer. The region where the second layer is present is evident from the moiré pattern. The reconstructed image in Figure 7-7 (e) excludes contrast from the base layer, leaving only second-layer graphene, for ease of analysis. A box profile is taken from the black boxed region along the arrowed direction, and is shown in Figure 7-7 (h). The region highlighted by the red dashed box shows the contrast-enhanced region, similar to what is observed from the multi-slice image simulation in Figure 7-7 (f). The increase in contrast is a result of multiple atoms under projection at the vertical direction when graphene fold back.^{31,44} As discussed earlier, different two layer structures could cause the enhanced contrast effect at the edge, it is therefore difficult to exclusively identify the atomic structure from a single frame of AC-TEM image.

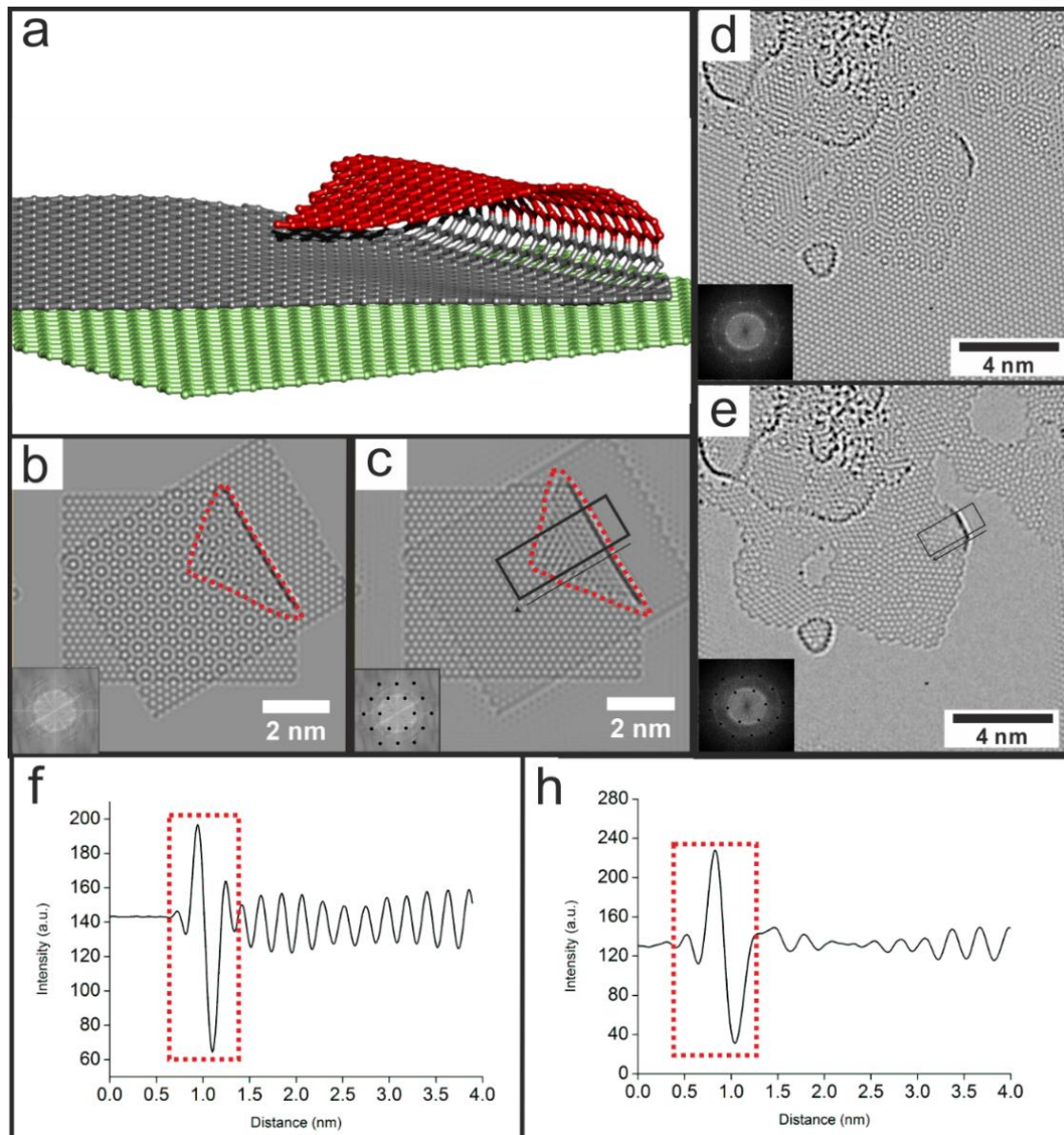


Figure 7-7. (a) Atomic model of a bilayer graphene structure, with the top layer folded back. (b) is the multi-slice image simulation of the atomic model shown in (a). The inset is the FFT of the simulated image. (c) Reconstructed images from the FFT covered with negative mask, shown in the respective inset. (d) An AC-TEM image of bilayer graphene with the second layer imposing a higher contrast line at the edge. (e) Reconstructed image from the FFT covered with negative mask, shown in the respective inset. (f) and (h) are intensity profiles taken from the boxed regions in (c) and (e) along the arrow indicated directions: the red rectangle highlighted region indicated the region of enhanced contrast.

It is therefore important to study the dynamics of second-layer graphene to gain further insight into the stacking nature of second layer graphene. The increase in temperature slows the rate of graphene growth, or even stops the whole process. Figure 7-8 is an example of second-layer graphene grown at 600°C. The temperature was then raised to 800°C to examine the second layer growth front. Figure 7-8 (a–d) are time series AC-TEM frames with red dashed lines highlighting the frontier of the second layer region. The respective insets show the FFT. Figure 7-8 (e–h) are reconstructed images from the negative-masked FFT shown in the insets: the mask blocks out the intensity that corresponds to the base graphene layer, allowing only the second layer to be shown, for ease of interpretation. Red rectangles highlight the area of interest, which is magnified and shown in Figure 7-8 (i–l). Figure 7-8 (i) shows a dark contrast line which was previously discussed as originating either by back-folding or bonding to the base layer. In this time series study, we can see in Figure 7-8 (j) the darker contrast along the edge fades away and in the subsequent two frames (Figure 7-8 (k,l)) an area of extra graphene extends from what used to be the darker contrasted border, over the course of just 10 seconds. This indicates the extra area came from the unfolding of the folded area: the red dashed line highlights the extra region formed from the unfolding process. Figure 7-8 (m–p) demonstrates this process with atomistic models: panel (m) shows the folded model and panel (n) shows the structure after unfolding. Panels (o) and (p) are side views of the two models, respectively. This dynamic study of the second layer-graphene edge confirms that the darker contrast arises from back-folding rather than edge bonding to the base layer.

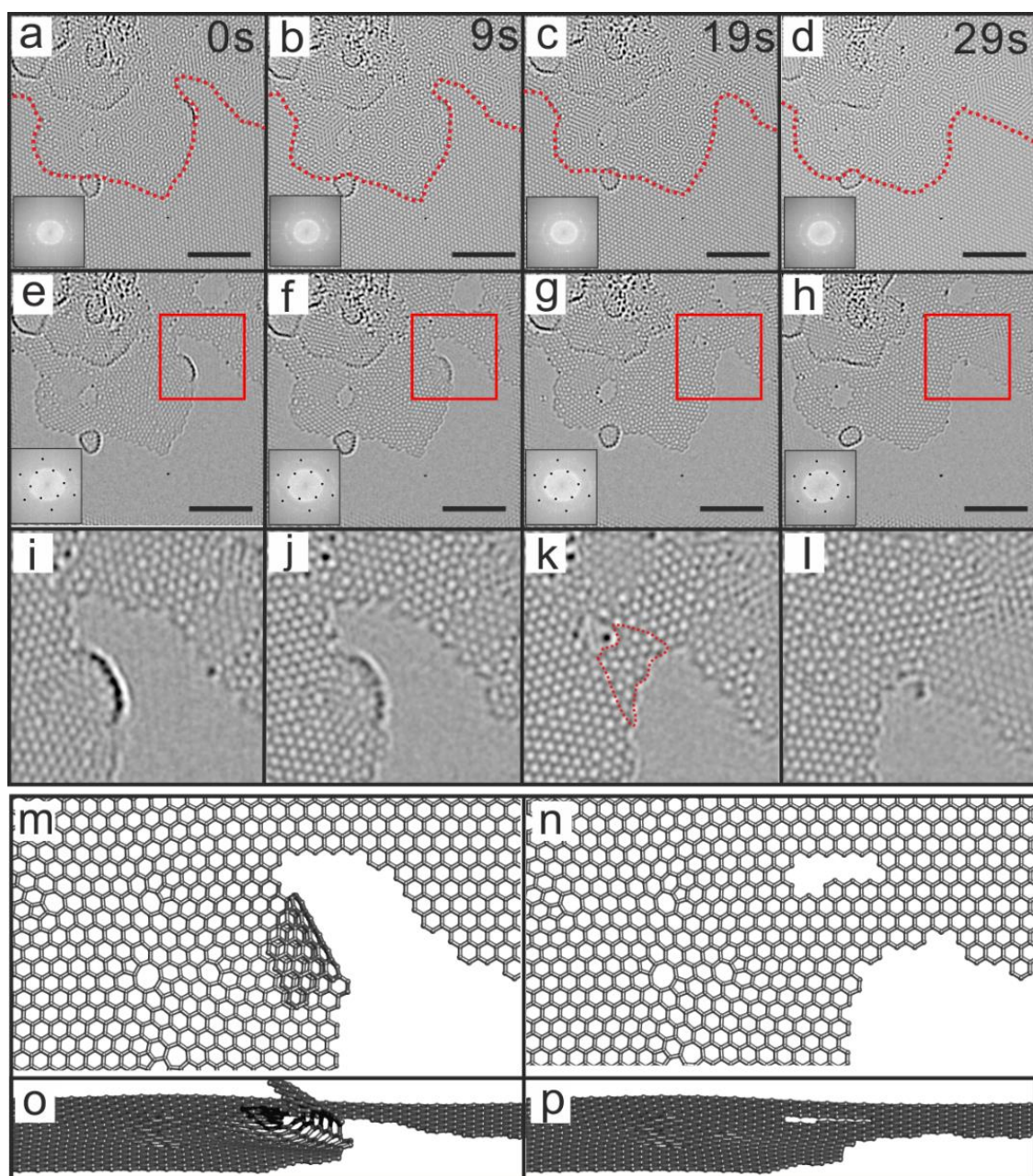


Figure 7-8. Dynamics of the unfolding process at 800°C. (a–d) are time series AC-TEM images of second-layer graphene grown at 800°C, with the FFT shown in the respective insets. (e–h) are reconstructed images from the FFT negative mask shown in the respective insets. (i–l) are magnified images taken from the red boxed regions in (e–h) to highlight the dynamics of the second layer unfolding process. The red dashed line highlights the area of graphene gain from the unfolding process. (m–p) are both front and side views of the atomistic model before and after unfolding. Scale bar = 4 nm.

