

SYNTHESIS AND CHARACTERISATION OF LARGE AREA GRAPHENE

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Submitted in conformity with the requirements

for the degree of DPhil in Materials Science

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March 2013

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Abstract

The pursuit of high quality, large area graphene has been a major research focus in contemporary materials science research, in the wake of the discovery of the multitude of exceptional properties exhibited by the material. The DPhil project was undertaken with the objective of developing an understanding of the growth of large graphene sheets by chemical vapour deposition (CVD), and also in the subsequent characterisation of their material properties.

By conducting atmospheric pressure CVD growth at high methane flow rates, it was found that few-layered graphene (FLG) could be deposited on a copper catalyst. It is demonstrated that the self-limiting property of a copper catalyst is not universal to all deposition conditions, and shown that FLG grows in a terrace-like configuration.

In depth transmission electron microscopy (TEM) studies were carried out on FLG. By selective image reconstruction from the inverse power spectrum of the TEM images, it was possible to elucidate the inter-grain connectivity of few-layer graphenes. It was determined that there were two possible inter-grain configurations possible; specifically an overlap of graphene layers or a discrete atomic bonding edge. The perturbation of the few-layer structure when subject to an out of plane distortion was found to incur a shift in the conventional AB-Bernal stacking of FLG.

By utilising the aberration corrected TEM (AC-TEM) at Oxford it was possible to resolve atomic detail in CVD synthesised monolayer films, including atomic bond rotations and vacancies. The use of a high current density at low accelerating voltage (80 kV) was demonstrated to allow for the controlled defect creation in graphene sheets. This permitted the creation of monovacancies and iron doped vacancy complexes suitable for further study. The behaviour of these two defect types under electron beam irradiation was subsequently studied.

Acknowledgements

Executing the research outlined in this thesis would not have been possible without the contribution, advice and support of my supervisors and fellow academics, or indeed from friends and family. Firstly, I would like to express gratitude and profound thanks to my supervisor, Dr. Jamie Warner, for providing me with patient guidance and tuition throughout the project. The success of this PhD project owes a considerable amount to his excellent supervision. Prof. Andrew Briggs, in his role as my senior supervisor, was a valuable mentor and supported me throughout with encouragement and wisdom. As such he also deserves special thanks.

Several people have supported me during this project with their specialist expertise and knowledge when using certain facilities. Mr. Paul Pattinson was always convivial and quick to assist with experiments conducted in the Physics Department's clean room facilities. Dr. Radka Chakalova was consistently kind and helpful when using the Materials Department's clean room equipment. Dr. Sverre Myhra provided a deep insight into the workings of the AFM, which greatly aided in its use. The expertise and generous support of Dr. Judy Kim on the use of the AC-TEM was greatly appreciated, as well as for her assistance in analysing graphene TEM data.

Some of the work in this thesis would not have been possible without the input from collaborators, and so I would like to thank Dr. Barbara Montanari and Prof. Nicholas Harrison for their modelling of defect structures that cast valuable insight into their behaviours. I would also like to thank Prof. Angus Kirkland for his support in using the Oxford AC-TEM facility, and also for provision of post-doctoral funding after thesis submission to do further research in this exciting area.

I would also like to thank my office and group mates, including Benjamin Farrington, Yimin Wu, Christopher Allen, Kuang He and others, whose continued friendship has been a pleasure. Finally, I would like to thank my family; my mother, father and sister all for their constant support and encouragement.

Publications

Presented here is a list of published works completed during the course of this project.

Following are brief notes on where the relevant section of the thesis may be found, if applicable. Some of the co-author work listed here lies beyond the purview of this thesis.

1. Wang, H.; Luo, J.; Robertson, A.; Ito, Y.; Yan, W.; Lang, V.; Zaka, M.; Schäffel, F.; Rummeli, M. H.; Briggs, G. A. D. *et al.* High-performance Field Effect Transistors from Solution Processed Carbon Nanotubes. *ACS Nano* **2010**, *4*, 6659–64.
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Ref. [4]. Chapter 4.

Ref. [5] and [8]. Chapter 5.

Ref. [10]. This work was led by other group members; however the resultant graphene growth method was used in Chapter 6 and Chapter 7. It is covered in section 3.2.2.

Ref. [11]. The Geometric Phase Analysis (GPA) method I used is covered briefly in section 3.7.

Ref. [13]. Chapter 6.

Ref.[14]. A section on exploiting graphene in devices was authored by me for this book, the research for which was used in writing section 2.3.2 - 2.3.7.

Section 2.6 uses writing from a review piece in ref. [16].

Chapter 7 is based on research published in ref. [15,17].

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Chapter 1

Introduction

1.1 Project Aims

The objectives for this doctorate project have been to establish and develop the facilities and techniques for the synthesis of large area graphene, and subsequently evaluate the material properties of the product by a range of characterisation techniques.

1.2 The Scope of this Thesis

The thesis covers the work that has been carried out over the course of 3½ years of EPSRC PhD funding at the Materials Department, Oxford. The literature review chapter includes discussions on graphene's properties, its synthesis, characterisation and some of the potential uses.

The chapter on chemical vapour deposition (CVD) synthesis of graphene is the result of the work involved in the establishing of a CVD system for the group, including the first results obtained from it. Later work on the CVD of graphene was subsequently led by other members of the group, principally Dr. Yimin Wu, and as such is beyond the scope of this writing.

The project focus later shifted toward the characterisation of the CVD grown graphene by transmission electron microscopy (TEM) study. By utilising the TEM facilities at IFW

Dresden, Dr. Jamie Warner obtained high quality data from our CVD grown few-layer graphene. The study and analysis of this data constitutes the chapter on TEM characterisation of few-layer graphene.

By harnessing the latest CVD graphene synthesis techniques developed in our group by Dr. Wu and Mr. Fan, it was possible to synthesise high quality monolayer graphene for study by TEM. The Oxford-Jeol 2200 aberration corrected TEM (AC-TEM) permitted up to atomic resolution capabilities when characterising these graphene samples. The final two results chapters are on the work accomplished by employing this facility. Images here were taken by Dr. Warner, Mr. He and myself over the course of four one week sessions.

A final chapter will attempt to summarise and conclude the presented work. Here also will be discussed the potential for future work, and a brief outline of a project that could be carried out.

Chapter 2

Literature Review

2.1 Introduction

In this chapter a review of the nascent field of graphene research is presented. Particular attention shall be paid to areas germane to the thesis subject; namely synthesis and characterisation. An overview of graphene's structure, properties and suitability for applications, a comparison of the currently available techniques for the synthesis of graphene, and how favourably these translate to various prospective uses, shall be discussed. Characterisation tools and techniques, with a particular skew toward transmission electron microscopy, comprises the last major component of this chapter, with a brief concluding discussion that together reviews the synthesis, characterisation and properties through the lens of bringing graphene from the laboratory to the factory production line.

2.1.1 What is Graphene?

Graphene is the two dimensional incarnation of graphite; a single layer cleaved from the graphite surface (see Figure 2.1). The sp^2 bonding hybridisation of the carbon atoms leads to the formation of a regular hexagonal lattice, akin to some of the other carbon allotropes such as carbon nanotubes and Buckminster fullerene. However, the two dimensional nature of graphene makes it nearly unique in materials science, barring a

few other examples; such as monolayer boron nitride, BSCCO - bismuth strontium calcium copper oxide -, niobium diselenide and molybdenum disulphide.¹ This intrinsic flatness, and the accompanying unique properties, has attracted as much attention from the theoretical physics community as it has from experimental scientists.²

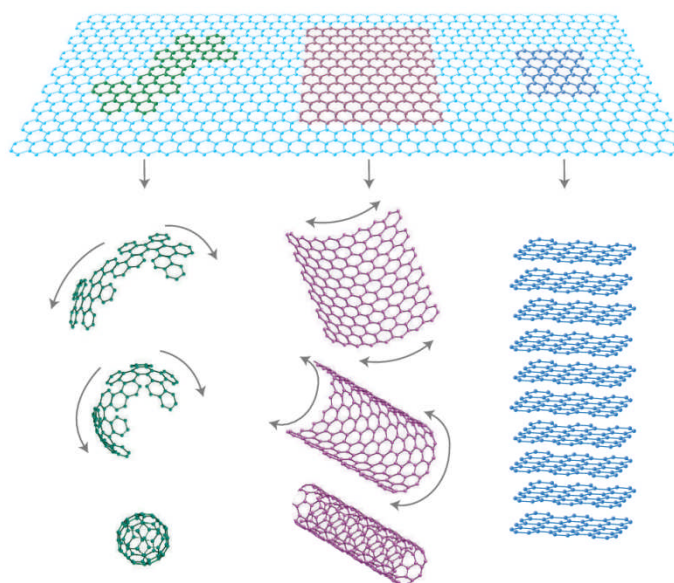


Figure 2.1. Graphene has the same hexagonal ‘chicken wire’ structure as unwrapped carbon nanotubes. The parent graphite structure constitutes many layers of graphene stacked in parallel. Reprinted by permission from Nature Publishing Group: Nature Materials [3], copyright (2007).

The two dimensional structure of graphene allows for a peculiar quirk in its electronic properties, in that the charge carriers behave as massless Dirac fermions, akin to charged neutrinos. The virtually massless nature of the carriers leads to exceptionally high intrinsic mobilities, reaching $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K for graphene on SiO_2 .⁴ Suspended graphene, detached from the deleterious effects of substrate interaction, has been shown to exhibit carrier mobilities as high as $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁵⁻⁷ The study of graphene's peculiar electronic properties also provides a means of observing quantum

electrodynamics through experiment, such as the fractional quantum hall effect (QHE).^{8,9}

2.1.2 History

The Nobel laureates Prof. Andre Geim and Prof. Konstantin Novoselov, based at the University of Manchester,⁴ are widely attributed as the first to successfully isolate free standing graphitic films, which was accomplished by the micromechanical cleavage of highly oriented pyrolytic graphite (the ‘Scotch tape’ method). While it is certainly the seminal publication that catalysed the present flurry of interest, it was not the first mention of graphene, or exfoliation of graphite, in historical literature. Indeed it was perhaps less the exfoliation of graphite yielding graphene, and more the confluence of a cheap and facile synthesis technique with the discovery of novel electrical properties further pursued by Profs. Geim and Novoselov in their paper. The later experimental confirmation of the Dirac fermion nature of the charge carriers,¹⁰ with further critical work carried out by Prof. Philip Kim at Columbia University,¹¹ guaranteed the rapid rise in interest and subsequent development of the field.

The earliest record of the exfoliation of graphite comes from a paper published in 1840 by Schafhaeuti,^{12–14} where he treats graphite flakes with nitric acid followed by sulphuric acid and yields “a graphite so much swollen as to fill up the whole lower part of the crucible”. Over a century later in 1962, Boehm identified single graphene sheets by TEM,¹⁵ and determined their thickness by measuring the relative absorbencies. These flakes were obtained by oxidising graphite, which increased the interlayer spacing of the graphene planes considerably, thus permitting the intercalation of polar fluids in between the planes and yielding graphene oxide films. The oxide product could be

subsequently reduced to give graphene. Boehm went on to write the IUPAC (International Union of Pure and Applied Chemists) definition for graphene, stating that:¹⁶

A single carbon layer of the graphitic structure can be considered as the final member of the [naphthalene, anthracene, coronene, etc.] series and the term graphene should therefore be used to designate the individual carbon layers in graphite intercalation compounds.

Despite the above IUPAC definition, the term graphene is often used to describe graphitic structures of up to ten layer thickness; the justification for this is that the electronic structure of the graphene layer system only approaches that of bulk graphite above ten layers. Monolayer graphene has a linear dispersion relation around the K-point of its band structure (see section 2.2.1), and in bilayer graphene the linear dispersion relation becomes parabolic and has a slight semimetal band overlap. The band overlap increases with the number of layers, approaching close to the overlap of bulk graphite above ten layers.^{3,17} Thus in practice one finds references to monolayer graphene, bilayer graphene and few-layer graphene (between three to ten layers) in the literature.

It is worth briefly considering the fundamental stability of the two-dimensional structure of graphene, as certain theoretical proposals suggested that completely two dimensional crystals should be unstable.^{18–20} Furthermore, attempts to grow thin films have shown that once films decrease in thickness below tens of layers they begin to degrade, by breaking up into isolated islands or by decomposing.^{21–23} However, by

extricating the graphene sheet directly from a bulk crystal of graphite the stability issues are evidently bypassed. It has been suggested that observed nanometre scale corrugations in the third dimension of the structure may allow graphene to be stable (see section 2.6),²⁴ although graphene has not been observed in free space, and as such it is possible that such corrugations are influenced by the substrate or tension with the edges from which it is suspended.

2.1.3 Why is Graphene Important?

The research interest in graphene stems from its novel properties; its two-dimensional nature make it of interest in everything from studying novel physical phenomenon such as the quantum Hall effect^{8,9} to its use as a supporting membrane structure in atomic resolution TEM,²⁵ its electrical properties could lead to a viable replacement of indium tin oxide in transparent conducting electrodes,²⁶ as well as in novel next generation transistor designs, such as bilayer pseudospin field-effect transistors (BiSFETs).²⁷

The two-dimensional character of graphene gives an advantage over the other novel carbon nanomaterial in the field, carbon nanotubes, in that it can be processed by already established planar techniques, which are extensively used in the silicon based microelectronics sector, with none of the issues of sorting for chirality of nanotubes and other properties that inhibit the fabrication of a device. If a synthesis method that can generate large areas of high quality graphene can be found then one of the main obstacles to implementation of graphene into devices will have been overcome.

2.2 The Properties of Graphene

For this section some of the properties of graphene shall be discussed. While it is reasonable to say that the majority of research interest has been on graphene's novel electronic properties, such as the exceptional measured carrier mobilities or the physical existence of a massless Dirac fermion system, the other properties of graphene could also lead to interesting commercial applications, as shall be reviewed here and later in section 2.3.

2.2.1 Electronic Properties

Graphene, much like its parent graphite, is a lattice of sp^2 hybrid bonded carbon. This yields a planar structure with a hexagonal symmetry, with the bonds spreading out to their maximum 120° separation. The strong σ bonds of the hybrid states produces a rigid structure, whilst the remaining p_z orbital forms a partially filled π bond with its neighbours, with each carbon contributing a single electron to the graphene system.²⁸ These π states are the key to understanding graphene's electrical properties, forming a delocalised conduction and valence band through the graphene system.