Parallel to the unfolding process, the edges were also found to fold themselves at high temperature. Figure 7-9 (a–c) are time series AC-TEM images of second layer graphene folding back at 700°C under electron beam irradiation. In Figure 7-9 (a), the edge of second-layer graphene still has weak contrast, which corresponds to an open edge. Over the course of 378 seconds, the dark contrast line slowly propagates around the boundary of the second layer and finally reaches the states shown shown in Figure 7-9 (c). The yellow shaded area in Figure 7-9 (b) shows the difference in area after back-folding. The three atomic models schematically illustrate the edge initially being lifted and then back-folded to form the dark contrast. This verifies further that the second-layer graphene edge did not bond with the layer below it.

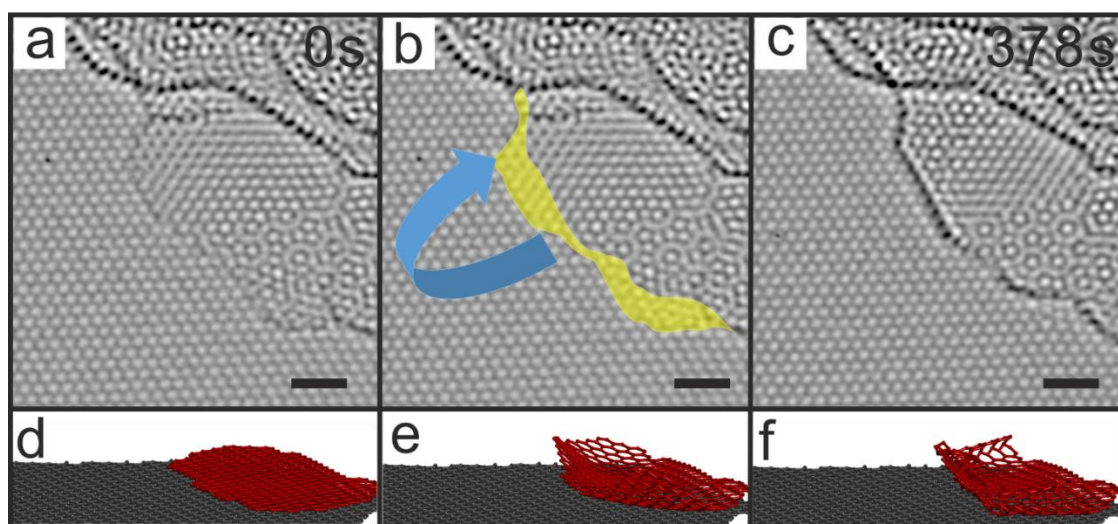


Figure 7-9. Dynamics of the second layer folding process at 700°C. (a) Second-layer graphene grown at 600°C, with its atomistic model shown in (d). (b) Yellow shaded area highlights the ‘missing’ area comparing before and the after edge folded back. The atomic model in (e) demonstrates the initiation of the folding back process. (c) The edge of the second layer shows an increase in contrast, indicating the completion of the folding back process, with the atomistic model shown in (f). In (d–f), the grey coloured lattice represents the initial base layer of graphene, the red coloured lattice represent second-layer graphene grown at 600°C. Scale bar = 2nm.

7.6 Multilayer growth

It was also found that extra layers (≥ 2 layers) could form when the temperature stayed at 600°C. In Figure 7-10 (a–f), the red dashed lines show the growth front of the newly-formed extra layer, which either originates from the folded second layer or simply from extra heterogeneous nucleation steps. The growth rate of this specific layer is estimated from fitting a linear equation to the six data points acquired from areas measured in AC-TEM images: the layer is estimated to grow at a rate of 0.03nm²/s, slower than the second layer growth. CVD of graphene on Cu substrate is known to be self-limiting due to the surface adsorption nature of the reaction, this process is explained in section 2.3.2.^{5,9,45} However, multilayer graphene still forms on Cu if the parameters for gas introduction and reaction temperatures are not adjusted correctly. By correlating this with the multilayer growth results obtained in this experiment, we may potentially be able to shed light on a new possibility: that some of the multilayer graphene is formed during the CVD process. When the copper surface is fully covered with graphene, and no more active sites are available to catalyse graphene growth, multilayer graphene can still form by either an edge folding back and growing in the opposite direction, or by extra layer growth activated by heterogeneous nucleation; that which occurred in Figure 7-10, but on a larger scale and at a faster speed in a CVD system. When CVD-grown graphene is transferred onto a TEM grid by the standard PMMA-assisted transfer method, the edges of graphene are mostly found to be folded edges.⁷ These edges are widely used to determine the number of layers. This reflects the importance of graphene back-folding, and indicates new prospects regarding the multilayer graphene growth mechanism.

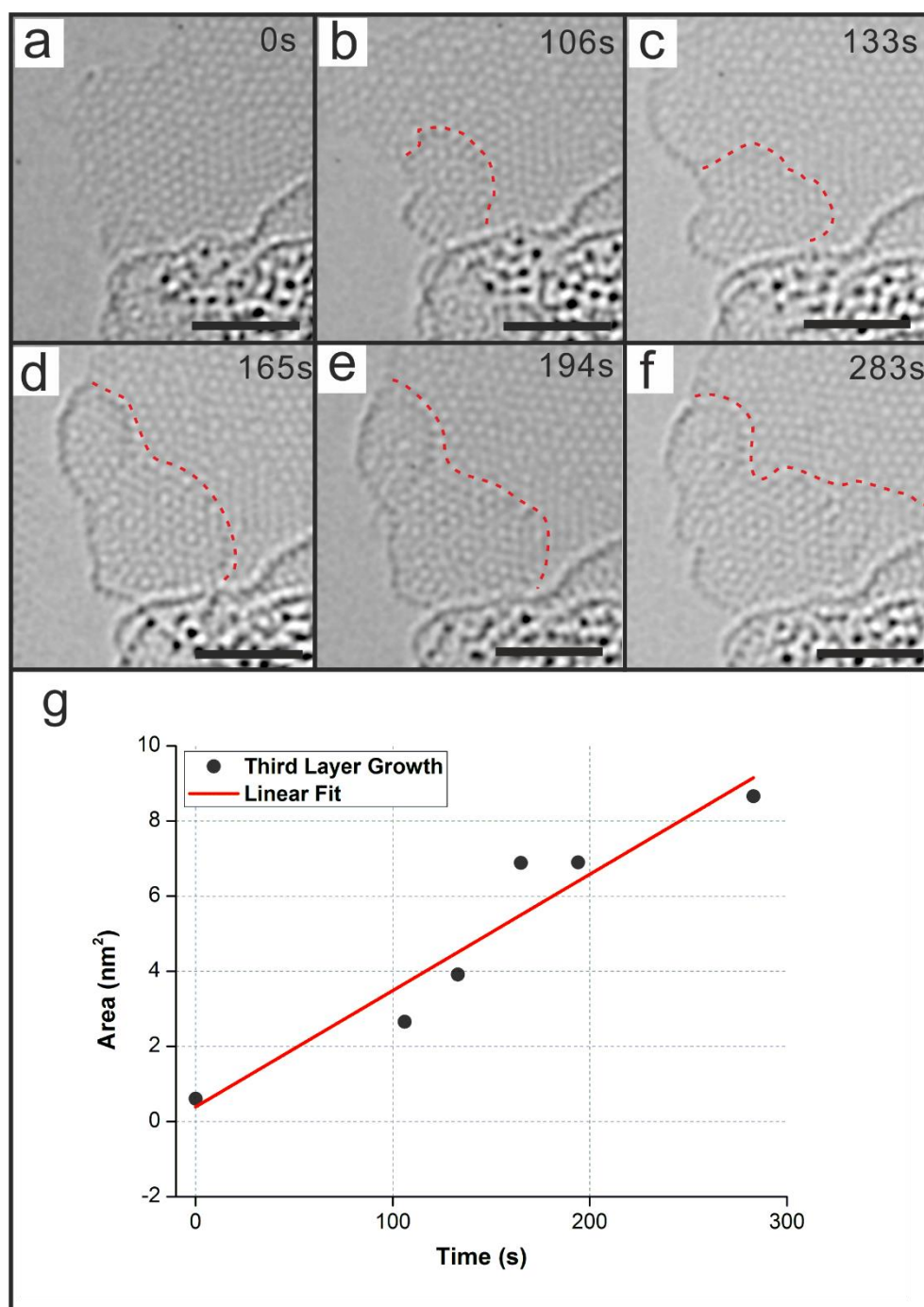


Figure 7-10. (a–f) Sequential FFT negative mask reconstructed frames showing the growth of folded second-layer graphene. The dashed red lines indicate the new growth frontier of the folded second-layer graphene at 600°C. Scale bar, 2 nm. (g) The area of back-folded second layer graphene and growth at 600°C, plotted against time and fitted with a linear equation. Scale bars, 2nm.

7.7 Conclusion

My results have demonstrated that heating graphene to 800°C, followed by reducing the temperature to 600°C using a high temperature *in situ* holder, removes the surface contamination on graphene and enables examination of graphene lattice. We found that graphene starts to nucleate around the Au nanoparticles and continues growing while the electron beam keeps irradiating the sample. This is consistent with classical nucleation theory. The mechanism for growth front propagation is found to be an alternating process of atom cluster deposition and indentation filling. A more detailed study of the edge reveals that the darker contrast lines that are occasionally observed arise from back-folding. They are also observed to continue growing at 600°C in a TEM environment.