2.2.1.1 Band Structure

A nearest-neighbour, tight-binding approximation for the band structure of graphite was first calculated in 1947,²⁹ and a number of papers have since developed on this work further,^{30,31} such that graphene's band structure was already well understood prior to its isolation. Graphene is made of two equivalent carbon sublattices, A and B, as shown in Figure 2.2, which between them contribute an electron state to the valence and conduction band, respectively. The band structure about the K/K' point of graphene

exhibits a characteristic zero-gap linear dispersion relation that is described by the Dirac Hamiltonian, formed from the partially filled p_z π/π^* orbitals. These electrons can be seen as relativistic quasi-particles, as opposed to the typical charge carrier with a finite effective mass.

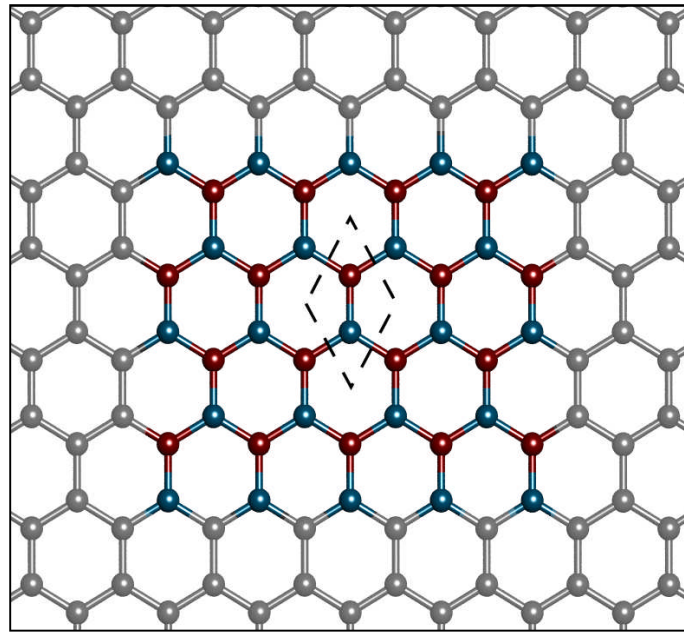


Figure 2.2. A graphene atomic lattice, with red and blue atoms denoting the two equivalent carbon sublattices. The dashed line shows the unit cell, containing a carbon atom from each sublattice.

Nearly all electronic systems can be approximated by the Schrödinger equation (Equation 2.1, showing the time independent equation), with the carriers, of effective mass m^* , following a parabolic dispersion relation.

$$E\psi = -\frac{\hbar^2}{2m^*}\nabla^2\psi \quad \text{Equation 2.1}$$

E is the energy eigenvalue of the Hamiltonian, ψ is the wave function (probability amplitude) of the system and $\hbar$ is the Dirac constant; Planck's constant h over 2π . In the case of graphene the π carriers move at relativistic speeds through the graphene lattice,

and as such behave according to the Dirac equation, a relativistic wave equation for describing electrons. Equation 2.2 describes the Hamiltonian for the Dirac equation.

$$\hat{H} = \frac{\hbar}{i} c \boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta m^* c^2 \quad \text{Equation 2.2}$$

where $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}$

$$\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

α_k and β describe the shown matrices, $\sigma_k = (\sigma_x, \sigma_y, \sigma_z)$ are the appropriate Pauli matrices, $\hat{H}$ is the Hamiltonian operator describing the total energy of the system, $\boldsymbol{\nabla}$ is the vector differential operator del, c is the speed of light in a vacuum and i is the imaginary unit. Carriers in graphene have negligible effective mass, and so the Dirac equation can be written to eliminate the β term, and substituting for the momentum operator ($\hbar/i \boldsymbol{\nabla} = \hat{\mathbf{p}}$), as shown in Equation 2.3.

$$\hat{H} = \frac{\hbar}{i} c \boldsymbol{\alpha} \cdot \boldsymbol{\nabla} = c \boldsymbol{\sigma} \cdot \hat{\mathbf{p}} \quad \text{Equation 2.3}$$

These quasi-particle charge carriers are known as massless Dirac fermions, and travel at an effective speed of light of $v_F \approx 10^6 \text{ms}^{-1} \approx c/300$ (where v_F is the Fermi velocity).^{3,28,32,33} The Hamiltonian can be rewritten as shown in Equation 2.4, which shows the linear dispersion relation that is seen in the graphene band structure.

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{k} \quad \text{Equation 2.4}$$

In typical material systems the electron carriers would be described by a separate Schrödinger equation from the holes, with different effective masses. However, in graphene the two carrier systems are related in a way which can be seen as analogous to C-symmetry (charge conjugation) in quantum electrodynamics. This arises from the interaction of the two sublattices discussed earlier; each unit cell contains two carbon atoms, each with its own π electron which contributes to the overall band structure. The energy bands of each of the two sublattices are described by a pair of out of phase sinusoidal waves oscillating about the $E = 0$ level along the hexagonal first Brillouin zone edge (see Figure 2.3c). These sine waves cross over at zero energy on the K/K' points. Thus, for energies of $|E| < 1$ eV, there are conical dispersion relations about the K (and K') point. This two component nature that arises from the two sublattices requires the wave function describes both, and hence the spinor notation is used. However, since the wave equation is not describing a real spin, but rather two distinct charge carrier bands (the π and π^* bands), it is typically referred to as a pseudospin. Similarly, the use of σ in Equation 2.2 does not refer to a real spin, but a pseudospin.

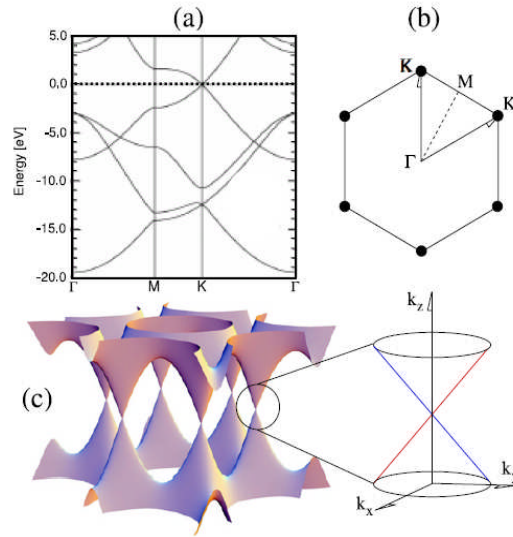


Figure 2.3. (a) The band structure of graphene from *ab initio* calculations conducted in ref. [34]. Copyright American Physical Society. (b) The first Brillouin zone of the reciprocal space of graphene, with the K, K', M and Γ points shown. (c) The energy surface of graphene. The focus is the band structure at each of the K points, with the characteristic conical Dirac like dispersion relation. Reprinted from ref. [35] (copyright Institute of Physics).

Following directly from graphene's symmetrical (for low E) band structure is the observation of a strong ambipolar effect, with an applied gate voltage (V_G) shifting the Fermi energy through the bands. The shift is able to induce carrier concentrations for electrons (or holes for corresponding negative voltages) as high as 10^{13} cm^{-2} ,³³ with a Hall effect sign change at $V_G = 0$.¹⁰ However, contamination by water, for instance from the atmosphere, can cause unintended p type doping and lead to a shift in the resistivity maximum to a positive gate voltage.⁴

2.2.1.2 The Quantum Hall Effect

An analogous system to the two dimensional structure of graphene can be seen in the two dimensional electron gas (2DEG) found in systems such as high electron mobility transistors, which exhibit a quantisation of the Hall conductivity.^{36–38} At suitably high magnetic fields one observes a similar phenomenon in graphene Hall bars.^{10,11} The

observed plateaus in conductivity (σ_{xy}) in graphene Hall bars occur at intervals governed by Equation 2.5, which is notably different from that observed for the integer quantum Hall effect.

$$\sigma_{xy} = \pm \frac{4e^2}{h} \left(n + \frac{1}{2} \right) \quad n = 1, 2, \dots \quad \text{Equation 2.5}$$

This is the anomalous quantum Hall effect, so called due to the occurrence of plateaux at filling factors of an integer plus a half instead of just integers. Figure 2.4 shows the quantum Hall measurements of a mono- and a bi-layer graphene system. The factor 4 in Equation 2.5 arises from spin degeneracy and the two Dirac points; and the anomalous nature of the effect can be attributed to the pseudospin of graphene arising from the two carbon sublattice. An expression for the energy E of massless relativistic charges in a magnetic field is shown in Equation 2.6, with an applied magnetic field B and Fermi velocity v_F .

$$E_n = \sqrt{2e\hbar v_F n B} \quad n = 0, \pm 1, \pm 2, \dots \quad \text{Equation 2.6}$$

One can readily see from this equation that a Landau level exists at $E = 0$ (for $n = 0$). This effectively acts as a constant offset of $\frac{1}{2} \frac{4e^2}{h}$, due to the shared occupation of the $n = 0$ Landau level of both holes and electrons; i.e., both carriers offer solutions for $E = 0$ and so share the filling of the Landau level, halving the filling factor.

Two dimensional systems in magnetic fields can exhibit a further property; the fractional quantum Hall effect (FQHE),³⁹ which arises from strong electron interactions forming a quantum fluid. The FQHE is expected only in two dimensional systems of exceptional

quality, at very low temperatures and high magnetic fields, and can be observed in between the plateaux caused by the integer QHE at fractional filling factors. The effect was first experimentally measured in graphene by two groups simultaneously;^{8,9} both groups used a two contact, suspended graphene device. This type of device had been shown previously to yield devices of high mobility,^{5,6,40} with the reduction in electron scattering permitting the electron-electron interactions necessary for the FQHE to manifest.

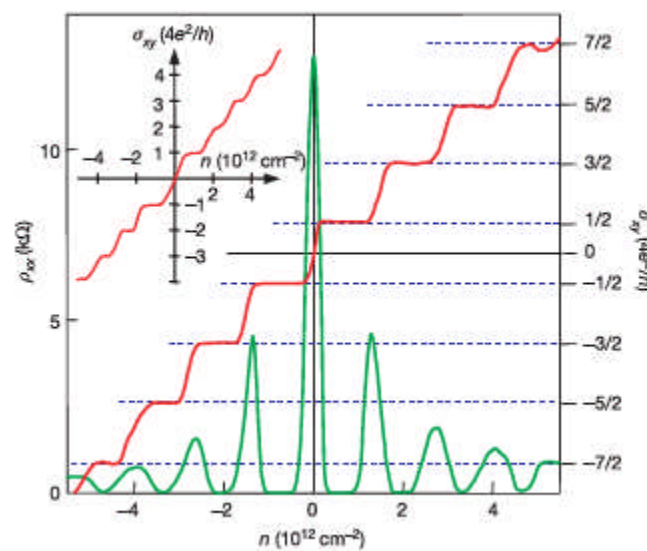


Figure 2.4. The anomalous quantum Hall effect observed in monolayer graphene and the longitudinal resistivity. The insert shows the result of the same experiment carried out on bilayer graphene, demonstrating the typical integer behaviour of a regular 2DEG, as opposed to the anomalous integer plus a half behaviour observed for the graphene monolayer. Reprinted with permission from ref. [10]. Copyright Nature Publishing Group 2005.

2.2.1.3 Klein Tunnelling

The unique properties of graphene allowed, for the first time experimentally, the observation of the Klein tunnelling phenomenon,⁴¹ also sometimes known as the ‘Klein Paradox’ due to the counter intuitive behaviour. The phenomenon arises when considering the effect of the Dirac equation, as applied to a massless relativistic particle,

upon a potential barrier scenario. Non-relativistic quantum mechanical considerations of a particle interacting with a potential barrier, for a barrier of higher potential than the particle energy, return the result of an exponentially decaying transmission coefficient that is dependent on the barrier length and height (Figure 2.5a). However, in the case of the Klein paradox the relativistic particle will penetrate through the barrier of potential height $V_0 = mc^2$ (the particle's rest energy), with a transparency tending to unity as the barrier height increases (Figure 2.5b,c).⁴² In the case of graphene, Klein tunnelling can be explained by the effect of charge conjugation across the potential barrier, with the same dispersion relation describing the behaviour of both electron and hole carriers. In the case of an incident electron, hole states that form inside the barrier (a barrier that is repulsive to electrons would be attractive to holes) would be strongly conjugated with the electron waves outside the barrier, as a consequence of the charge-conjugation symmetry that arises from the two sublattices (Figure 2.5d).^{2,43} Or, alternatively, the transmission is a consequence of the inability for a potential step to reflect a massless particle. The linear dispersion relation of graphene, the two component wave function arising from the sublattice symmetry and its massless charge carriers, allows the observation of this effect in a physically realisable system.⁴⁴

2.2.1.4 Minimum Conductivity

It has been experimentally observed that graphene exhibits a minimum conductivity of $\sim \frac{e^2}{h}$, although there is a measure of uncertainty over the exact value.^{3,10,45} Even though the band structure of graphene would suggest that the density of states vanishes at the Dirac point, these experiments show that undoped and unbiased graphene is still conductive, with no sign of an insulating state.⁷