7.8 References

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Chapter 8

Formation of Closed Edge Nanopores in Graphene

8.1 Introduction

Graphene nanopores have been extensively studied, both experimentally and theoretically, primarily in relation to application in emerging technologies for single-ion channels,¹ single-molecule detection,² and liquid purification.^{3–7} The experimental sequencing of DNA using graphene technology is also rapidly advancing.^{8–10} Folded and non-folded DNA molecules can be distinguished by their different levels of conductance when passed through graphene nanopores. Moreover, theoretical studies suggest that the conformation of DNA nucleotides in a graphene nanopore can be controlled through precise engineering of the nanopore surface. In consequence, strand sequencing of DNA by measuring the ionic current blockade in graphene nanopores is possible, enabling fast and inexpensive DNA sequencing technology.^{11–14}

Due to these important potential applications, the introduction of a nanopore into a graphene sheet in a controlled way has been widely studied.^{15,16} Helium ion drilling, EBL, focused electron beam irradiation, block copolymer lithography, defect-selective electron recoil sputtering, and focused ion beam direct writing are among many approaches that have been applied to the creation and size control of graphene nanopores.^{16–22} However, small nanopores are often back-filled with both carbon and

foreign atoms in a self-healing process due to the dangling bonds at the edge of the nanopore,^{23–26} and this instability is detrimental to the functionality and lifetime of the nanopores. Thus, the development of approaches to prevent the filling of graphene holes after creation is a crucial step to improving their lifetime and consequently their application in solution environments. One way to do this is to eliminate the highly reactive dangling bonds associated with the edges of graphene holes. A previous study has utilised Si atoms to stabilise graphene nanopores by bridging the dangling bonds around the perimeter of the hole.¹⁵ However, functionalisation of graphene edges still results in polar functional groups that are attractive to ionic species in solution. Elimination of polar or dangling bonds could be achieved by forming closed edge pores in bi-layer graphene, similar to the edge of a carbon nanotube or a back-folded graphene layer, where all C-C bonds are sp^2 in nature, but where their flexibility enables bending and curvature of the lattice, and subsequently sealing of the edges.

The utilisation of electron beams within the TEM for drilling holes into multi-layered graphene is well established.^{18,27–31} The additional use of an *in-situ* heating holder can also be applied to control the deposition of amorphous carbon.^{29,31} To selectively remove the layers in multi-layered graphene, a top-down approach can be applied in which an electron beam at an energy beyond the graphene sputtering threshold voltage (>80 keV) is focused onto an area of interest to decrease the number of layers, eventually leading to the formation of nanopores of the desired size.^{28,30} However, the nature of electron beam sputtering is such that the back layer of a multi-layered graphene sheet is eroded first.³² This leads to the back layer having a larger pore size, which in turn means that the holes in each layer do not have aligned edges and it is hence difficult for the edges in adjacent layers to bond, forming a closed edge nanopore.

To overcome this challenge in forming closed edge nanopores within monolayer graphene, I have exploited hydrocarbon surface adsorbates that are known to condense on graphene at room temperature. I show that a combination of controlled electron beam irradiation and variable temperatures can lead to stable closed edge nanopores in graphene. Using an *in situ* heating holder has enabled me to study the structural changes of the same atoms between room temperature and 800 °C. This ability to track the same group of atoms reveals the detailed transformation of a nanopore and consequently demonstrates control over the size of the closed edge nanopores.

8.2 Schematic illustration of closed edge nanopore formation

Open or closed edges and folded edges, have been extensively studied in graphene.^{33–36} The schematic model in Figure 8-1 (a,b) shows bi-layer graphene in its intrinsic open edge state and in its closed edge form, with bonds between the upper and lower layer that saturate the dangling bonds. Monolayer graphene is typically covered with a surface layer of hydrocarbons at room temperature, forming a pseudo-bi-layer material, in which one layer is amorphous. Heating to ~ 500°C removes surface adsorbates to leave clean graphene. Understanding these temperature dependent surface chemistry interactions has enabled me to develop a process by which to convert surface adsorbates into a stable secondary layer that includes edge bonds suitable for closed nanopore formation. This process is schematically illustrated in Figure 8-1 (c). The graphene sample was initially heated to 800 °C to allow surface contamination to evaporate, leaving clean graphene, the lattice structure of which could be imaged. Using a previously reported fabrication technique,^{37,38} the electron beam (80keV) was focused to maximise the beam current density($\sim 10^8 \text{ e}^{-1}\text{nm}^{-2}\text{s}^{-1}$),³⁸ to create a, as shown in process 1, Figure 8-1 (c). The sample was then cooled down to room temperature, process 2,

Figure 8-1 (c) which results in hydrocarbons from the microscope environment accumulating on the surface of the graphene.

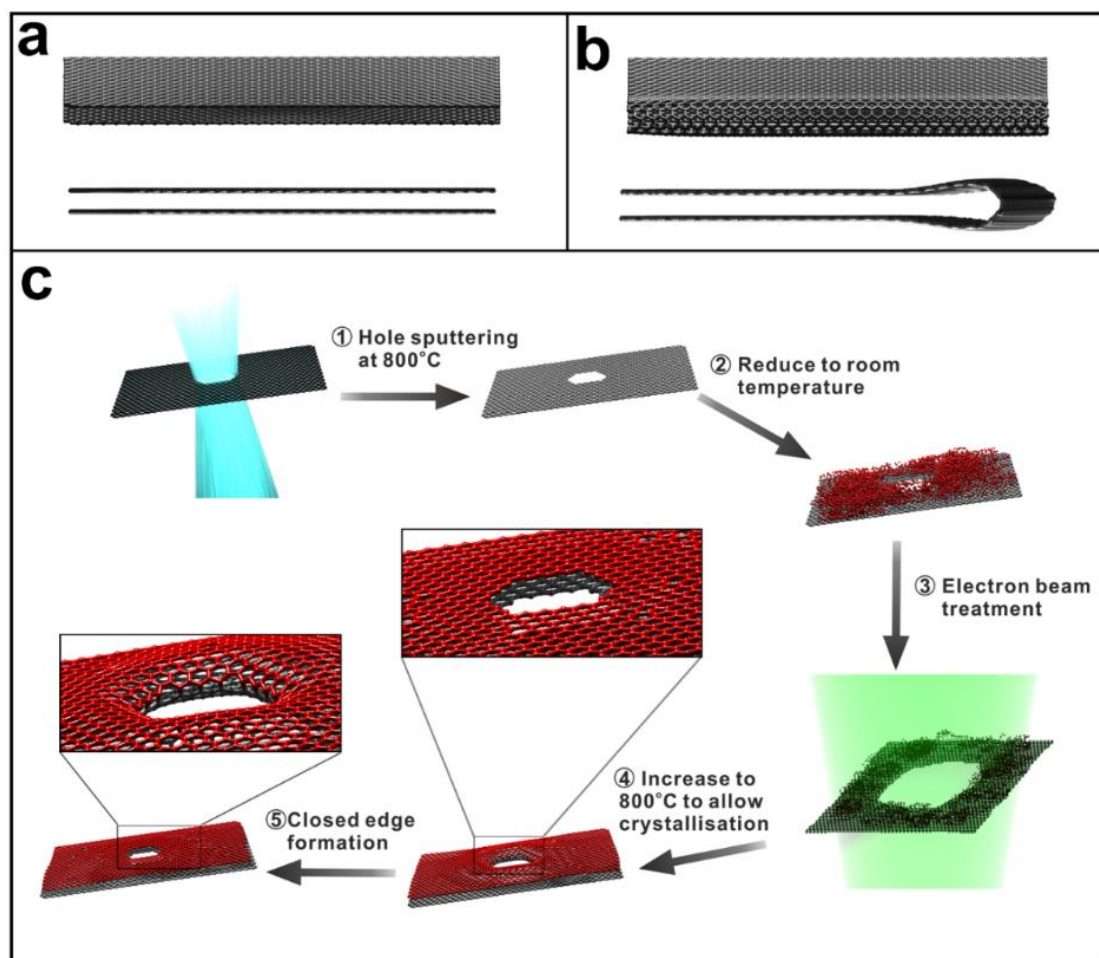


Figure 8-1. Closed edge graphene nanopore fabrication. (a, b) Atomic models of open and closed graphene edges (3D perspective front and side views). (c) Schematic illustration of temperature controlled formation of a stable closed edge graphene nanopore.

The rapid accumulation of the hydrocarbon residues has the effect of surrounding the hole and partially filling some of the nanopore. Exposure to the electron beam for extended periods at room temperature causes the nanopore to be completely filled. Electron beam irradiation of the hydrocarbon residue causes interlayer bonding to the underlying graphene layer, as shown in process 3 and 4, Figure 8-1 (c), in addition to sputtering of hydrogen from the adsorbates to leave primarily carbon atoms, together

with small amounts of residual elements such as nitrogen and oxygen. Reheating the sample to 800 °C causes the bound surface carbons to crystallise, forming a polycrystalline secondary layer. The carbon atoms at the edge of the nanopore consequently bond to eliminate the dangling bonds (process 5).