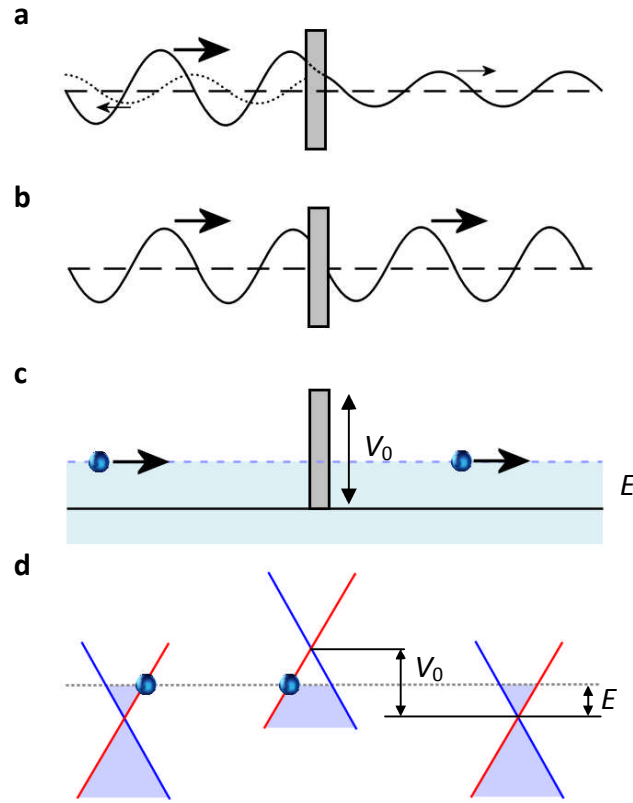


Figure 2.5. (a) The non-relativistic quantum mechanical potential barrier scenario, with an incident wave of energy $E < V_0$ resulting in a transmitted wave of amplitude dependent on the level of exponential decay within the barrier. A portion is also reflected by the barrier (dotted line). (b) For a massless, relativistic particle solving the Dirac equation shows the transmission probability is effectively unity for $E < V_0$. (c) In the particle picture this translates to the transmission of a particle with unchanged energy. (d) The low energy dispersion relation for the graphene carriers, with red and blue contributions from the two equivalent sublattices. The electron couples with a hole of equal pseudospin inside the barrier.⁴³

The minimum conductivity is speculated to arise from the difficulty of reaching the Dirac point experimentally, with the effect of sorbed contaminants from the environment, such as hydrocarbons and hydrogen, as well as defects, such as extended Stone-Wales-divacancy defect structures (see section 2.6),⁴⁶ resulting in charged regions. A suitably large number of random defects results in a series of potential barriers, ordinarily preventing the propagation of charge carriers through the system; this is known as

Anderson localisation.^{47,48} However in graphene, due to the nature of Dirac fermions and the associated Klein tunnelling effect, the pockets of charge that accumulate about these defects (charge ‘puddles’) are able to pervade relatively freely through the system by tunnelling between disorder induced potentials, essentially generating carriers in the vanishing density of states (DOS) limit near the Dirac point.^{49,50} The inability to remove these sources of disorder ultimately limits the experimental understanding of the origin of the minimum conductivity in an ideal graphene system (see section 2.2.1.6 for a discussion on scattering mechanisms and the charge mobility in graphene).⁷

A minimum conductivity of $\frac{4e^2}{\pi h}$ is predicted for the ballistic limit in graphene,^{51,52} which has yet to be realised by an experimental system, with most tending to $\frac{4e^2}{h}$. The closest to a perfect experimental system, with negligible intrinsic defects, that has been realised is reported in ref. [7], however this still yielded a minimum conductivity higher than the ballistic limit. The sample inhomogeneity in this case was verified to be minimal for the measured devices, thus there should be negligible charge puddles to provide carriers. The mismatch with theory is attributed to scattering at the metal-graphene interface.

2.2.1.5 Polycrystalline Effects

As techniques for synthesising large area graphene mature, an issue to contend with is the effect of grain boundaries on the electrical properties of the graphene films. There are two principle defect types to consider when looking at grain boundaries; a five-membered carbon ring and a seven-membered ring. The number refers to the carbon atoms making up the enclosed loop, with the standard, defect free graphene comprising of many linked six-membered rings in a characteristic hexagonal configuration. Individual five- or seven-membered rings are rare, as they would induce either a positive

or negative curvature in the overall crystal structure due to the strains induced. However, it is possible for five- and seven-membered rings to pair up, with no net effect on the curvature and a minimal energy cost.⁵³

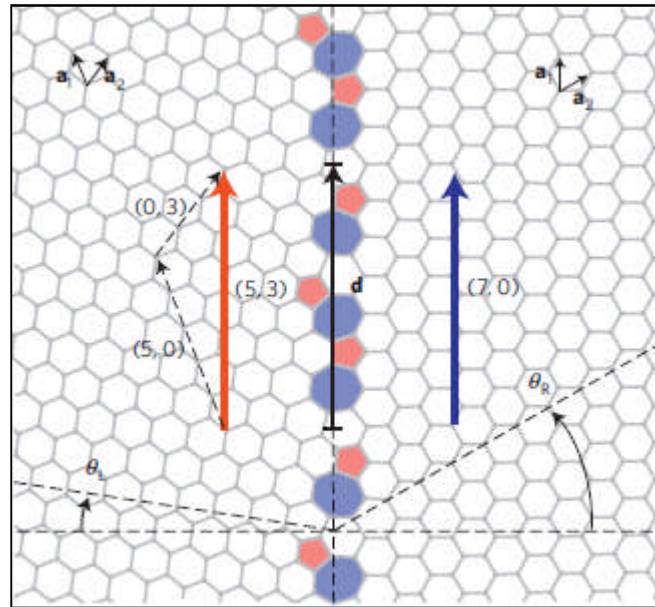


Figure 2.6. A grain boundary in graphene can be defined by the two angles (here θ_L and θ_R) of rotation of the grains to the normal of the grain boundary. The boundary is described by a vector $\mathbf{d}$, which is itself defined by matching vectors from each grain. Here they are such that $(n_L, m_L) = (5, 3)$ and $(n_R, m_R) = (7, 0)$. Reproduced with permission from ref. [54]. Copyright Nature Publishing Group 2011.

The conjoined defective rings can be found at grain boundaries, forming an axis between grains of differing rotation angles (see Figure 2.6). The grain boundary itself is defined by the repeat vector $\mathbf{d}$, which is characterised by matching vectors from each grain, composed of translation components (n_L, m_L) and (n_R, m_R) for the left and right grain, respectively. The orientation of the grain boundary has important implications for the band structure.⁵⁴ For instance if the vectors $n_L - m_L = 3q$ and $n_R - m_R \neq 3q'$ (for integer values of q), or vice versa, then a band gap arises due to the non-conservation of momentum across the boundary at low energies. Other chirality conditions provide

conduction channels for carriers of all energies. The band gap magnitude is characterised by Equation 2.7, where d is the periodicity.

$$E_g = \hbar v_F \frac{2\pi}{3d} \quad \text{Equation 2.7}$$

This leads to band gaps in the range of 0.3 - 1.4 eV.

2.2.1.6 The Carrier Mobility

The carriers in graphene are massless, relativistic Dirac fermions (section 2.2.1.1), and thus graphene exhibits exceptionally high mobilities. The highest mobilities are reported in samples where the graphene is suspended, as charged impurities and other scattering centres from substrate interactions are minimal, and where current annealing has removed contamination. These mobilities are of the order of $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at temperatures up to 240 K,^{5,6,40} with near ballistic transport at 20 K and mobilities as high as $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported in strained suspended samples.⁵⁵ In the work on suspended graphene, evidence suggests that flexural phonons are the limiting factor for mobility at room temperature, which requires straining to suppress.

For useful electronic devices it is more important to understand the behaviour of graphene at room temperature, also taking into account the effect of the substrate and the gate dielectric. In these devices mobilities are typically within the range of $1 - 2 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³ Within the graphene itself, the effect of charged impurities and disorder on scattering becomes important at room temperature,⁴⁵ although if these sources of disorder are removed intrinsic room temperature mobilities of $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ could be achievable for particular carrier concentrations, due to the

weak effect of electron-phonon scattering.⁵⁶ The substrate can be expected to contribute further extrinsic scattering sources, in the form of substrate roughness and impurities,^{57–61} ultimately leading to an inhomogeneous distribution of charge localisation throughout the sample. These Dirac point charge localisations are often referred to as electron and hole puddles.⁴⁹ Even after minimising these extrinsic sources of disorder, however, the effect of polar optical phonons of the most frequently used graphene substrate, the dielectric silicon dioxide, can severely limit the carrier mobility.⁶² This is known as remote polar phonon scattering,⁶³ where the SiO₂ polar optical phonons couple with the graphene charge carriers, and would also be expected to occur with any additional polar top gate dielectric. Selection of appropriate substrates and gate dielectrics should minimise this effect.⁶⁴ Hexagonal boron nitride (h-BN) may prove to be such an ideal insulating substrate, due to its atomically smooth surface, large optical phonon modes and a lattice constant comparable to that of graphene. By employing h-BN with graphene devices mobilities of $6 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been achieved,⁶⁵ some three times greater than with equivalent silicon dioxide substrate samples. Encapsulation of the graphene in a h-BN sandwich structure, thus providing both a gate and a body electrode, as well as isolating the graphene from unwanted environmental doping, lead to mobilities in the $1 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ range.⁶⁶ On conventional SiO₂ based substrates an aluminium oxide top gate dielectric initially yielded mobilities of $8 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to the low end of the range reported for non-top gated devices.⁶⁷ More recently, mobilities of $2.3 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achieved,⁶⁸ with negligible measured change in device mobilities before and after gate deposition now possible,⁶⁹ although this is likely due to the mobility limiting factors being elsewhere in the fabricated devices.

2.2.2 Mechanical Properties

Before experimental measurements of its mechanical properties were performed, it was predicted that graphene would be the strongest of known materials.⁷⁰ The first thorough experimental measurements used a graphene sheet suspended over an array of micrometer scale perforations in the underlying substrate,⁷¹ a technique first outlined in a study of few layer graphene.^{72,73} By applying a force with a diamond atomic force microscope (AFM) tip on the free-standing area of graphene it was possible to determine its elastic and inelastic breaking strength. A Young's modulus of 1.0 ± 0.1 TPa and an intrinsic strength (i.e., assuming no defects or flaws) of 130 ± 10 GPa were found. The extraordinarily high strength can be attributed to the covalent sigma bonds, and that the measurement is of a defect free atomic-scale region. The measured breaking forces were justified as being representative of an ideal defect free graphene due to their good agreement with *ab initio* calculations performed for monolayer graphene,^{74,75} and the distribution of breaking forces recorded was narrow; a defective sheet would have a large variance in measured values due to the differing number, size and type of defects one would find under the tip.

Graphene's flexibility, elasticity and mechanical stability have been tested in the fabrication of a flexible film on a PET substrate.⁷⁶ The resistance was found to not change for a bending radius of up to an equivalent tensile strain of 6.5%, and reverted completely to its original state after. Further, it was found that the original resistance could be restored when strains of up to 18.7% were applied. The resistance was also seen to be stable for up to 11% stretching. Theoretical work has shown that a strain

induced gap in the band structure should only manifest for strains in excess of 20%,⁷⁷ and that graphene should be perfectly elastic for deformations in excess of 20%.⁷⁴

2.2.3 Thermal Properties

Theoretical predictions and experimental measurements have found that freely suspended single-layer graphene exhibits among the largest known thermal conductivity of any material, of over $3,000 \text{ W mK}^{-1}$ at room temperature.^{78–81} This was measured using a non-contact optical technique that was reliant on graphene's characteristic Raman signal, specifically the temperature dependence of the G peak position (see section 2.5.2). Thermal conductivity is a critical issue for microelectronics, as the power dissipation needs have risen with increased miniaturisation.

The practical use of graphene will require its interaction with a substrate, rather than suspended in ideal conditions. Such measurements yield a thermal conductivity of 600 W mK^{-1} for graphene on a SiO_2 substrate at room temperature.^{82,83} This is a reduction of several times that over suspended graphene samples, and likely arises due to phonon coupling with the substrate.⁸⁴ Of the three graphene phonon modes (longitudinal, transverse and flexural), coupling with the flexural (ZA) mode to the substrate is argued to mitigate its contribution to the overall thermal conductivity, as well as phonon leakage to the substrate.^{84,85}

2.3 Applications of Graphene

The excellent electrical and thermal conductivities, and exemplary strength and elasticity, should make graphene an exceptional candidate for a number of applications.

However, graphene needs to justify the upheaval of a switch over to a new material from an already employed incumbent. Indeed, because of this it is logical to speculate that any major uses of graphene are likely to be from novel applications that are purposely designed to exploit the particular properties of graphene, rather than trying to force graphene into an existing area where it would struggle to compete with any established benchmark materials. This section will discuss a selection of the possible applications of graphene, including transparent conducting films, electronic devices and others.

2.3.1 Transparent Conducting Films

In the booming display, touch and solar panel markets, as well as future nascent products such as augmented reality displays, materials that are both transparent (> 90%) and conductive are keenly sought; indeed the transparent conducting film (TCF) materials market is predicted to reach a value of \$10 billion in 2016.⁸⁶ Graphene has the potential to be a replacement for the incumbent TCF materials, such as indium tin oxide (ITO), as it possesses a competitive sheet resistance and exhibits a high transmittance of 97.7% per layer.⁸⁷ ITO is well established as a TCF, however the inherent rigidity of the ceramic is a disadvantage when compared to graphene. The flexibility of graphene should enable the development of next-generation technologies that require device flexibility; as well as improving existing mobile telecommunications handsets and electronic readers, flexible devices could open up entire new industries, such as wearable computing or mobile, storable solar cells. Furthermore, the high mechanical strength of graphene makes it very durable; ideal for touch-screens or foldable e-paper.

There are two major limiting problems with regards to implementation of graphene in this sector; the low cost production of high quality graphene and the subsequent transfer into the production line without damaging the graphene. For the first point, there are currently two viable synthesis methods for the production of large area graphene; chemical vapour deposition (CVD) and chemical exfoliation, both of which are discussed in detail in section 2.4. The former, CVD synthesis, provides higher quality and more uniform graphene, however at significantly higher costs than the solution exfoliation route, where lots of small, overlapping flakes are deposited to produce a relative low quality film. The chemical exfoliation route will likely be suitable only for applications which do not require high electrical quality; applications such as smart windows and low-end touch-screens. Higher grade applications will require significantly better electrical quality than possible from chemically exfoliated graphene, which may be provided by continuous CVD grown sheets, but at a high cost incurred due to the need for significant elevated temperatures. The second major issue is incorporating the use of graphene into existing production lines, or modifying them in a cost efficient manner. Again, the chemical exfoliation technique lends itself to relatively facile and low cost integration, due to the ability to drop cast directly from solution, which would lend itself well to organic electronics applications. The problems arise for high quality applications that would demand CVD quality graphene, and the issues in transferring the graphene from the seed catalyst to the host device in a cost-effective and repeatable manner.