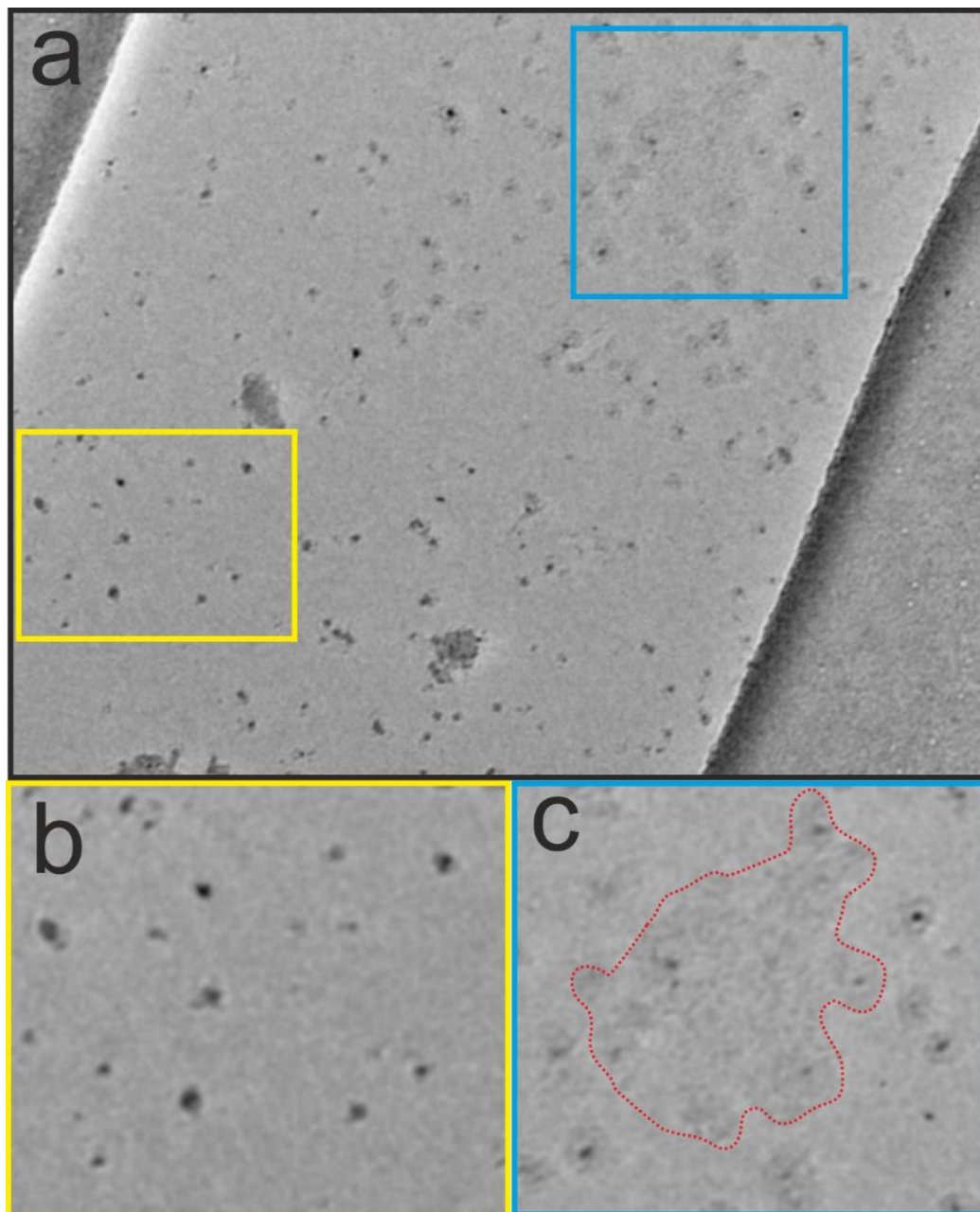


Figure 8-2. Low magnification electron beam sputtering effect study. (a) Low magnification image of graphene suspended across a window on a SiN TEM grid for heating experiments. (b) and (c) correspond to the magnified image of the yellow and blue highlighted regions in (a).

When this temperature cycle is applied to the sample, the nanopore structure is stable in response to further temperature and vacuum level changes, as the added layer does not evaporate due to electron beam irradiation. This is evident in Figure 8-2, which shows that only areas (at 800 °C) that have been exposed to extended electron beam irradiation have kept added layers, whereas carbon sources on the surface of other areas vanish as the temperature is increased from room temperature to 800 °C. Similarly, the treated graphene nanopore can now be reduced to room temperature without being back-filled. The low magnification image shown in Figure 8-2 (a) demonstrates the contrast between the electron beam irradiated area and pristine area. Figure 8-2 (b,c) are magnified images of the yellow and blue boxed regions, respectively. The darker contrast dots are the inorganic nanocrystals on the surface of graphene. Panel (c) shows the electron beam sputtered region and the red dotted line highlighted region shows the surface hydrocarbon layer created during imaging at room temperature, which still remains when temperature is increased back to 800 °C. Panel b is the non-irradiated area and the surface carbon contamination evaporates off again when temperature increases.

8.3 *In situ* TEM of closed edge nanopores formation

Phase contrast AC-TEM images can be used to identify differences between open and closed edges, based on their contrast profiles. I have compared multi-slice image simulations of both atomic models with experimental data. Atomic models of a nanopore in bilayer graphene with both open and closed edges are shown in Figure 8-3 (a,b) and (e,f) respectively, and were used to generate the multi-slice image simulations in Figure 8-3 (c,g). Simulated images of the open and closed edges (Figure 8-3 (d,h)) and analysis of these (Figure 8-3 (i,j)) show that the closed edge gives rise to stronger contrast than the open edge relative to the contrast in the bulk lattice. The ratio between

the intensities of the outermost atoms to the bulk atoms is 1.17 for the closed edge and 1.06 for the open edge.

A further example of several graphene nanopores, which shows the closed edge formation process, is shown in Figure 8-3 (k). This edge structure is similar to the image simulation of a closed edge nanopore. Analysis of a closed edge nanoribbon in Figure 8-4 provides further evidence that bi-layer graphene forms closed edges. The nanoribbon created between two graphene nanopores is seen in Figure 8-4 (a). This helps us further identify the atomic configuration of the edges, i.e. open or closed edge. In Figure 8-4 (b), the lower boundary of the nanoribbon shows an array of periodically separated bright spots, indicating a closed edge. Multi-slice image simulations are shown in Figure 8-4 (c-i). This analysis helped us to further confirm the closed edge formation on the edge and to identify that closed edges are also formed on other nanopores based on the unique feature of the periodic array of bright dots.

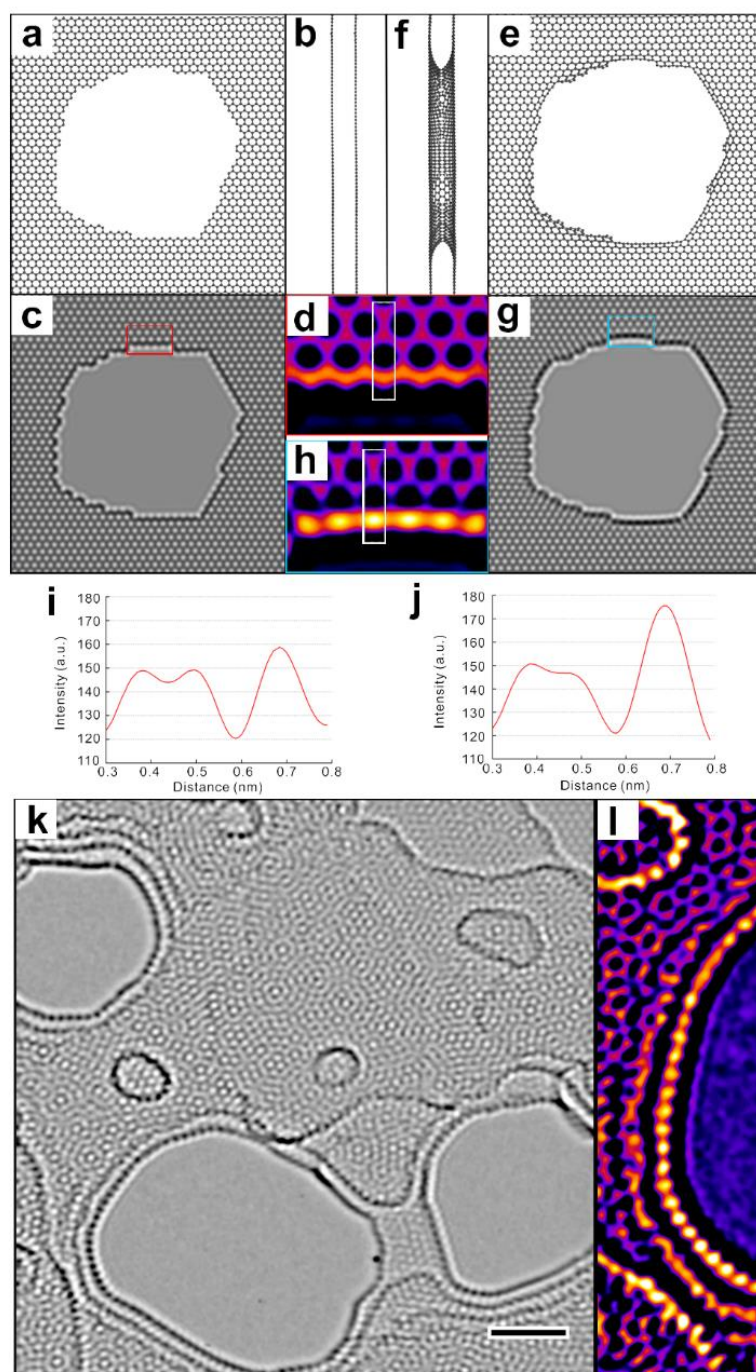


Figure 8-3. Modelling and simulation of open and closed edge graphene nanopores. (a, b) Front and side views of an open edged graphene nanopore. (c) Multi-slice image simulation of the model in (a) with the region in the red rectangle enlarged in (d). The same analysis applied to a closed edge nanopore, shown in (e – h). (i) and (j) Box profiles taken from the white rectangular regions in (d) and (h). (k) AC-TEM image of graphene nanopores with closed edges, magnified in (l). Scale bars, 2 nm.

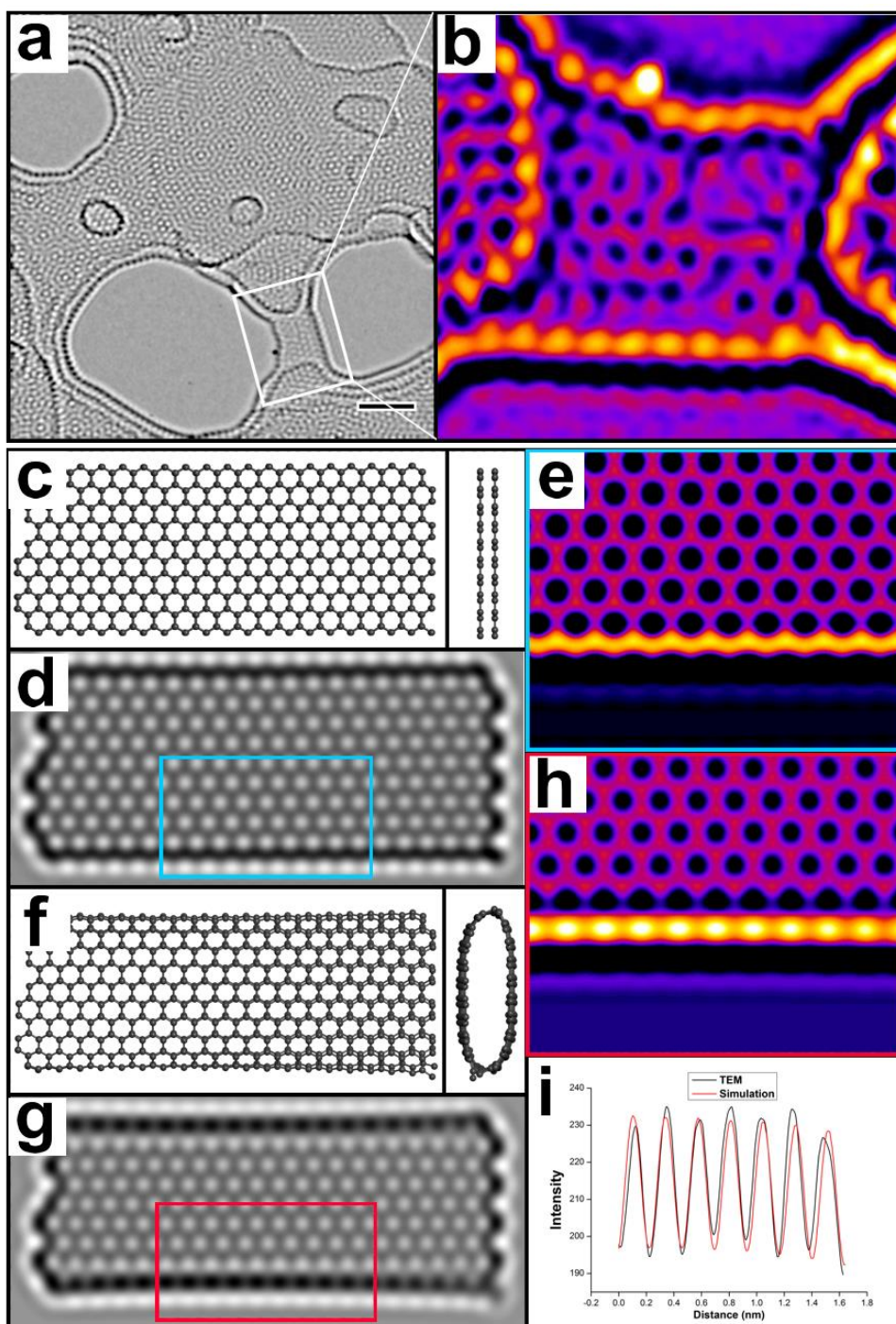


Figure 8-4. Modelling and simulation of open and closed edge GNR. (a) A TEM frame, with the white box highlighting a closed edge bi-layer GNR. A magnified image is shown in (b). (c) is the atomic model of an open edge bi-layer nanoribbon, with its side view shown in the inset. The multi-slice image simulation of the model is shown in (d), and the magnified area of the region highlighted by the blue box is shown in (e). (f-h) are the same analysis applied to the closed edge nanoribbon.

Figure 8-5 shows AC-TEM images of the same area during consecutive stages in the closed-edge nanopore formation process (schematically outlined in Figure 8-1 (c)). A 4 nm diameter nanopore was sputtered from pristine graphene sheet at a temperature of 800°C, as shown in process 1 in Figure 8-5. The temperature was then reduced to room temperature (process 2) and the residual hydrocarbons were allowed to aggregate on the surface of graphene around the nanopore area, followed by further electron beam irradiation. The temperature was increased again to 800 °C to promote crystallisation and the construction of a closed edge (process 3). Finally the sample temperature was lowered to room temperature (process 4) showing that the structure of the closed edge is preserved at the probable working temperature for nanopore applications. Visual comparison between the nanopore edge after process 4 and the edge after process 2 shows significantly stronger edge contrast, typical of closed edge formation.

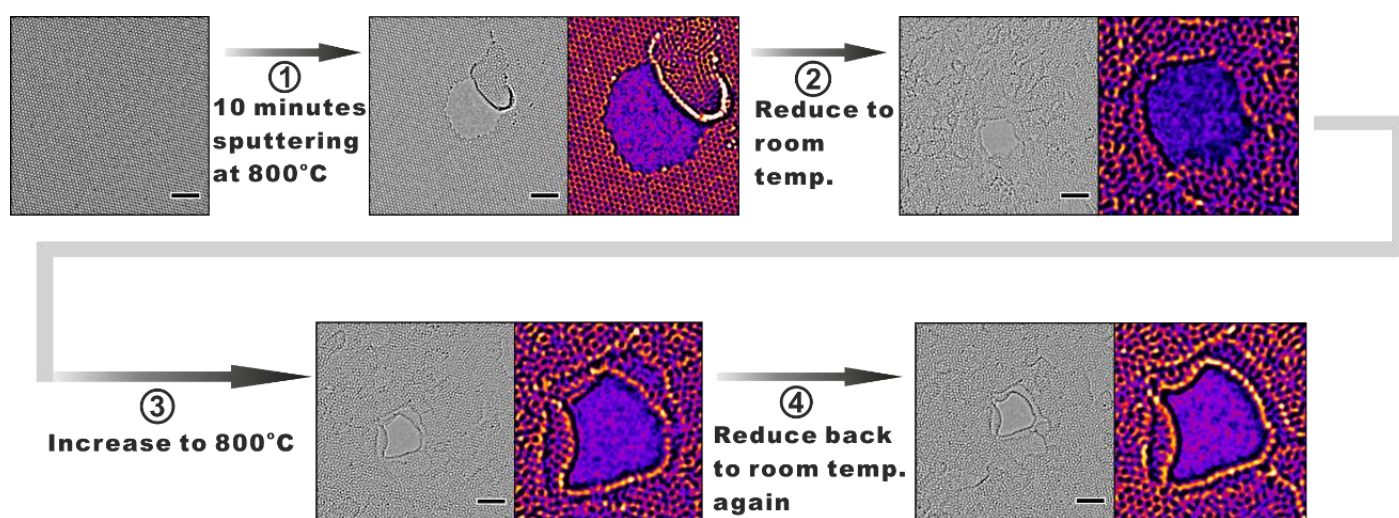


Figure 8-5. AC-TEM images showing the closed edge graphene nanopore experimental fabrication process. All scale bars = 2 nm

8.4 Temperature dependent study of graphene nanopores

Figure 8-6 provides further details that show how the surface hydrocarbons transform from amorphous to nanocrystalline sp^2 regions as the temperature is increased. A nanopore was again initially sputtered at 800 °C (Figure 8-6 (a)). The temperature was then reduced, allowing amorphous hydrocarbons to condense on the surface, as shown in Figure 8-6 (b), and irradiated with the electron beam. The temperature was then increased progressively, in order to monitor the structural evolution of the nanopore. The accumulated hydrocarbons were present in an amorphous state at both room temperature and 400 °C. However, as the temperature was increased from 500 °C to 700 °C (Figure 8-6 (d–f)), the surface carbon starts to crystallise. This is evident from the power spectra shown in Figure 8-6 (g,i) calculated from the highlighted boxed regions in Figure 8-6 (b and f) respectively. The box profile across the central region of the power spectrum (Figure 8-6 (j)) shows two peaks ($d=0.21\text{nm}$) and is characteristic of a polycrystalline sp^2 lattice which is also evident from the Moiré patterns in Figure 8-6 (f). Figure 8-6 (g) has a relatively uniform intensity across the centre of the power spectrum (Figure 8-6 (h)) indicative of an amorphous region. In Figure 8-6 (f), it appears that more than one layer has formed from the crystallisation of the surface adsorbates, but the nanopore still has a closed-edge structure.

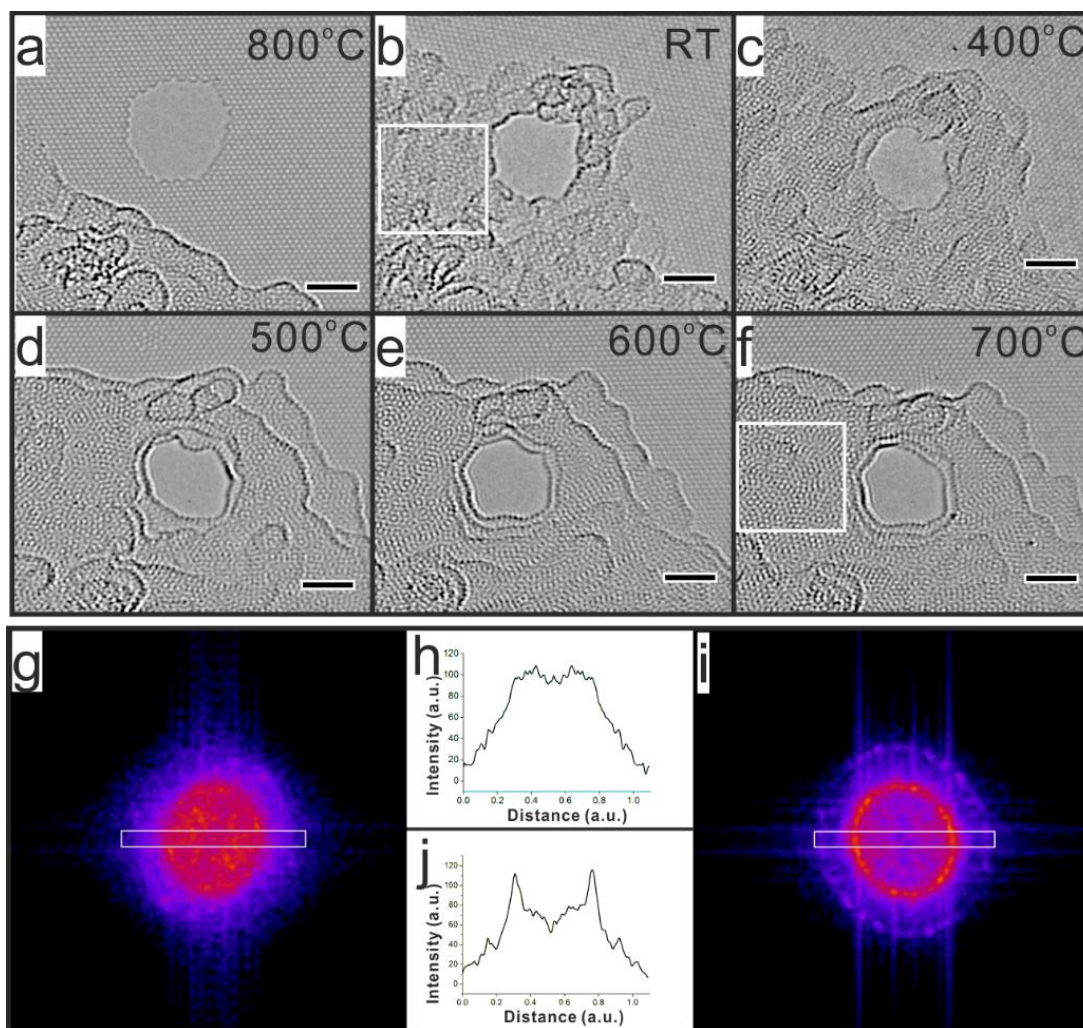


Figure 8-6. Temperature dependent study of graphene nanopores. (a – f) AC-TEM images of the same graphene nanopore at various temperatures indicated. (g) and (i) Power spectra calculated from the highlighted region of (b) and (f) respectively. (h) and (j) Profiles from the white boxed region in (g) and (i). All scale bars = 2 nm.

8.5 Nanopore stability characterisation

Improving the stability of the nanopores is the primary objective of this study and therefore I have examined the stability of closed edge graphene nanopores at room temperature under electron beam irradiation and for a longer period of time without electron beam irradiation. To achieve this a nanopore was created at 800 °C (Figure 8-7 (a)) and subsequently reduced to room temperature (Figure 8-7 (b)). When the

temperature was again increased to 800 °C a closed edge nanopore was created. The temperature was then finally reduced to room temperature and a sequence of images recorded, to monitor the nanopore stability.