2.3.2 Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs)

The bedrock of modern computer hardware technology is the concept that the semiconductor industry works to double the number of transistors per integrated circuit every two years; colloquially known as “Moore’s Law” (Figure 2.7).^{88–90} CMOS (Complementary Metal-Oxide-Semiconductor) is the incumbent technology used for integrated circuits, and currently relies on using silicon as the semiconducting channel layer in the MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistors) that comprise the logic gates of the circuit. These transistors have been shrunk continuously over the past several decades, to the stage where the physical limit of silicon based devices is inexorably approaching.

The promise of graphene as a straight semiconductor replacement in CMOS chips, one that could beat the silicon limit, was first mooted in the same paper that announced the initial electronic characterisation of isolated monolayer graphene,¹ and has remained an often cited potential application of graphene in both the scientific literature and the wider popular press. It is not difficult to appreciate why; graphene research builds on the expertise developed in the study of fullerene film transistors and high performance single carbon nanotube transistors.^{91,92} The ultrahigh carrier mobility and monatomic thickness of graphene make it an attractive CMOS candidate, as these properties are two of the key fundamental limits of silicon.⁹³ Furthermore, a critical advantage that graphene possesses over other alternative channel materials, such as carbon nanotubes, is the capability to process in a planar form.

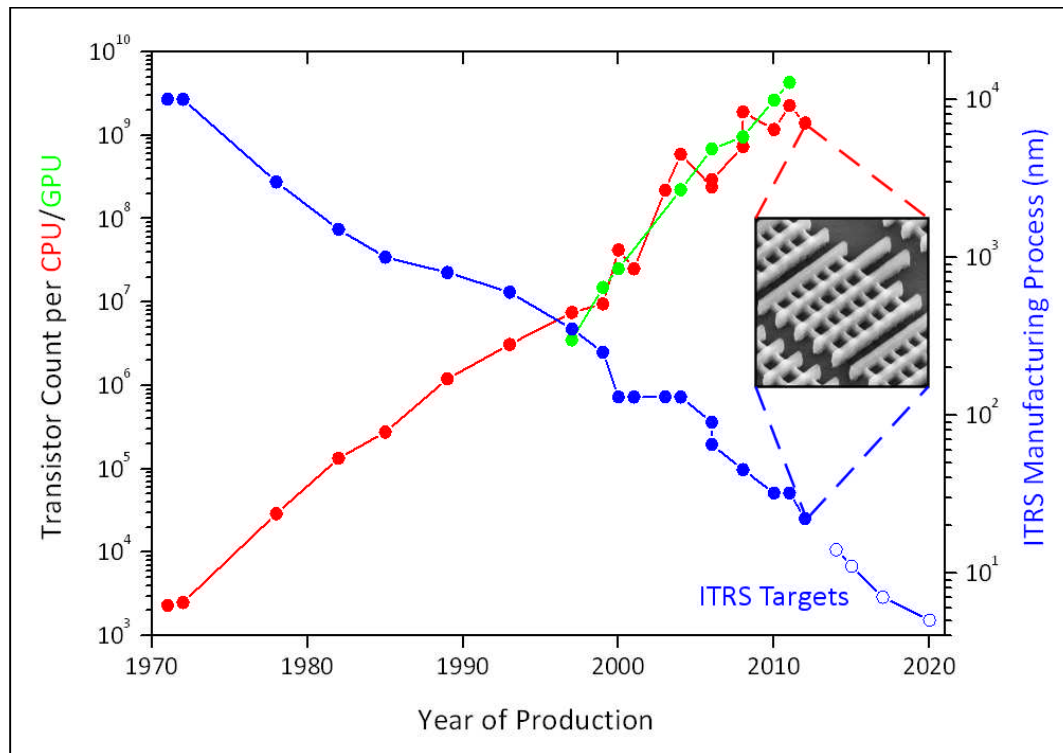


Figure 2.7. The exponential increase in transistor count per central/graphics processor unit (CPU/GPU) with time. On the right (blue) is shown the International Technology Roadmap for Semiconductors (ITRS) designated name for the characteristic scale of the manufacturing process, typically referring to the gate length. Hollow blue circles denote the future ITRS targets. The insert shows an SEM image of Intel’s 2011 IvyBridge 22 nm process tri-gate transistors.

With the continued miniaturisation of silicon channel MOSFETs, the reduction to the channel lengths eventually falls below that of the depletion region widths around the source and drain junctions, leading to adverse “short channel effects”.^{94,95} These include both reductions to the gate oxide thickness, necessary to maintain device reliability, and drain induced barrier lowering. The atomically thin gate oxides used result in quantum tunnelling of electrons across the insulator into the gate, increasing the power consumption. The reduction in the channel length results in a significant electric field originating from the drain in the channel, which acts to reduce the threshold voltage.

This drain induced barrier lowering effectively causes the device to allow current flow under the subthreshold (OFF) condition.

Of particular interest with regards to graphene are two short channel effects that act to impede the charge mobility; namely the field dependence of charge carriers in the inversion layer, leading to carrier scattering at the dielectric-semiconductor interface,⁹⁶ and also carrier velocity saturation, where the high electric fields limit the drain current before pinch off.⁹⁷ Both of these can be partly mitigated by using a channel made from materials exhibiting higher mobility.⁹⁸ This would also result in improved device transconductance, as increasing the mobility leads to a concomitant increase in drain current. The ultrahigh electron mobilities of $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ recorded in suspended graphene devices at low temperature make it a prime candidate in high mobility devices.^{5-7,33}

Two other attractive features of graphene are the single atomic thickness and the planar nature of the graphene sheet. The thickness of a semiconductor is a crucial consideration in CMOS scaling, as the depletion width (the depth into the channel that charge is depleted by the action of the gating field) must also scale down with channel length.⁹⁹ The threshold voltage of the device is only affected by the channel length and drain potential in a manner that is strongly dependent on the depletion width,¹⁰⁰ hence minimising the channel thickness should assist in optimising the device transconductance.¹⁰¹ Furthermore, the planar nature of graphene allows for the transfer of many standard techniques to graphene from existing CMOS fabrication processes, such as lithographic patterning, etching and layered structures from deposition.

However, in spite of the advantages outlined above, there are numerous obstacles to the implementation of graphene in this capacity. The International Technology Roadmap for Semiconductors (ITRS) outlined in their 2011 Emerging Research Materials document the following critical issues to the incorporation of graphene in FETs:⁹³

1. Graphene deposition over large areas with controlled grain size, thickness and crystallographic orientation. See section 2.4.
2. A method for manifesting a band gap in graphene.
3. Controlling surface and interface effects on carrier mobility and scattering.
4. Achieving a high mobility on a silicon compatible substrate.
5. Deposition of a high k dielectric with a high quality passivated interface.
6. Forming reproducible low resistance contacts to graphene, without damage to the graphene layer.
7. Integration, doping and compatibility with CMOS.

A number of these challenges also apply to the wider field of graphene research, not just with regards to incorporation of graphene into CMOS, and whilst they are significant a great deal of progress has been made in a relatively short time. Arguably the most critical problem is the lack of a band gap, with the band gap generation methods (constraining into nanoribbons,^{102–108} strain engineering,¹⁰⁹ a field induced gap in bilayer systems^{110–113}) remaining commercially unviable or unproven. The reported band gaps in graphene have been limited to the narrow regime, short of the 1.14 eV of silicon, and more akin to the other high mobility, narrow gap semiconductors, such as indium arsenide at 0.35 eV. This would prohibit the naive direct replacement of silicon with graphene in the current inversion based MOSFET CMOS architecture, as the device

cannot be efficiently turned off.¹¹⁴ Issues with performance limits from scattering caused by silicon dioxide substrates have been addressed by employing h-BN,⁶⁵ although it remains to be seen if h-BN is sufficiently compatible, and scalable, for use in CMOS.

To be a competitive consideration for the replacement of silicon, academia will need to have demonstrated solutions for all of these issues by around 2014.⁹³ In spite of the rapid progress it seems unlikely that this will be achieved, and as such graphene transistor research has increasingly shifted focus toward both radio-frequency analogue devices, section 2.3.3, and novel architectures that are specifically designed to harness graphene's unique properties, section 2.3.4.

2.3.3 Radio-Frequency (RF) Electronics

The low on-off ratios of graphene channel transistors, stemming from their lack of a band gap, would not prove to be such a fatal shortcoming in radio-frequency, or analogue, applications, such as amplifiers and transmitters. These devices benefit from graphene's high transconductance and carrier mobility, as the transconductance is the crucial parameter when considering an amplifiers performance. A further important parameter in the RF field is the frequency cut-off; the frequency at which the current gain for the device is reduced to one, and is thus the limiting frequency at which a signal will be carried through. Higher maximum operating frequencies (> 100 GHz) would permit the use of graphene electronics in radar applications. Current commercial technology for wireless communications in the 60 GHz regime already exists, however high frequency graphene electronics (122 GHz and 240 GHz) could allow for the commercial exploitation of these bands,¹¹⁵ as demand for spectrum bandwidth ever increases.¹¹⁶ Figure 2.8 shows a comparison of graphene high frequency FETs to several

competing technologies,¹⁰¹ with promising progress having been achieved in a short period; currently devices exhibit cut-off frequencies as high as 427 GHz,⁶⁹ with performances into the terahertz regime thought possible in ideal cases.¹¹⁷

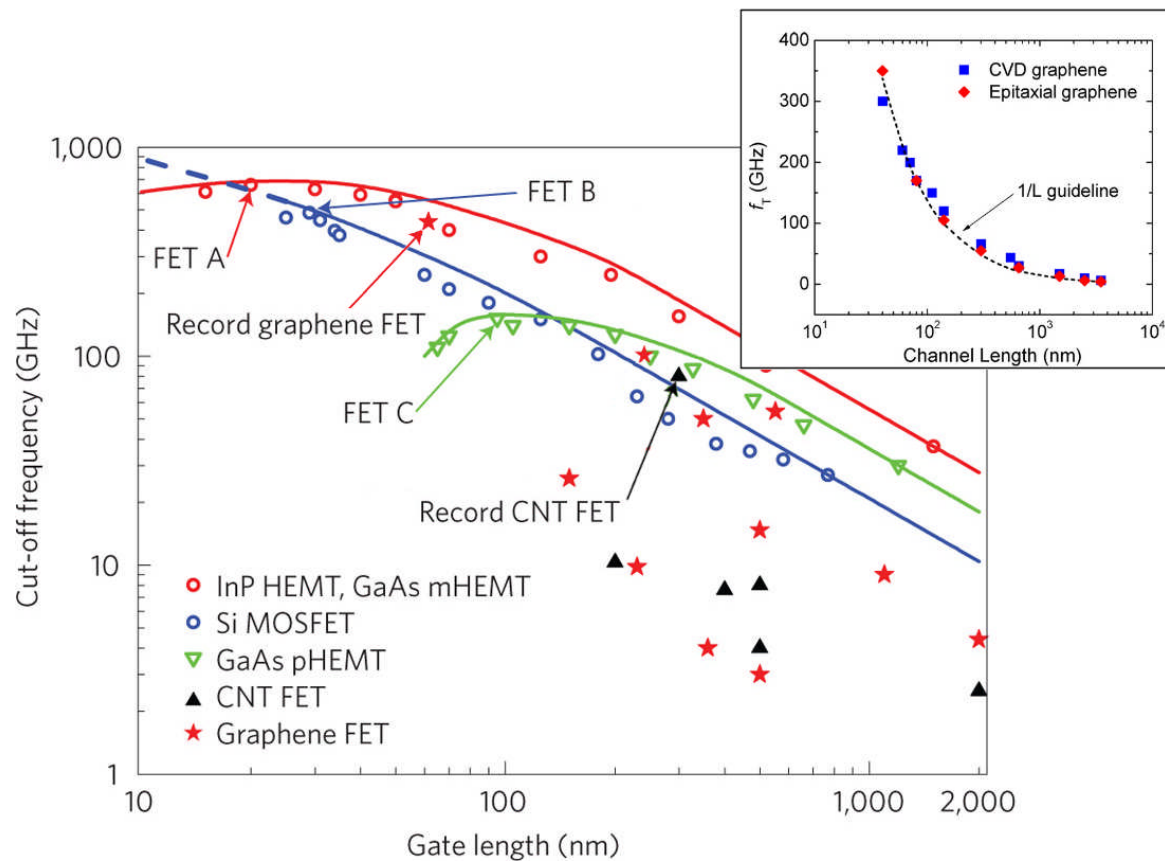


Figure 2.8. Cut off frequencies of different FET materials against gate length. FET A refers to InP HEMT (High Electron Mobility Transistors) and GaAs metamorphic HEMT, FET B to silicon MOSFETs and FET C to GaAs pseudomorphic HEMT. Figure adapted and updated with new results from ref. [101] with permission. Copyright Nature Publishing Group 2010. The record graphene transistor performance is 427 GHz at a gate length of 67 nm.⁶⁹ The insert illustrates the reciprocal relationship between the channel length and the cut-off frequency (f_T). Reprinted with permission from ref. [118]. Copyright 2012 American Chemical Society.

There are several recent papers which display the current state of the art in graphene radio frequency devices. The work by IBM researchers has consistently lead the field, with successive papers pushing device performance forward, with cut-off frequencies of

26 GHz in 2009,¹¹⁹ 100 GHz in 2010 (both on epitaxial SiC graphene),¹²⁰ 155 GHz with CVD grown graphene in 2011,¹²¹ and 300 GHz with both CVD and SiC epitaxial graphene in 2012.¹¹⁸ Recent work from Duan *et al.* has demonstrated innovative ways to overcome the problem of deposition of a quality gate dielectric in order to achieve superior devices.^{69,122} Progress has also been made toward graphene based integrated circuits, with a broadband radio-frequency mixer fabricated on silicon carbide that operates at 10 GHz,¹²³ which shows great promise toward future integration of graphene into existing technologies.

The current limiting factors with regards to device performance and commercial exploitation are principally the same as those outlined in section 2.3.2 (MOSFETs); such as graphene synthesis, dielectric deposition and mobility debilitating sources of scattering. Further problems unique to RF FETs are the comparatively poor maximum oscillation frequency performance, a measure of the maximum power transmission, stemming from the weak saturation behaviour.^{101,124–126}

2.3.4 Novel Transistor Designs

The problems arising from the attempts to develop logic MOSFET type transistors with graphene encourage the querying of whether the conventional device architectures are the best way to utilise graphene's properties. Three novel transistor designs have been put forward; the tunnel FET, the triode barristor and the bilayer pseudospin FET (BiSFET), that exploit these properties.