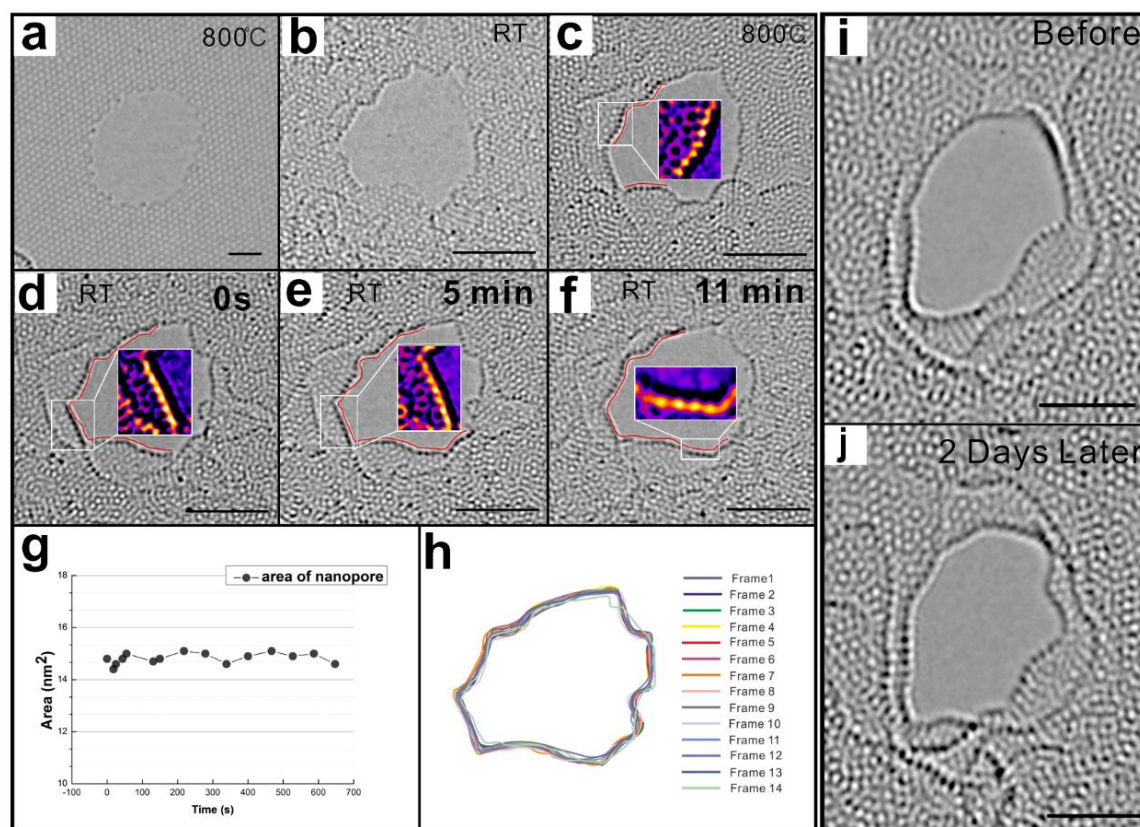


Figure 8-7. Graphene nanopore stability at room temperature. (a) Graphene nanopore in single layer graphene produced at 800 °C. (b) The same pore imaged after the temperature was reduced to room temperature. (c) Increasing the temperature again to 800 °C enables the formation of closed edges. The temperature was then returned to room temperature for a second time and a time series of images was recorded over 11 minutes (d – f). (g) The area of the nanopore during the time series. (h) Perimeter of the nanopore during the time series using 14 frames in total, illustrating the stability of the nanopore shape at room temperature under electron beam illumination. (i) Nanopore directly after fabrication and before exposure to atmosphere. (j) The same nanopore as in (i), but after two days of exposure to atmospheric conditions (outside the TEM). All scale bars = 2 nm.

A total of 14 frames were recorded over 11 minutes and a selection of these are shown in Figure 8-7 (d–f) with the comprehensive data set provided in Figure 8-8. The insets (Figure 8-7 (c–f)) are magnified images from the white boxed regions and the periodic bright features at the edge strongly suggest that these are closed edges. The area of the nanopore in successive frames has been measured and is plotted against time in Figure 8-7 (g). The values fluctuate at around 15 nm^2 with no significant decrease or increase over the course of my observations. The nanopore perimeters in the 14 frames recorded are shown superimposed in Figure 8-7 (h) and no significant deviation from the initial shape is observed. These data indicate that once closed edges are formed, the dangling bonds diminish and edge stability is consequently increased.

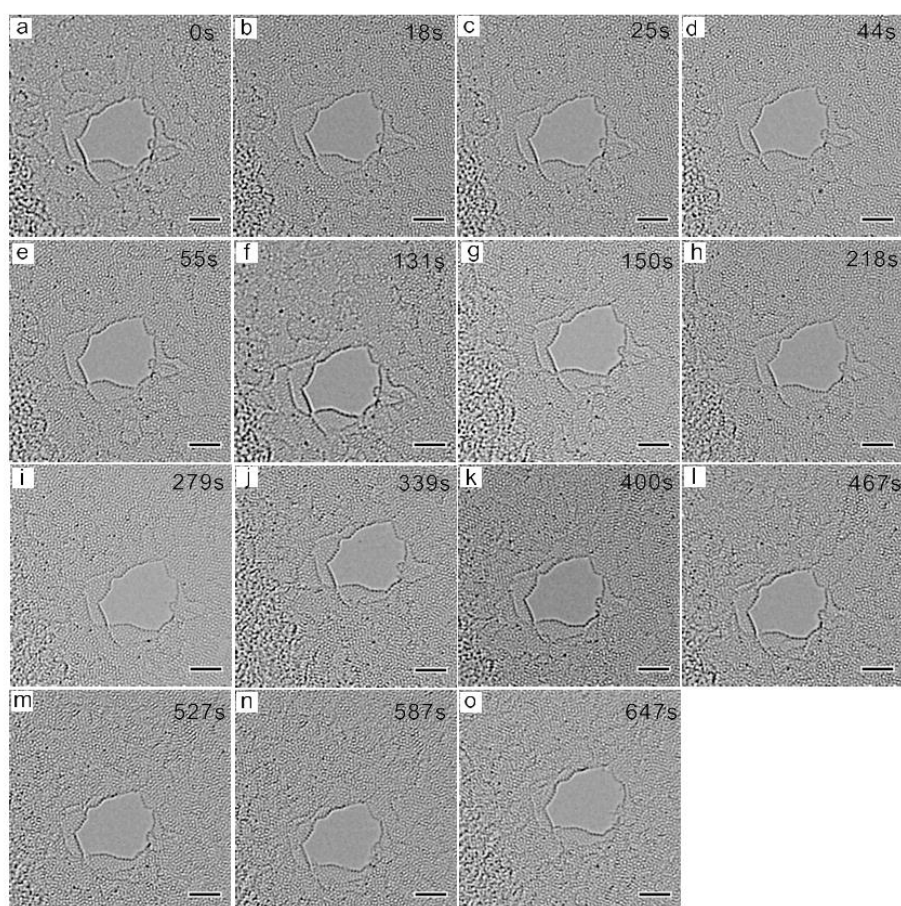


Figure 8-8. (a–o) Full times series of AC-TEM images from which three were taken for Figure 8-7(d–f). All scale bars, 2nm.

This process is effective in preventing the as-created nanopore from being back-filled by ambient carbon sources. The closed edge nanopores have also been tested for stability over an extended period of time. As shown in Figure 8-9 six nanopores were initially created at 800 °C and the previously described closed edge fabrication process was applied. After two days of exposure to atmospheric conditions, the as-fabricated nanopores and their closed edges were intact and showed no signs of clogging. Figure 8-7 (i and j), respectively, show the same nanopore directly after fabrication and then after two days of exposure to the atmosphere outside the TEM. The closed edge nanopore has barely changed, showing that it is extremely robust to exposure to ambient conditions. It was important that the same nanopore was observed both before and after exposure to atmosphere for two days, as the imaging process in the TEM requires electron beam irradiation which can create new holes in the sample that could be mistaken for the nanopores initially fabricated. However, since I have recorded the exact location of the initial nanopore created I am confident that the nanopore shown in Figure 8-7 (j) is the same one seen in Figure 8-7 (i). Constant electron beam irradiation of the closed-edge nanopores also had little effect on their size once they had formed, indicating that the edges are robust against sputtering due their closed nature.³⁹ In contrast, open edge holes are known to be continually sputtered and increase in size with exposure to an electron beam.

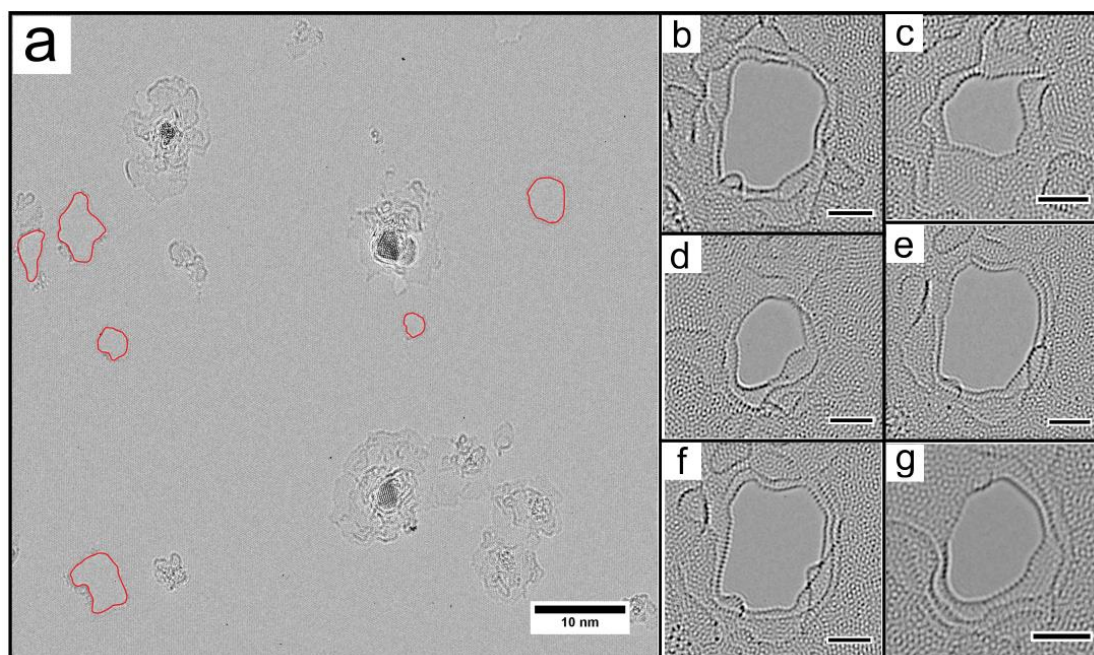


Figure 8-9. Long term stability test of closed-edge nanopores. (a) Low magnification TEM image of the as-created nanopores in graphene at 800 °C. These were then turned into closed edge nanopores using the fabrication method mentioned, and left in air for two days. (b–g) show the same nanopores after two days in air. Scale bars = 2 nm

8.6 Nanopore size control

The ability to control nanopore size is important as it affects the size of molecules that can pass through the nanopores. I demonstrate in Figure 8-10 that the size of the nanopore can be adjusted during both the initial sputtering fabrication step at 800 °C and the carbon source aggregation process at room temperature (process 2 in Figure 8-5). Figure 8-10 (a-d) show four selective AC-TEM frames that form part of the graph shown in Figure 8-10 (q) at 800 °C. In this sequence electron beam irradiation strips off carbon atoms at the edge of the nanopore and this results in an increased size, with a growth rate of $0.01\text{nm}^2/\text{s}$ for the beam current density used. This is a relatively slow process and the average size of the nanopore at this stage could therefore be controlled with nanometre precision. When the temperature is reduced to room temperature,

hydrocarbons adhere and slowly start to fill the nanopore and decrease its area linearly with time, as shown in Figure 8-10 (r).

The four frames shown in Figure 8-10 (e-h) demonstrate the appearance of the nanopore during this process, with the complete dataset shown in Figure 8-11. The area of the nanopore decreased from $\sim 5.2\text{nm}^2$ to $\sim 3.0\text{nm}^2$ over 10 minutes, at a rate of $0.004\text{nm}^2/\text{s}$ (Figure 8-10 (r)). This gradual decrease also allows adjustment of the size of the nanopore with nanometre precision during this process. When the desired nanopore size is reached the temperature was raised to $800\text{ }^\circ\text{C}$ to fix the nanopore size and initiate closed edge formation, which limits any further size modification. Using the techniques described here, closed edge nanopores with sizes ranging from $\sim 1.5\text{nm}^2$ to $\sim 70\text{nm}^2$ were constructed using controlled exposure to the e-beam to determine the initial hole size followed by fixed time at room temperature to control the degree of hole shrinking by carbon adsorbate filling (Figure 8-10 (i-p)).

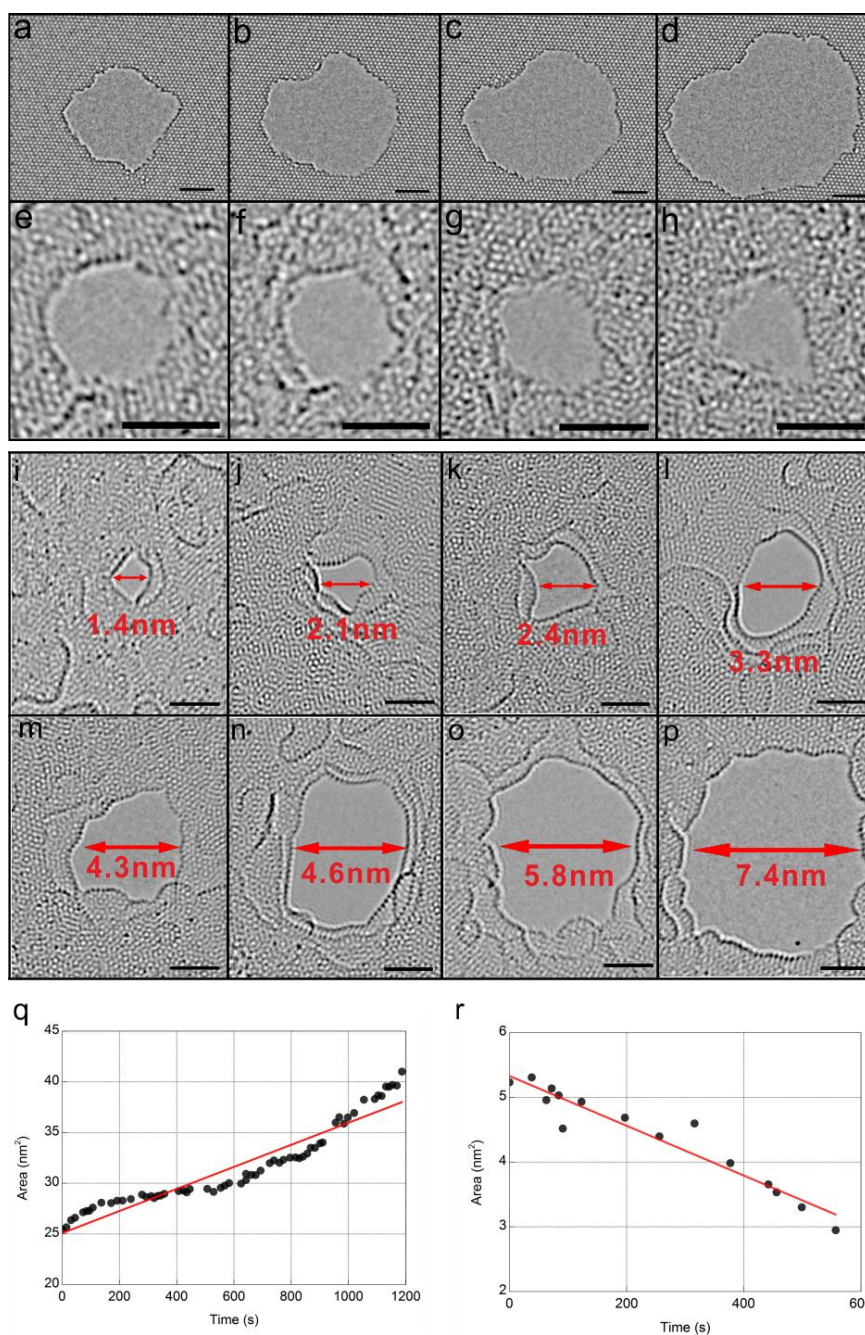


Figure 8-10. Nanopore size control. Nanopore sizes controlled during two separate stages: electron beam sputtering at 800 °C and nanopore shrinkage at room temperature. (a–d) Four selective frames from hole sputtering at 800 °C with the area trend plotted in (q) together with a linear fit. (e–h) Four selective frames from room temperature nanopore shrinkage with the area trend shown in (r) together with a linear fit. Utilising these two control parameters closed edge nanopores with diameters ranging from 1.4 nm to 7.4 nm were fabricated in a controlled manner as shown in (i–p). All scale bars = 2 nm.

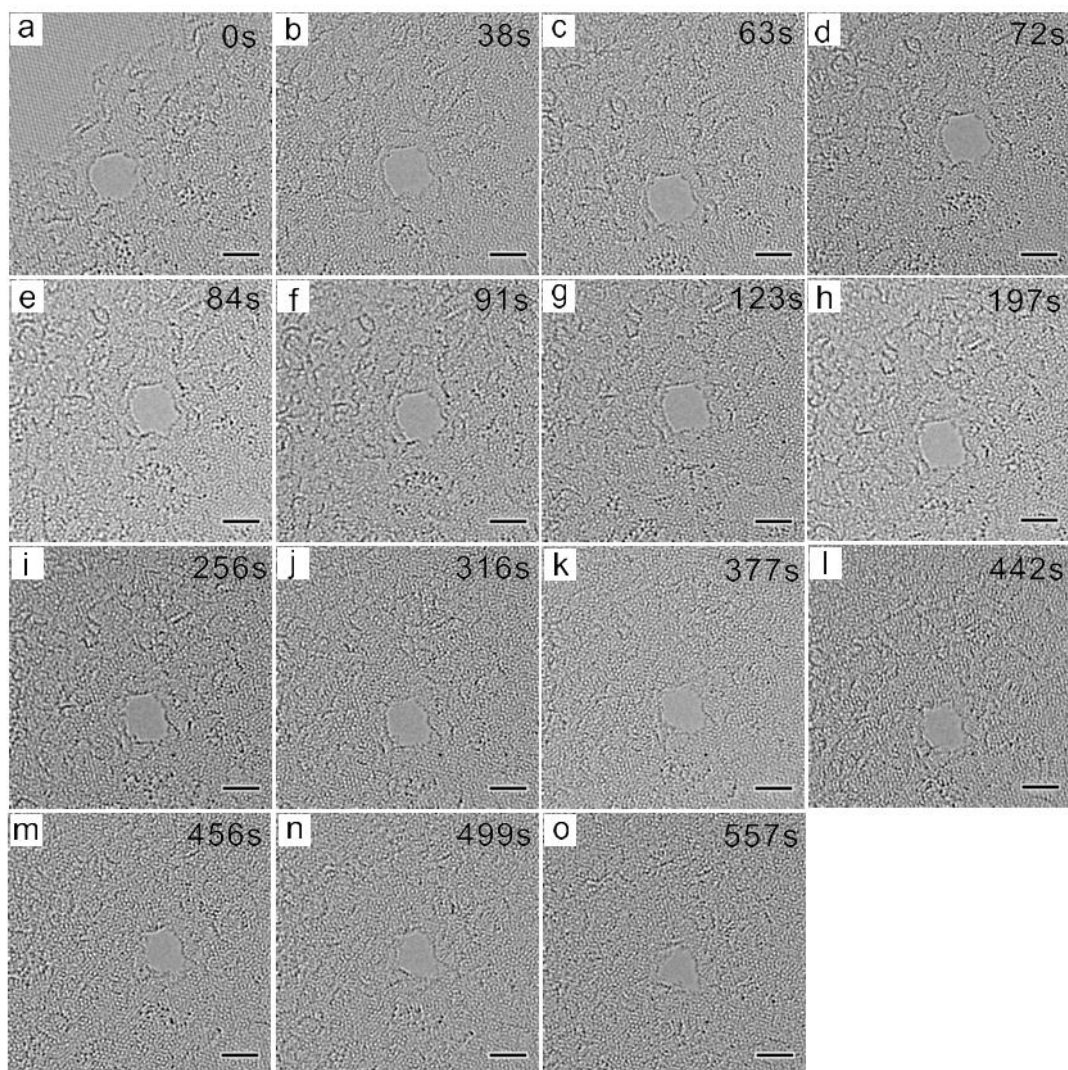


Figure 8-11. Images of graphene nanopores at room temperature after open edge nanopore fabrication at 800 °C. All scale bars = 2nm.