It is possible to fabricate a high on/off ratio device by harnessing the quantum mechanical tunnelling effect across a potential barrier in a tunnel FET device. A gating

field is applied across a layered device, with two layers separated by a thin dielectric, and is used to tune the tunnelling rate, with the gate voltage in the ON state permitting tunnelling between the source and the channel, and inhibited in the OFF state.^{127,128} The experimental realisation of such a device using bilayer graphene intercalated with an atomically thin BN dielectric, manifesting switching ratios of up to 10^4 , demonstrates the strong potential of the concept.¹²⁹

Alternatively, the graphene barristor (see Figure 2.9) relies on the formation of a Schottky barrier between doped/biased metallic graphene and a semiconductor, such as silicon.¹³⁰ Critically, the graphene does not interact with the hydrogen terminated silicon employed in the barristor, and as such few interface states are formed. The gating field from the top gate can be used to mediate the Schottky barrier height, and thus control the drain current. Depending on the source-drain bias regime used, the barristor can work as a regular transistor, displaying current saturation behaviour and an on/off ratio of approximately 300 in the reverse bias. Or the bias can be flipped to forward, which whilst not showing any current saturation behaviour, still exhibits a low drain current leakage in the off state and a high on/off ratio of 10^5 .

A further device, the BiSFET, employs two semiconducting sheets, separated by a thin dielectric, that can couple across and form excitons. These excitons can condense into a Bose-Einstein condensate, giving coherence of states across both layers and thus acting as one unified layer, ignoring the intermediate insulator. The term “pseudospin” arises as a way of addressing which layer the carrier inhabits, so that top and bottom are analogous to spin up and down (not to be confused with the pseudospin of the graphene band structure).¹³¹ It may be possible to observe this effect at room

temperature in a graphene BiSFET system, with one p-type and one n-type graphene layer, where the charge concentrations in each layer are roughly equal.²⁷ The switching effect would be caused by controlling this charge density, likely with a gating field, with imbalances in the relative charge densities between the two layers leading to decoherence, and thus lower current flow. Such a device would exhibit different digital logic operations to a MOSFET; however conventional logic functions can be imitated. Rough simulations suggest that such a graphene BiSFET device in an inverter circuit would consume 8×10^{-21} J per clock cycle, 2 – 3 orders of magnitude less than current silicon CMOS technology.¹³² As of yet though, no graphene based BiSFET has been experimentally tested.

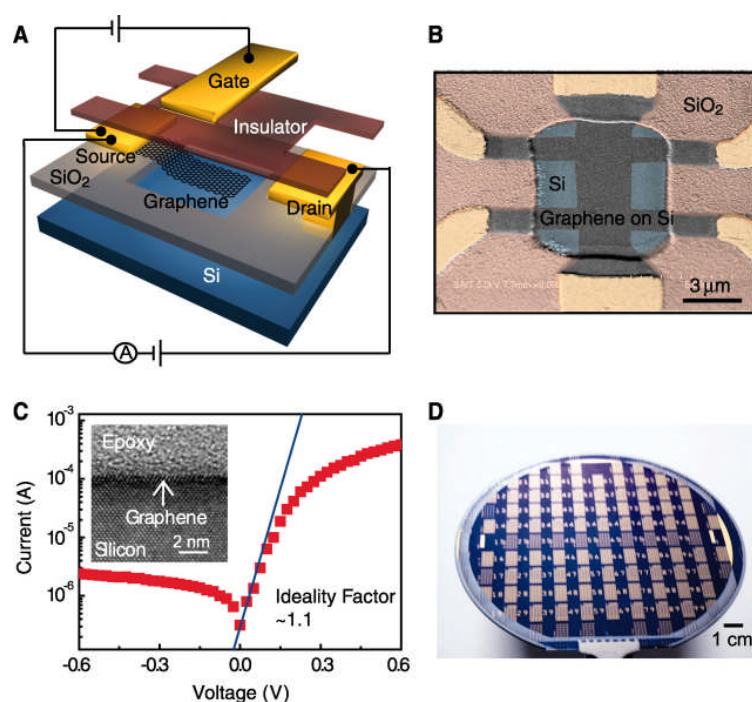


Figure 2.9. A: A blown-up schematic of the graphene barristor. B: False colour scanning electron micrograph of the barristor before gate dielectric deposition. C: Drain current versus drain voltage at zero gate voltage, displaying Schottky diode behaviour. Insert shows a transmission electron microscope image of the graphene-silicon interface. D: Large scale device processing on a 6-inch wafer. Reprinted with permission from ref. [130]. Copyright American Association for the Advancement of Science 2012.

2.3.5 Interconnects

With increased device scaling demands the current copper based interconnect technology suffers from several problems: Electromigration,¹³³ the movement of the copper ions stemming from the high current densities and operating temperatures; parasitic resistance, increasing dramatically with device scaling into the nanometre regime; and also general conformity issues, an inherent problem when patterning at such high resolution. As a candidate replacement, graphene offers excellent current carrying capacity of up to 10^9 A cm^{-2} , compared to 10^6 A cm^{-2} for copper,¹³⁴ and high thermal conductivity,⁸¹ important for heat dissipation, as well as an intrinsically high carrier mobility. However, the conductivity of nanometre scale graphene ribbons is currently short of that of the incumbent copper technology by an order of magnitude, and furthermore there is still considerable variance between ribbons of identical geometries.¹³⁵ These ribbon structures are thought to be limited in their electrical quality by a combination of impurities and edge roughness, and the failure of graphene interconnects due to oxygen etching seems to be mediated by point defects in the graphene.¹³⁶

2.3.6 Gas Sensors

The two-dimensional and readily dopable nature of graphene makes it a promising potential candidate for the use in sensor applications.¹³⁷ Interactions of various gas molecules with the graphene slightly modify its electronic properties by doping, which can subsequently be measured.¹³⁸ It has been shown that this technique can be used to detect individual gas molecule binding events with the graphene. This is possible due to the low electronic noise found in graphene, the quality of the graphene crystal used and

the ability to employ four-probe measurement geometries.¹³⁹ A scalable gas sensor fabricated from reduced graphite oxide has been demonstrated.¹⁴⁰ Surface Acoustic Wave (SAW) sensors from graphene oxide/graphene nano-sheets have been employed to detect carbon monoxide and hydrogen gas, responding both to the doping and also to mass, with the sorbed molecules perturbing the acoustic wave.¹⁴¹

2.3.7 Metrology and the Definition of the Ohm

In metrology, the field of standards and defining of SI units, the quantum Hall effect (QHE) seen in the 2D electron gas (2DEG) formed in semiconductor GaAs/AlGaAs heterojunctions has been used to define the ohm. Graphene also exhibits its own variety of the QHE (section 2.2.1.2), and as such it has attracted interest as a potential calibration standard; one that can leverage the potential low cost of QHE graphene devices to be widely disseminated beyond just the few international centres for measurement and unit calibration. The employment of graphene in the QHE metrology is particularly prescient, with SI units for mass and current to in future also be defined by h and e .¹⁴²

Epitaxially grown graphene on silicon carbide has been used to fabricate Hall devices that reported Hall resistances accurate to a few parts per billion at 300 mK, comparable to the best incumbent Si and GaAs heterostructure semiconductor devices.^{143,144} The maturity of graphene as a QHE standard has allowed for the fine comparison of the quantisation behaviour with that of GaAs heterostructures. Experiments demonstrated no difference in the resistance values between the two device types within the experimental uncertainty of $\sim 10^{-10}$, thus both verifying the value of the QHE quantum of

resistance and demonstrating the universality of the QHE in fundamentally different material systems.¹⁴⁵

2.3.8 Further Applications

There are multiple other potential applications for graphene which have not been discussed here. Some of the largest potential fields are composite materials, photonic devices (photo detectors, solid state lasers) and supercapacitors. These applications are mostly dependent on the development of suitable synthesis technologies, and as such it is realistic to expect that those applications that can exploit relatively low quality graphene will be the first to market.¹⁴⁶

2.4 Synthesis of Graphene

There are four principle methods for the synthesis of graphene. Mechanical exfoliation of graphite by the use of adhesive tape led to the opening up of the field of graphene research,⁴ and is still the most viable method for fundamental study by academia. Chemical vapour deposition (CVD) of graphene by the thermal decomposition of carbon containing precursor gases on to metal catalysts had been studied prior to the first isolation of graphene,¹⁴⁷ and has recently benefited from a strong surge in research due to two publications in 2009.^{76,148} Epitaxial growth of graphene on silicon carbide by thermally induced desorption of silicon could potentially be ideal for device fabrication, due to graphene being already formed on a dielectric substrate, removing the need for a transfer stage.¹⁴⁹ Colloidal suspensions of graphene, and chemically modified graphene derivatives, have potential advantages due to being readily chemically functionalisable and cheap to scale.¹⁵⁰

2.4.1 Mechanical Exfoliation

The most readily available way for fabricating graphene is by mechanical exfoliation of graphite. For instance, it is possible to find graphene sheets among the debris in a pencil trace. The first formal isolation of graphene was instead by the somewhat more scientific method of using Scotch tape to peel graphite apart, and then applying the graphitic residue from the tape to a silicon substrate, with an oxide layer of 300 nm thickness; this is essential for locating the graphene fragments (see section 2.5.1). Whilst the basic principle is simple to grasp, the technique requires iteration and practice in order to reliably obtain graphene layers, as opposed to thin graphite. Furthermore, the graphene layers are located amongst a plethora of graphitic debris, and as such the locating of isolated graphene flakes can be particularly time consuming.

This technique has seen the best quality graphene fabricated to date, with a carrier mobility of $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature recorded for non-suspended graphene,³ due to the exceptionally low level of defects that it is possible to achieve (borne out by the absence of a Raman disorder induced D-band peak). As such this technique is widely used by researchers investigating graphene's properties.

2.4.2 Chemical Vapour Deposition

2.4.2.1 Catalytic Growth

Chemical vapour deposition (CVD) uses volatile precursor gases that contain the desired elements, and either breaks them down under high temperature or initiates a reaction over a substrate, upon which a product is deposited. Often this process uses a transition metal catalyst, and rates can be further improved by use of low pressure systems, to

remove waste gases, and by ignition of a plasma, which can also serve to reduce the deposition temperature. As a process it is currently used extensively in the micro-fabrication industry for the deposition of thin films, such as silicon and high-k dielectrics, as well as for synthetic diamond¹⁵¹ and carbon nanotube production.¹⁵²

Synthesis of graphene has been reported on a variety of transition metals, such as copper,¹⁴⁸ nickel,^{76,153,154} on the (0001) face of ruthenium,^{155–157} and on the (111) face of iridium.¹⁵⁸ There are some reports of graphene grown directly on to dielectric surfaces; however these currently lack quality and uniformity.^{159–162} Copper and nickel films are the most promising candidate materials, and as such shall be considered in more detail. Both copper and nickel CVD procedures are similar, in that they typically use a methane precursor gas as the carbon source mixed with hydrogen and argon. After an annealing and reduction phase to treat the metal, the precursor gas is heated at 1000 °C whilst it passes over the catalyst, causing decomposition of the gas and leading to carbon deposition on the catalyst surface. Subsequent cooling leads to the observation of few layer graphene in the case of nickel, or single layer graphene in the case of copper, on the catalyst. The role of hydrogen is to inhibit the formation of non- sp^2 bonded carbon,¹⁶³ and argon acts just as a carrier gas. The deposition can be carried out at atmospheric ambient pressure,^{76,164,165} or under low vacuum (500 mTorr – 50 Torr).^{148,166,167}

It is notable from the literature that CVD graphene grown on copper foils is typically limited to a mono- or bi- layer, whereas nickel catalysed depositions are often few layer, and are strongly dependent on nickel film thickness and post deposition cooling rate. Carbon precipitation from nickel has been studied before, and it is recognised that

carbon is highly soluble in nickel at high temperatures,¹⁶⁸ thus it is essential to limit the nickel thickness in order to minimise the volume of carbon adsorbed, and to suppress multiple layers forming by rapid cooling.⁷⁶ Investigation by using mixed isotopes of carbon (^{12}C and ^{13}C) in the precursor methane gas was carried out by ref. [169] to further elucidate the differences between the growth mechanisms of copper versus nickel catalysed graphene. Figure 2.10 illustrates the two possible routes. Segregation refers specifically to the thermodynamic equilibrium process by which impurities preferentially diffuse out of the lattice and toward grain boundaries or, in this case, the surface in order to minimise the free energy of the system.^{170,171} Precipitation, or non-equilibrium segregation, refers to the effects of cooling on the surface composition. It was found that nickel catalysed graphene growth followed a surface segregation - precipitation route, while copper a surface adsorption route. This is due to the solubility of carbon in copper being significantly lower than in nickel; the completed d-shell in copper limits the chemical affinity with carbon.¹⁷² As a result, carbon is inhibited from diffusing far into the copper surface, and thus copper effectively acts solely as a catalyst for the decomposition of methane, as well as a high mobility surface for the carbon precursor species.¹⁷³ When the copper surface is covered with a graphene layer the catalyst is prevented from interacting with the methane; it is effectively passivated and stops deposition of further layers. However, the nickel system is able to absorb more carbon, and thus during cooling further carbon can precipitate out of the surface, increasing the thickness and decreasing the uniformity of the graphene. It can be said that the copper CVD mechanism is that of a true catalyst – the copper provides empty 4s orbitals for the graphene π electrons to bind with by a charge transfer mechanism, rather than forming a chemical intermediate.¹⁷²

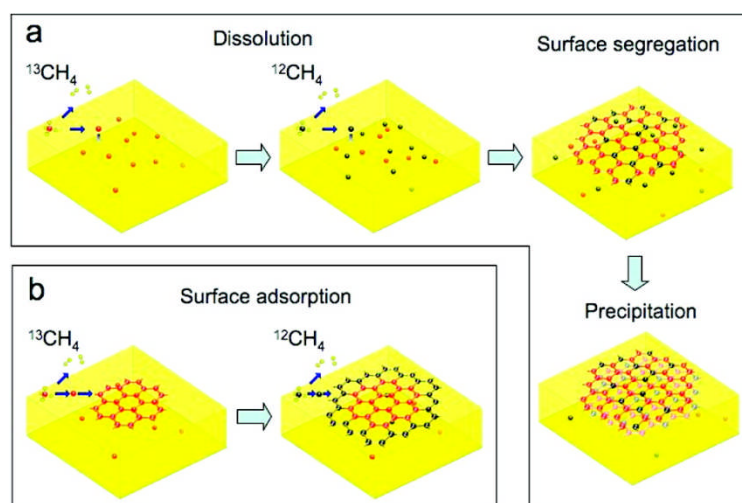


Figure 2.10. The location of carbon isotopes after sequential gas flows of isotopes of methane on a grown graphene film inform which growth route was taken. Isotopes mixed together suggest a surface segregation followed by precipitation pathway (a), whilst distinct zones of isotopes would suggest surface adsorption (b). Reprinted with permission from ref. [169]. Copyright American Chemical Society 2009.

It has been noted, however, that under ambient pressure conditions the copper catalyst loses its self limiting properties, and as such multilayer graphene domains can be observed to have formed.¹⁷⁴ The multilayer formation was found to be inhibited by using particularly low methane precursor concentrations of 100 ppm mixed into an argon carrier gas, in addition to the standard hydrogen flow. It was concluded that the marked increase in graphene thickness when deposition was performed at ambient pressure was due to the behaviour of the boundary layer; the layer of gas that is in immediate proximity to the surface. The critical consideration is that the rate of diffusion of reactants through the boundary layer is strongly dependent on the pressure of the gas flow, and as such acts as the limiting step for the deposition in the ambient pressure regime. This is as opposed to the surface reaction rate limiting the deposition rate, which is the case for low pressure deposition. The lower pressure results in an increase in the diffusion rate through the boundary layer, which if increased far enough

will cause it to exceed the surface reaction rate, and hence no longer act as the limit to deposition rate. With a surface reaction rate limited deposition graphene should form as a limited, continuous monolayer, which does not occur with higher gas pressures unless the carbon species supply is throttled.

An important limit in the quality of copper catalysed CVD grown graphene has been the presence of grain boundaries, which diminish the properties of the film. By limiting the nucleation density and tuning the CVD process to preferentially grow existing seeds, rather than forming new crystals, has proven effective. By forming an enclosure with the copper foil, and conducting the growth under low pressure and reduced methane flow rates combined with prolonged growth time, 100-500 μm scale graphene grains were found to grow on the inside surface of the enclosure. It is hypothesised that the low methane concentration coupled with the stable environment, allowing for static equilibrium to establish, may have been the important factors.¹⁷⁵ Reduction of the number of nucleation sites can also be achieved by extensive pre-treatment of the copper to ensure that it is both clean and smooth, as step edges and contaminants can act as nucleation centres.^{176,177} Careful and extensive pre-annealing can help mitigate these effects.¹⁷⁸ A recently demonstrated method yields >200 μm scale grains by increasing the growth temperature to over 1090 °C, which is above the melting point of copper.^{179–182} It is presumed that by melting the copper the surface irregularities are effectively removed, allowing for nucleation to occur on a perfect copper surface and thus helping to reduce the nucleation rate.

2.4.2.2 Post-Growth Transfer

A key step in the practical use of graphene films prepared by CVD is the transfer of the film from the metal catalyst to an appropriate substrate. The most common transfer methods utilise PMMA (poly [methyl-methacrylate]) as a temporary scaffold for the graphene, with the PMMA applied to the graphene side of the catalyst by spin coating from anisole solution.⁷⁶ The metal can then be safely removed by the action of an appropriate etchant, such as iron (III) chloride solution, which does not damage the graphene layer. The graphene/PMMA film is subsequently rinsed with DI water, hydrochloric acid solution (to fully remove iron contamination)¹⁷⁴ and DI water once more. It has been found to be preferential to then transfer the sample to isopropanol (IPA), before moving to the desired surface, as this eliminates trapped water.¹⁸³ It has been shown to be beneficial to apply an extra coat of PMMA in anisole solution to allow the film to relax to the substrate.¹⁸⁴ Once transferred, the PMMA can be removed by the action of a solvent such as acetone or by baking in atmosphere at 300-350 °C. This method can result in cracks in the film, which may be avoided by first evaporating a thin protective gold layer to the top face of the graphene before applying PMMA and removing the underlying copper.¹⁸⁵ A similar method to the standard PMMA transfer utilises a supporting tape film around the perimeter of the copper/graphene/PMMA. Here, once the copper etching and cleaning stages are performed the graphene/PMMA structure can be dry transferred to a desired substrate.¹⁸⁶

A more elegant, but limited, solution is to use the surface tension effect of the evaporation of IPA to adhere a TEM grid to the graphene/catalyst surface and then etch the metal away, thus removing the need for any PMMA scaffold stages.¹⁸⁷ Recent reports of the use of an electrochemical method demonstrate the advantage of a non-

destructive transfer technique, allowing for the reuse of the catalyst and minimising the level of etchant waste.^{188,189} This permits the use of expensive high purity, single crystal copper platinum catalysts. The process relies on the electrolysis of water into hydrogen at the cathode, thus placing the graphene/metal sample as the cathode leads to the gentle intercalation of hydrogen bubbles between the metal and graphene layers.

2.4.3 Chemical Processing

The graphene chemical exfoliation methods divide into two camps; the intercalation of graphite oxide and the subsequent reduction to graphene,¹⁹⁰ or the direct exfoliation of graphite.^{191,192} Graphite oxide can be formed by several methods, which typically use a mixture of strong oxidising agents and acids.^{193–195} It has a similar layered configuration to the parent graphite, however its specific structure is still not well understood due to the level of the disorder and disruption. The name graphite oxide is something of a misnomer, as the compound is made of several different functional groups, such as carbonyl and hydroxyl groups, as well as epoxide groups, with the edges terminated by carbonyl and carboxylic groups. The layers of graphite oxide have a greater separation to that of graphite, and can be separated further readily by the intercalation of polar solvents such as water, due to the strong hydrophilicity of the layers.¹⁵⁰ As such the interlayer distance depends strongly on humidity, and varies from 6 to 12 Å.¹⁹⁶

Graphite oxide can be fully exfoliated, as confirmed by AFM measurements after deposition, into a stable suspension by ultrasonication and stirring for a prolonged time.¹⁹⁷ Polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and ethylene glycol,¹⁹⁸ among several others,¹⁵⁰ have also been used successfully. Graphene oxide is a dielectric; however it is possible to reduce it

to graphene. Reduction of the suspension can be done by the use of reductants; such as hydrazine,^{199,200} dimethylhydrazine,²⁰¹ and hydroquinone;²⁰² by the use of an UV photocatalyst,²⁰³ or by thermal reduction.²⁰⁴ Even after reduction sizable quantities of oxygen remain in the product,¹⁵⁰ and reduction past a C:O ratio of 16 has been shown to be difficult by theoretical calculations.²⁰⁵

Once the exfoliated graphene oxide is suspended in solution it needs to be deposited. It is possible to produce a film of graphene oxide, by filtration techniques, and then reduce to graphene. Alternatively one can conduct the reduction while the graphene oxide is still in solution; however the graphene product does not share the oxides hydrophilicity, and as such does not remain suspended in polar solvent and thus typically requires the actions of dispersion agents. This can then be followed by filtration and thermal treatment. Conductivity measurements of pressure filtrated reduced solution, leaving a graphene paper, has yielded results on the order of 10^2 S cm^{-1} .^{206–208} Work on exfoliating graphene, without the oxidation and reduction stages, using strong solvents (such as NMP) have led to conductivity measurements of the same magnitude to those of the reduction method.¹⁹¹

2.4.4 Epitaxial Growth on Silicon

Epitaxial graphene can be grown by the thermal decomposition of silicon carbide, leaving single to few-layer graphene on the SiC surface after the sublimation of silicon.^{64,110,149,209} Typically the graphene is grown on the silicon terminated (0001) face (see Figure 2.11), using either the 6H-SiC or 4H-SiC polymorph, by desorption of silicon under high temperature vacuum/argon annealing,^{210,211} although growth on the carbon terminated face (000 $\bar{1}$) is possible, leading to larger domain size but some orientation

disorder.²¹² Prior to the growth stage, preparation of a smooth surface is best achieved by use of hydrogen etching,^{149,213} which leads to a surface of uniform, large (300 nm - 700 nm) and highly flat terraces. The heating treatment stage is carried out at temperatures in the region of 1200 °C for up to 20 minutes in ultra high vacuum,¹⁴⁹ or, more recently, by heating in the range of 1500 – 2000 °C under near ambient pressure conditions with argon atmosphere.²¹³

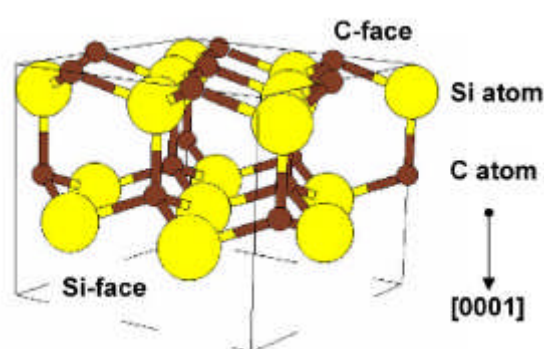


Figure 2.11. The crystal structure of 4H-SiC, showing the carbon terminated (000 $\bar{1}$) and silicon terminated (0001) faces. Reprinted with permission from ref. [214]. Copyright IEEE 2008.

While epitaxial graphene may be grown on either face of SiC, silicon face growth is notably slower than carbon face growth and has an orientation phase relative to the under lying silicon carbide of 30°,²¹⁵ whereas carbon face growth leads to multiple orientation phases.^{210,216,217} As a result of the apparent disorder in carbon face synthesis most research focused on silicon face growth, however recent research has shown that the carbon face provides superior quality graphene.²¹⁴ Problems with silicon face growth include the roughening of the surface during the growth phase, which has been shown to be independent of pre-treatment of the silicon carbide surface,^{35,218} although this issue may have recently been resolved by the use of rapid sequential heating steps to control silicon desorption.²¹⁹ The roughening reduces the pre-growth step size of 1 –

2 μm to 200 – 500 Å, although graphene has been shown to grow across step edges,²²⁰ and as such silicon face graphene sheets are estimated to grow up to 100 nm.²²¹ It is speculated that the surface roughening occurs due to the inhibition of silicon desorption from the silicon face, leading to silicon nucleation at the surface, forming islands and then eventually leading to roughening.^{215,222}

The roughening process has been shown to not occur during RF induction furnace growth of graphene on the carbon face, with up to three times the terrace size.²¹² Carbon face growth seems to only be viable in a narrow temperature band of around 1430 °C, as nanocaps form below this temperature and nanotubes above it.²²³ This leads to the hypothesis that a delicate balance exists between the rate of silicon decomposition and the rate of carbon migration.²¹² The epitaxial graphene quality grown by the carbon face method is high, with an atomically flat profile and large scale continuous films,^{35,213} with devices fabricated with room temperature mobilities of up to 5,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and on/off ratios of up to 7.²¹⁴

2.4.5 Discussion

The above descriptions of the four principle synthesis techniques lack any critical comparison. There are several things to consider in comparing the techniques. Most obvious is the quality of the graphene synthesised, which is most readily quantified by electrical measurements such as the conductivity (or carrier mobility) and is critical in several important applications, such as transparent conducting films (see section 2.5). The viability of economies of scale for bulk manufacture depends on both the systems used in the synthesis and the size of the graphene produced. The size of the graphene is

important when considering the types of applications available for its use, with larger areas allowing for greater flexibility in its use.

Mechanical exfoliation is the flagship for producing high quality graphene, setting the benchmark with a carrier mobility of $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K recorded for non-suspended graphene.¹⁰ Further to this, the technique is readily accessible to almost any academic research group, with no prohibitively expensive or difficult to acquire equipment or skills, and the graphene can be transferred directly to the silicon/silicon dioxide substrate after the exfoliation. The requirements increase for synthesis of high quality graphene, with reactive ion etching and a clean room required, however even these are available to most groups. To offset the advantages are the inherent issues of scalability; this would be a technique that would be very difficult, if not impossible, to scale up to an industrial throughput via automation, principally due to the nature of locating the graphene flakes on the substrate, and crucially the acute difficulty and lack of repeatability in making isolated flakes of much greater than 10-100 μm . Furthermore, it lacks well defined parameters that can be controlled and adjusted to alter the conditions of graphene formation, with instead the exfoliation and pressure-transfer being a more nebulous skill; a “knack” that is acquired through experience. This is almost certainly a technique that will remain only for research, and not in industrial applications.

Room temperature carrier mobilities measured on epitaxial graphene devices are up to $5,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1,200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the carbon and silicon terminated faces, respectively.²¹⁴ These compare favourably to the best mobilities reported for mechanically exfoliated graphene of the order of $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{10,11} Landau level

spectroscopy of epitaxial graphene layers grown on the carbon face has shown carrier mobilities of up to $250,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$,^{224,225} which suggests comparable quality to that of suspended exfoliated graphene, and originates due to decoupling of the layers, allowing for each layer to act as an isolated system. Coupled with the respectable electrical quality indicated by the mobility results is the nature of the synthesis method, namely that growth is epitaxial on an insulating surface, suitable for direct fabrication into devices without need for a transfer step. As important is that the graphene grows over the entire face of the crystal. This potentially lends this method to being well suited toward the fabrication of integrated circuits, as the graphene would be readily patternable by standard lithographic techniques widely used in the existing VLSI silicon chip industry. A potential drawback is that while it is possible to transfer the grown graphene from the SiC substrate,²²⁶ it is not as straight forward as in other synthesis methods, which is an important consideration for applications such as transparent contacts. The use of ultra-high vacuum and very high temperatures also makes it potentially more costly to manufacture epitaxial graphene, which is an important consideration when compared to current cheap silicon devices, and may put off uptake of this method by a VLSI industry who are both reluctant to change from the well established silicon route and see a potential increase in overheads.