Figure 8-12 shows that back filling from carbon condensation at low temperature (200 °C) occurs when the edges of nanopores are left open which illustrates the significance of closed edges in stabilising nanopores for practical applications. I now show a comparison experiment to demonstrate the effect of back-filling at low temperature (200 °C) if a closed edge had not been formed. Figure 8-12 (a–c) show three selective frames in the AC-TEM time series, the pore size again decreases with time because carbon atoms trapped by the electron beam continue to adhere to the reactive

open edge. The nanopore filled up completely from what was a 22nm² pore over the course of ~40 minutes. This experiment testifies to the significance of the closed edge formation technique developed in this study, to achieve stable and durable nanopores in graphene.

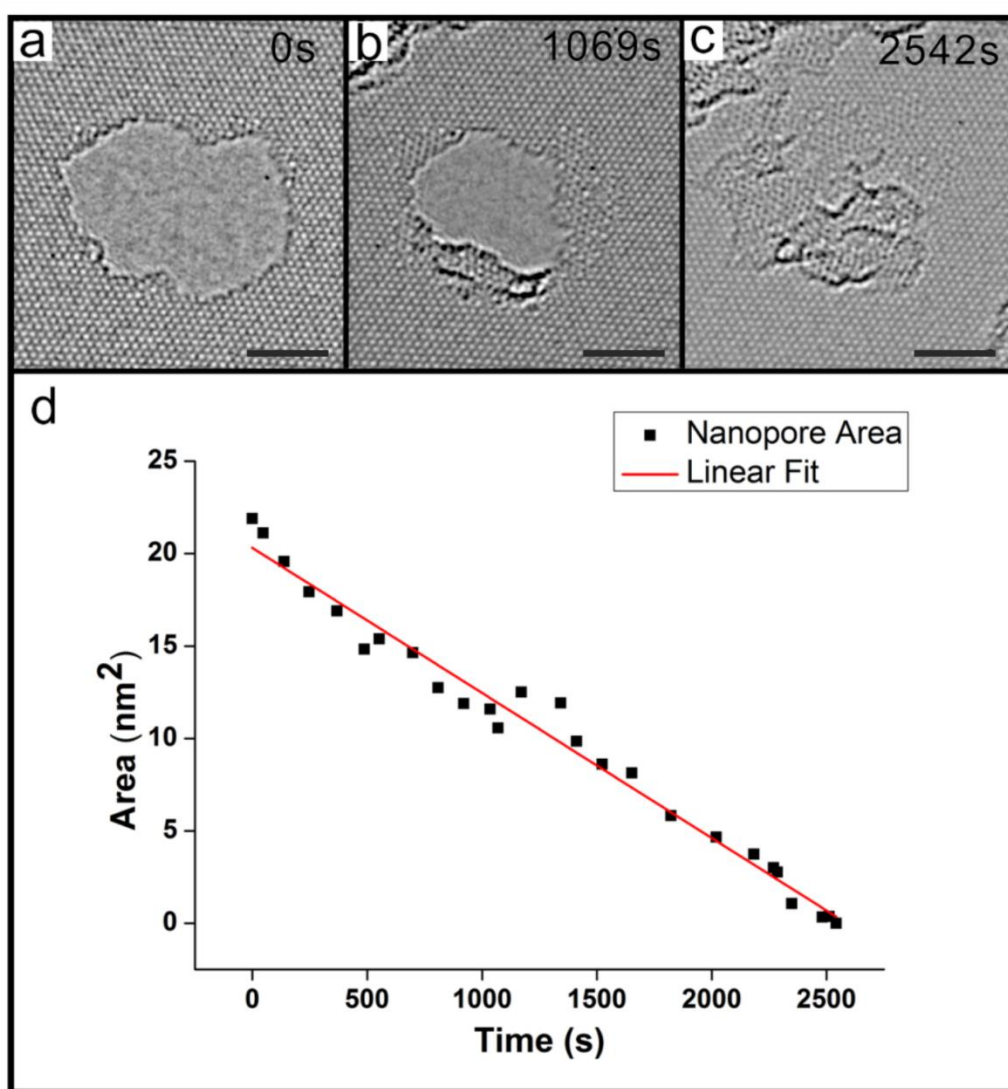


Figure 8-12. Hole-filling at 200 °C. A nanopore was created at 800 °C, then dropped to room temperature. (a–c) Time series of AC-TEM images of the nanopore at 200°C. The change in the area of the nanopore in each image as a function of time is plotted in (d) and fitted with a linear equation. All scale bars = 2 nm.

8.7 Conclusion

Using a stable SiN-based *in-situ* TEM heating chip that exhibits minimal drift, I have been able to accurately control the temperature of a graphene specimen, and to monitor the effect of this temperature on edge structures in graphene nanopores. This has enabled the development of a series of temperature assisted processes that form closed edges in graphene nanopores. The closed edge nanopores were stable during 11 minutes of observation and further experiments showed that they were also stable for up to two days in air. The size of the nanopore can be controlled with nanometre precision by adjusting the electron beam irradiation time at 800 °C during the fabrication process and the time spent at room temperature, during which additional carbon layers are added. This practical method of fabricating closed edges around graphene nanopores may make it possible to address issues arising from the uncontrolled back-filling of nanopores, leading to, for example, instability during DNA and single molecule detection using graphene nanopores.

8.8 References

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Chapter 9

Conclusions, and Future Outlook

9.1 Conclusion

This doctoral thesis has been composed of three broad sections with three broad areas of focus: the CVD method for the synthesis of large area, high quality, monolayer graphene; studying the behaviour of edge atoms at atomic resolution, and under various temperatures *via* AC-TEM imaging; and, finally, understanding the temperature dependent nature of graphene growth in a TEM, and utilising this understanding to fabricate stable nanopores for the purpose of graphene sensor technology and DNA sequencing.

Graphene has physical and chemical properties that are highly desirable for a variety of applications, especially in the electronics industry. However, the lack of a repeatable method to synthesise monolayer, defect free, and clean graphene has perplexed researchers, and has retarded the development of graphene applications. The graphene samples used in the experiments described in this thesis were fabricated using a novel CVD method whereby the temperature was sufficiently high that copper catalysts were in a molten state during reaction; this was then followed by an electrochemical etching process to transfer this graphene onto the desired substrate – in this case, TEM grid.

The atomic resolving power of the AC-TEM (OJ 2200MCO) equipped with monochromator offers a powerful tool to spatially resolve the position of each carbon atom in a graphene lattice – the atom positions at the edge are of specific interest. The

first part of the investigation was designed to understand the hydrogenation of graphene edges: theoretical calculations predict that saturating graphene edges with hydrogen lowers its energy and forms a more stable structure. Despite the importance of this area of study, experimental investigations of whether graphene edges are always hydrogen-terminated have been limited. I have, as described in Chapter 4, studied graphene edges produced by sputtering in vacuum. Direct measurements of the C-C bond lengths at the edge show ~14% contraction relative to the bulk. DFT reveals the contraction is attributed to the formation of a triple bond and the absence of hydrogen functionalisation. Time-dependent images reveal temporary attachment of a single atom to the armchair C-C bond in a triangular configuration, causing expansion of the bond length, which then returns to the contracted value once the extra atom moves on and the armchair edge is returned. Our results provide confirmation that non-functionalised graphene edges can exist in vacuum.

We then started to investigate the periodic structure of graphene edges. Graphene has three experimentally confirmed periodic edge terminations: zig-zag, armchair, and reconstructed 5-7. Theory predicts a fourth periodic edge of graphene, called the EK edge, which consists of a series of single C atoms protruding from a zig-zag edge. In Chapter 5, we confirmed the existence of EK edges in both GNRs and on the edge of bulk graphene, using atomic resolution imaging by AC-TEM. The formation of the EK edge occurs as a result of sputtering and reconstruction of the zig-zag edge. DFT reveals the minimal energy is needed for EK edge reconstruction and bond distortion, both in and out of plane, supporting our AC-TEM observations. The EK edges can now be included as the fourth member of the group of observed periodic edge structures in graphene.

After the study of the periodic structures that can exist at the edge of graphene, we then investigated the temperature dependence of graphene edge terminations at the atomic scale, using an *in situ* heating holder within an AC-TEM, as described in Chapter 6. The relative ratios of armchair, zig-zag, and reconstructed zig-zag edges from over 350 frames at each temperature were measured. Below 400°C, the edges were dominated by zig-zag terminations, but above 600°C, this changed dramatically, with edges dominated by armchair and rec. 5-7 edges. We showed that at low temperature chemical etching effects dominate and cause deviations in the thermodynamics of the system. At high temperature (600 and 800°C), adsorbates are evaporated from the surface of the graphene and chemical etching effects are significantly reduced, enabling the thermodynamic distribution of edge types to be observed. The growth rate of nanopores at high temperature was also shown to be slower than at room temperature, which is indicative of the reduced chemical etching process. These results provide important insights into the role of chemical etching effects in nanopore formation, edge sputtering, and edge reconstruction in graphene.

The next step was to investigate *in situ* second-layer graphene growth in a TEM. As described in Chapter 7, we investigated the use of an *in situ* heating holder to allow us to heat the sample to 800°C to achieve a clean graphene surface, and then to 600°C for graphene growth. Second layers were found to heterogeneously nucleate around gold nanoparticles. The growth mechanism were found to be an alternating process of atom cluster deposition and indentation filling to maintain the low energy of the growth front. By carefully studying the dynamics the darker contrast lines that were occasionally observed during growth these were correlated with back-folding. It was also found that graphene would keep growing in the opposite direction after the back-folding, leading to new possibilities as regards multilayer formation.

After the second layer study, I then attempted to develop a method to stabilise graphene nanopores, to make them more suitable for real life applications, as discussed in Chapter 8. Dangling bonds at the edge of a nanopore in monolayer graphene make it susceptible to back-filling by atmospheric hydrocarbons at low temperatures, leading to potential instability in nanopore applications, such as DNA sequencing. We showed that closed edge nanopores in bi-layer graphene are robust to back-filling under atmospheric conditions for days. A controlled method for closed edge nanopore formation, starting from monolayer graphene, was reported using an *in situ* heating holder and electron beam irradiation within an AC-TEM. Tailoring of the closed edge nanopore sizes was demonstrated from 1.4nm to 7.4 nm. These results should provide mechanisms for improving the stability of nanopores in graphene for a wide range of applications involving mass transport.

9.2 Future outlook

The logical next step of the experiments carried out in this thesis is to correlate the structure information gathered from AC-TEM imaging and the electronic properties of graphene nano-constrained structures. By utilising the *in situ* electrical measurement, it will be possible to directly quantify the types of edges and the effect edge roughness has on electrical measurement. This will allow better understanding of nano-engineering.