The chemical vapour deposition technique has developed at a pace since 2009 after the methods outlined in ref.[76] and ref.[148], which is likely in part due to the CVD equipment and skills being carried over from experience in nanotube synthesis by various research groups. It shows great promise in growing large, inch scale areas of graphene with good electrical properties, showing peak carrier mobilities of up to

7,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and sheet resistances of 30 Ω/sq at 90% optical transmittance when p-doped with nitric acid.¹⁶⁷ The potential for industrial scalability is strong; however the use of high temperatures in synthesis, a drawback not present in solution processed graphene, effectively increases the cost. The necessary transfer procedure from the metal catalyst is perhaps the most troublesome aspect of this process, however is potentially automatable by the use of a roll to roll production line. The likelihood is that CVD graphene will be used by industry in the longer-term future, particularly in the field of transparent conducting films.

Solution dispersed graphene's principle advantage is the comparatively low requirements for equipment and conditions. Unlike CVD or silicon carbide reduction no high temperatures are required, both reducing cost and ensuring there are no conflicts arising in a process flow for a given application, for instance where the growth temperature would exceed the melting point of an already deposited material. The ability to spray coat graphene membranes would be of great utility, however currently this results in high sheet resistances of $2 \times 10^7 \Omega/\text{sq}$.²⁰⁶ Filtration of the colloidal graphene solutions into graphene papers results in reasonable conductivities of $7,200 \text{ Sm}^{-1}$, and a high tensile strength of up to 35 GPa.²⁰⁶ Thus while the quality of the graphene produced by solution dispersion may be the lowest, due to the deposited film comprising many small graphene flakes rather than a single layer and the dominance of variable range charge hopping from residual oxygen sites,²²⁷ the simplicity of preparation, low cost, no potentially egregious temperature conditions and facile transfer procedure are all advantages over the alternatives. One further advantage of this method is the potential to readily functionalise the graphene in suspension to

modify its properties, as with carbon nanotubes.²²⁸ The low costs and ready scalability lend solution processed graphene to industrial application in the nearer term.

2.5 Characterisation of Graphene

The limiting factor in the study of graphene was not the isolation of sheets, but their identification and characterisation. In a fundamental sense the initial fabrication of graphene was trivial; it is probable that every pencil trace contains at least some isolated monolayers. However, identifying these monolayers required special optical microscopy techniques, and then understanding graphene's properties in detail utilised a wide range of characterisation methods; such as transmission electron, scanning electron, atomic force and scanning tunnelling microscopy, Raman spectroscopy and electronic device fabrication. It has been decided to limit this review to those methods which are germane to the research matter of the thesis, namely optical, scanning electron, and atomic force microscopy, as well as Raman spectroscopy. As transmission electron microscopy is such a major part of this work it shall be covered in its own section.

2.5.1 Optical Microscopy

Graphene is only an atom thick, with a transparency of 2.3% per layer, and thus one would expect it to be all but invisible to optical microscopy. This is typically the case, unless the graphene is located on a substrate with a thin-layer film of appropriate depth, which provides an additional distance for the optical path and thus causes interference, and stronger contrast of graphene layers with respect to the background. Using optical microscopy to find graphene, particularly when produced by mechanical exfoliation, is particularly useful. The high throughput and quick search speed allow for graphene

flakes to be located and their thickness semi-quantitatively identified by the level of contrast with respect to the background. Figure 2.12 shows an example of some graphene layers seen by an optical microscope.

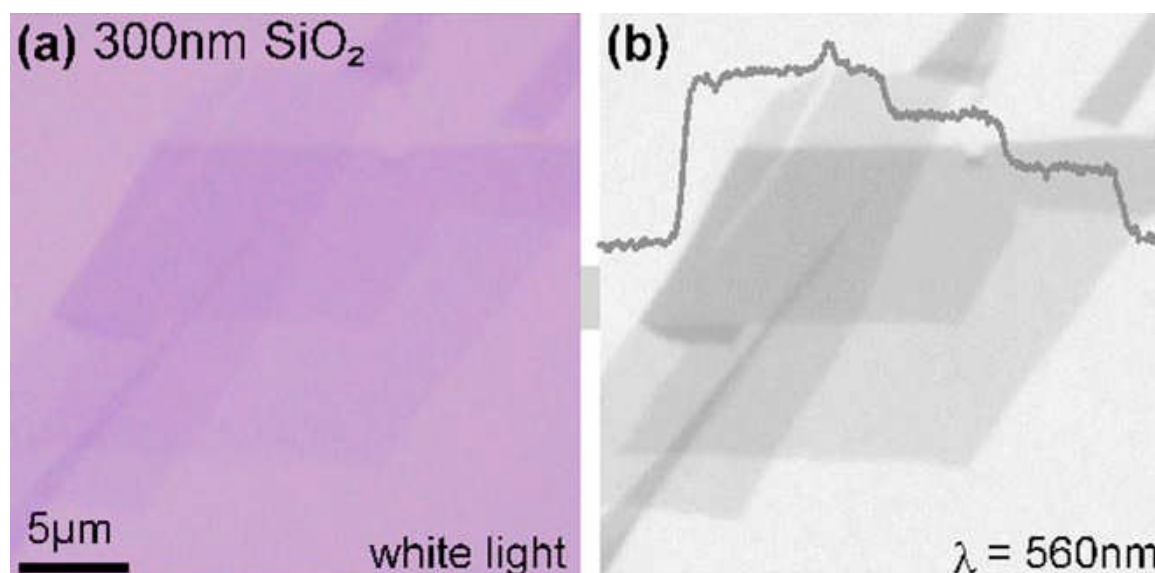


Figure 2.12. Several graphene layers on 300 nm SiO₂ as seen by optical microscope under (a) white light and (b) green light, illustrating the change in contrast with layer count. The darker regions are graphene of a greater number of layers. Reprinted with permission from ref. [229]. Copyright (2007) American Institute of Physics.

The majority of work with graphene is conducted using 300 nm thick silicon dioxide on silicon wafers, with the thin layer of oxide acting to increase the optical path length. Without this the contrast between graphene and the background would be insufficient to be observed. Using the Fresnel equations it is possible to derive the optimum oxide thickness for a range of optical wavelengths (see Figure 2.13).²²⁹ The contrast of graphene is dependent on the quality of the CCD camera used to record the image, and so the ease with which graphene can be identified will vary from system to system.

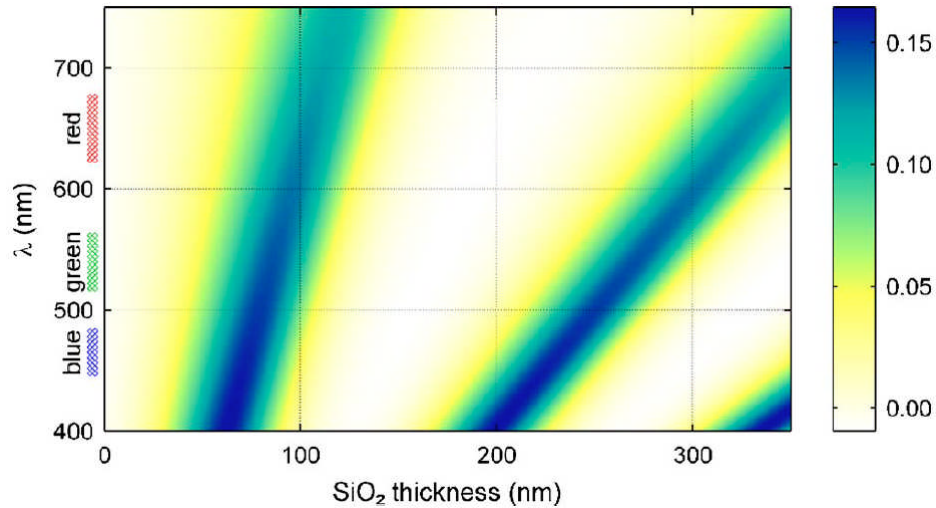


Figure 2.13. A plot showing the optimum filters to use on a microscope for a substrate of particular oxide thickness. The scale on the right indicates the level of contrast for a given colour on the plot. Reprinted with permission from ref. [229]. Copyright American Institute of Physics 2007.

2.5.2 Raman Spectroscopy

Raman spectroscopy is a non-destructive method for both positively identifying a material as graphene and for quantifying the layer count.^{230–232} When optically identified it is often difficult to discriminate between layers that are different by one purely by contrast, and even when it is possible a qualitative contrast measurement is not always ideal. The Raman spectrum exhibits different peak positions and profile shapes when the incident light interacts with particular graphene sheets, and hence can provide a quantitative means of thickness evaluation.

Raman spectroscopy relies on the inelastic scattering of optical photons from vibrational phonons in a lattice, which shifts the energy of the reflected probing beam. The interaction of the electric field E of the photon's electromagnetic wave over time t and the vibrational mode of a diatomic molecule vibrating at a frequency ν_m gives rise to an

induced dipole moment P , with the polarisability α approximated to be linear with displacement q from an equilibrium position q_0 by assuming small vibrations.

$$P = \alpha_0 E_0 (2\pi\nu_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \{ \cos[2\pi(\nu_0 + \nu_m)t] + \cos[2\pi(\nu_0 - \nu_m)t] \} \quad \text{Equation 2.8}$$

The first term of Equation 2.8 represents the Rayleigh scattered photons, and the two cosine terms represent the anti-Stokes (frequencies summed) and Stokes (difference of the frequencies) terms. If the partial derivative component is zero then the particular mode is not Raman active. Due to population levels the Stokes term is typically measured by a Raman system, which is where the final vibrational state of the molecule is higher than the initial (a phonon is created), and thus the released photon is of lower energy than the incident.

Raman spectra for mono- and bilayer graphene are shown in Figure 2.14a. The two spectra are readily distinguished by the profile of the 2D peak, as well as its relative position and intensity. The G peak, a signature of the carbon-carbon stretching mode and found in all sp^2 carbons, at $\sim 1580 \text{ cm}^{-1}$ and the 2D peak, originating from second order zone boundary phonons, at $\sim 2700 \text{ cm}^{-1}$ are the most prominent peaks in a Raman spectrum taken of graphene, or of bulk graphite. The G peak is down shifted slightly by $3 - 5 \text{ cm}^{-1}$ at higher thicknesses, and the full width half maximum (FWHM) begins to increase. The 2D peak up shifts markedly with incremental layer increases, and broadens into a shape composed of several Lorentzian peaks. As the layer count increases the lower frequency Lorentzian peaks comprising the 2D profile decrease in intensity, eventually leading to the shape found for bulk graphite, with an apparent “plateau” to the left of the peak (Figure 2.14b). Turbostratic graphene, that is graphene

that lacks the AB Bernal arrangement in its layering, shows a single Lorentzian 2D peak, however it is up shifted by some 20 cm^{-1} and has a FWHM of 50 cm^{-1} , double that of single layer graphene.

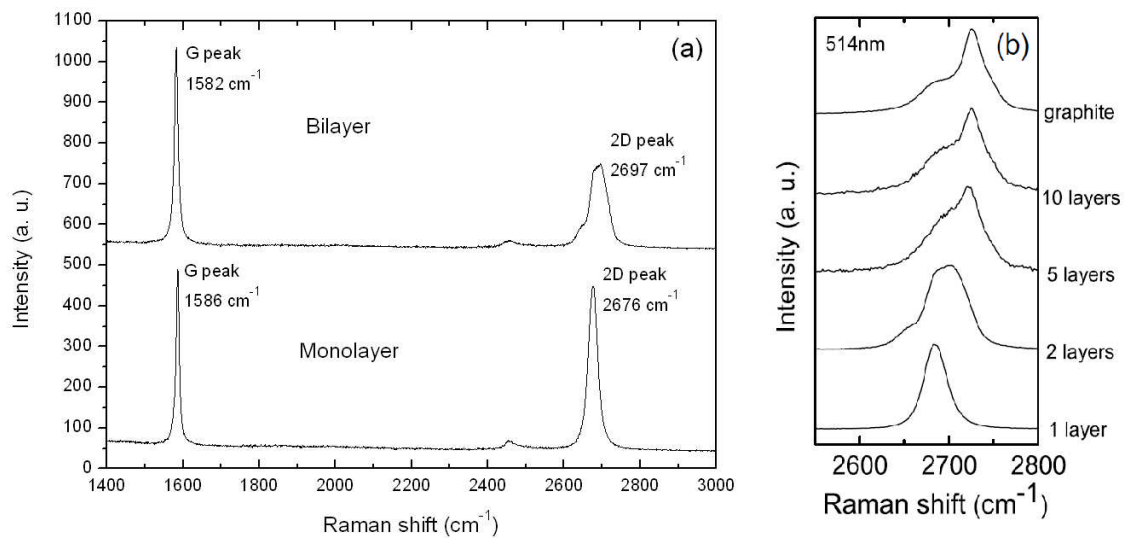


Figure 2.14. (a) Raman spectra for graphene and two layer graphene. The 2D peak for bilayer graphene has a significant up shift, and is composed of four Lorentzian peaks, rather than the monolayers single Lorentzian. Laser wavelength of 532 nm . (b) The change in Raman spectrum 2D peak with increasing graphene layer count (reprinted from ref. [230], copyright American Physical Society 2006). The FWHM of the peak increases, and the general shape tends to that of bulk graphite as the layer count increases.

Other peaks for graphene can occur at $\sim 1350\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$, and are the D and D' peak, respectively. The D' peak is normally seen as part of the much larger G peak, and is only apparent in strongly disordered graphene. The D peak, which is not present in theoretically ideal graphene due to polarisation symmetry, is visible at graphene edges as the mode only remains inactive for infinite crystals. An effective way of quantifying the quality of a graphene is to find the relative intensity of the D and G peaks.²³³

2.5.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is often used to measure the thickness of graphene layers by the use of non-contact (tapping) mode. However it has been noted that the step height measurements of graphene on silicon are variable.^{4,234} It has been shown that more reliable measurements are obtained by measuring across from one graphene sheet to another, for instance at a fold.¹ Unreliable AFM measurements of surfaces with changing material properties are due to changes in the attractive forces at work; for instance a thin film of water typically forms on graphitic substances due to its wettability, leading to a capillary force component in the attractive forces acting on the probe which is not present for the silicon dioxide substrate.²³⁵ This can be avoided by careful choice of measurement location, where possible using a folded or overlapping graphene edge, or by ensuring the AFM tip is acting in the repulsive, rather than the attractive, regime on both the graphene and the oxide surface. Contact mode AFM measurements lack this problem, however there is a minor (0.2 nm) deviation in the step height depending on the direction of the scan profile.²³⁴ The problems with thickness measurement do not necessarily effect the actual imaging however, and as such AFM can be used as a method of high-resolution imaging of graphene flakes in order to characterise their lateral dimensions, leaving thickness determination to an alternative technique, such as Raman spectroscopy.

2.5.4 Scanning Transmission Electron Microscopy

The scanning transmission electron microscope (STEM) is an operational mode possible with certain transmission electron microscopes, although some systems are bespoke to exclusively image in STEM mode. The imaging beam is focussed to a point, which is

raster scanned across the sample. The fine spot size and raster scanning make STEM ideal for spectroscopic mapping techniques, such as electron energy loss spectroscopy (EELS).

A powerful capability of STEM is the ability to map the sample with respect to the atomic weight, known as Z-contrast imaging, by employing annular dark-field detector. By collecting widely scattered electrons, which are strongly dependent on the atomic weight, it is possible to build an atomic resolution image where the contrast directly corresponds to the presence of atoms, circumventing the image interpretation issues inherent with phase contrast based HR-TEM. This technique is known as high-angle annular dark-field imaging (HAADF), and due to the position of the detectors off of the beam axis can be executed simultaneously with spectroscopic measurement, thus permitting direct mapping of the sample.

Some literature examples of STEM with regards to graphene research are covered in section 2.6.

2.5.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) occupies a strong position in between optical microscopy and more intensive processes such as AFM and TEM, providing sufficiently high resolution to resolve down to nanoscale features, whilst also offering a wide and continuous range of magnifications and a rapid imaging capability. These make SEM an excellent technique for examining just grown or transferred CVD graphene, permitting a fast assessment of the quality of the sample.

Difficulties arise in resolving the contrast signal of the graphene in many SEM systems, due to the single atom thickness of the layer rendering it effectively transparent to the electron beam. To analyse graphene in the SEM a low accelerating voltage is needed, which provides more surface information and thus increases the contrast of the graphene.²³⁶ Under these conditions, the SEM may be used to characterise the level of wrinkling and cracking in a transferred film. Wrinkles and creases show up clearly as regions of high contrast due to increased secondary electron emission from these topographic features, and similarly cracks can exhibit a fringe of bright contrast along the graphene edge due to more secondary electrons being scattered from these features, although this edge contrast may also be enhanced by an electron beam induced current (EBIC) effect.²³⁶

Typically SEMs utilise an Everhart-Thornley detector that is situated to one side of the system, hence the strong topographic contrast that is characteristic of an SEM image. However, by employing an in-column (also called in-lens) secondary electron detector it is possible to register significantly lower electron energies, which is ideal for studying thin surface structures such as graphene. Using an in-lens detector it is possible to delineate between graphene of different layer count by comparing the intensity of the secondary electron signal across the sample.²³⁷

2.6 Transmission Electron Microscopy of Graphene

High-resolution transmission electron microscopy (HR-TEM) is a powerful imaging tool, providing information down to the atomic level, whilst provoking minimal radiation damage at low accelerating voltages. Recent developments in correcting for spherical

aberration and reducing chromatic aberration have been crucial in permitting this leap forward to angstrom scale resolution at accelerating voltages that do not simply annihilate an organic sample.^{238–243} Furthermore, with TEM it is possible to take rapid consecutive images in a series, permitting the capture of the specimen's evolution at a high temporal resolution. Alongside these capabilities are some significant disadvantages, perhaps the biggest of which is the need for the material specimen to be electron transparent, so that the electrons may be transmitted through to the detector. This normally necessitates extensive sample preparation, with etching and milling procedures to thin the sample sufficiently to be imaged. However, graphene's inherent atomic thickness negates many of the conventional sample preparation issues, and thus is a perfect specimen for study by low-voltage aberration corrected HR-TEM (AC-TEM), allowing the probing of atomic scale defects in the graphene structure at high spatial and temporal resolution.

2.6.1 HR-TEM Background

HR-TEM relies on the interference of multiple transmitted electron beams through a thin specimen in order to construct an image that shows the variation of phase. This is as opposed to other optical and electron microscopy techniques, where sample information is typically derived from variation of the beam amplitude due to absorption by the specimen. Measuring the interference of multiple beams passing through the sample, instead of the relative amplitude attenuation of a single beam, means it can be significantly more difficult to interpret an HR-TEM image.^{244,245} For instance it is possible for an image to display different contrasts for atoms, rather than all atoms being of dark

contrast, due to the phase of the contrast transfer function. The background of the contrast transfer function is explored in Appendix A.

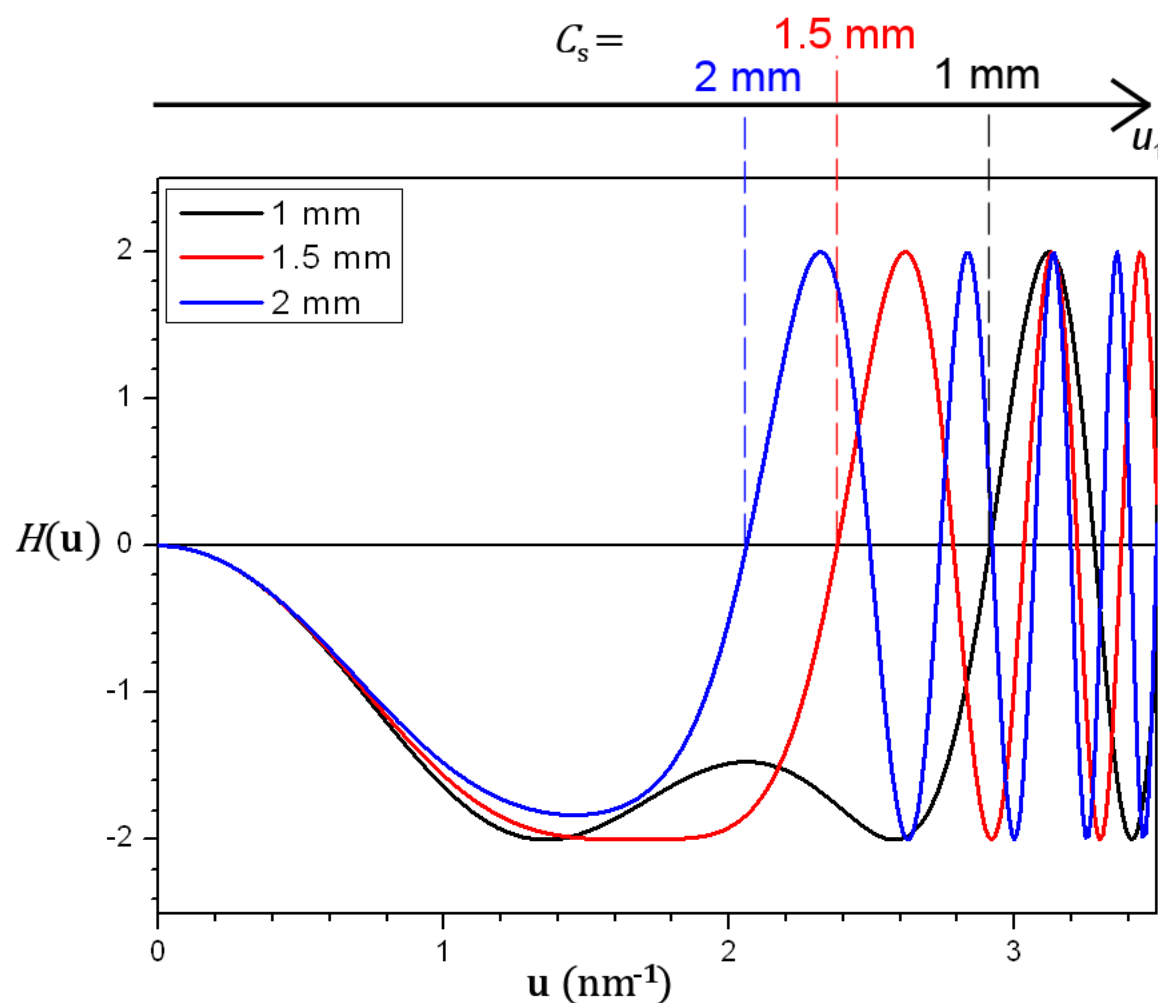


Figure 2.15. The effect of spherical aberration (C_s) on the contrast transfer function. Lower C_s values give a wider region of constant phase and a larger u_1 . Curves calculated for a microscope at 80 kV and defocus of -80 nm.

In AC-TEM systems it is possible to control the spherical aberration coefficient, a capability not available in ordinary HR-TEMs (Appendix B). Figure 2.15 illustrates how reducing the objective lens C_s broadens the frequency region that is in constant phase, and increases the point of first crossover, u_1 . Thus a smaller C_s yields better image resolution, and pushes the resolution limit nearer to the information limit. This is further

improved by operating the microscope at the Scherzer defocus (Appendix A), where the increase in the size of the uniform phase region permits the intuitive interpretation of images taken of thin specimens.

2.6.2 Imaging Graphene

Due to graphene's mono-atomic thickness, it is legitimate to interpret monolayer graphene samples as weak-phase objects, allowing us to approximate that the phase of transmitted electrons corresponds to the crystal's field potential. Thus at the Scherzer defocus one can simply interpret regions of dark contrast in an image as regions of high electron density, although this approximation breaks down for extremely low accelerating voltages (20 kV), due to the increased interaction between the electron beam and the carbon atoms.²⁴⁶ However, obtaining consistent atomic resolution images of graphene remains non-trivial, even with high quality TEMs, due to the intrinsic instability of the corrected state.²⁴⁷ This necessitates constant fine tuning of the microscope to compensate for small fluctuations in the correctors.

The effect of electron irradiation on TEM specimens is an important consideration when imaging,^{248,249} particularly for samples comprised of light elements such as carbon.^{250–256}

Whilst irradiation effects are typically a hindrance with regards to obtaining high quality images, it also presents a potential opportunity for engineering the properties of materials on the nanoscale. By controllably sputtering atomic vacancies and reconfiguring the structure it should be possible to tailor a range of properties.^{257–261} In the specific case of graphene it has been well established that imaging at or below an accelerating voltage of 80 kV reduces the knock-on damage suffered by a pristine graphene,^{262,263} due to the electrons imparting energy below the minimum threshold

energy of approximately 22 eV.^{254,264,265} This low voltage still does not prevent electron mediated chemical etching or the sputtering of under-coordinated carbons.²⁶⁵ Further care needs to be taken with controlling the electron dose that an area of graphene receives, with higher doses leading to some defect formation even at 80 kV.^{265,266}

In the following sub-sections a brief review of the literature of TEM done on graphene is presented.

2.6.3 Dislocations

The plasticity of graphene, as with all crystals, is critically affected by the presence and movement of dislocations. This fundamental defect is of great interest to material scientists in general, as the study of dislocation dynamics in graphene could present a valuable window to validating universal dislocation models in other materials.²⁶⁷ Due to graphene's two-dimensional nature one can only find edge dislocations,²⁶⁸ a complimentary pair of which can be formed by the removal of a zigzag chain of carbon atoms, as in Figure 2.16a-c.²⁶⁹ The pentagon-heptagon dislocation core, a (1,0) dislocation, adds a semi-infinite row of atoms along the armchair axis in which the defect points, or two semi-infinite zigzag rows (Figure 2.16d-f).

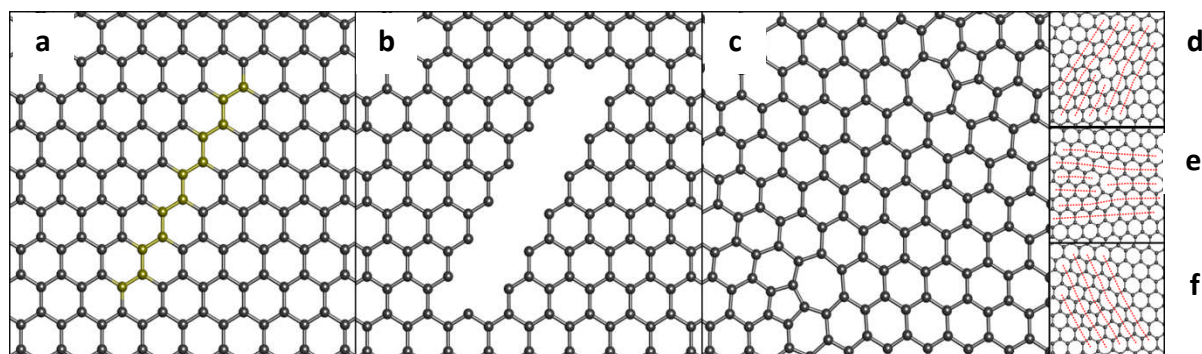


Figure 2.16. (a) Atomistic model of a graphene sheet. The highlighted zigzag chain of atoms removed, as in (b), yield a dislocation pair with two pentagon-heptagon cores, modelled in (c). (d-f) Atomistic models of a pentagon-heptagon dislocation core, with red line annotations for each of the three zigzag direction (100) graphene planes. The planes in (d) and (e) both gain a zigzag row, and (f) does not.

HR-TEM of graphene layers exposed to electron irradiation have been shown to form edge dislocations,²⁷⁰ however the lack of spherical and chromatic correctors prevent the resolution of the atomic structure. Atomic resolution AC-TEM studies of dislocations in graphene permit the observation of electron beam mediated displacement in real time. Figure 2.17(a-c), models in (d-f), shows a dislocation pair that first moves closer together through shifting a lattice position via the green highlighted atoms undergoing a Stone-Wales rotation (a glide process), before separating along the common zigzag axis by the removal of the two yellow highlighted atoms (a climb process). The dislocation core can be clearly seen to comprise a 5- and 7-membered carbon ring, with the atomic resolution permitting the direct measurement of the C-C bond lengths of the pair (Figure 2.17d). This shows a significant extension and compression of the bonds of up to 27%, with the strain field extending into the surrounding lattice for up to several Angstroms from the 5-7 structure.²⁷¹

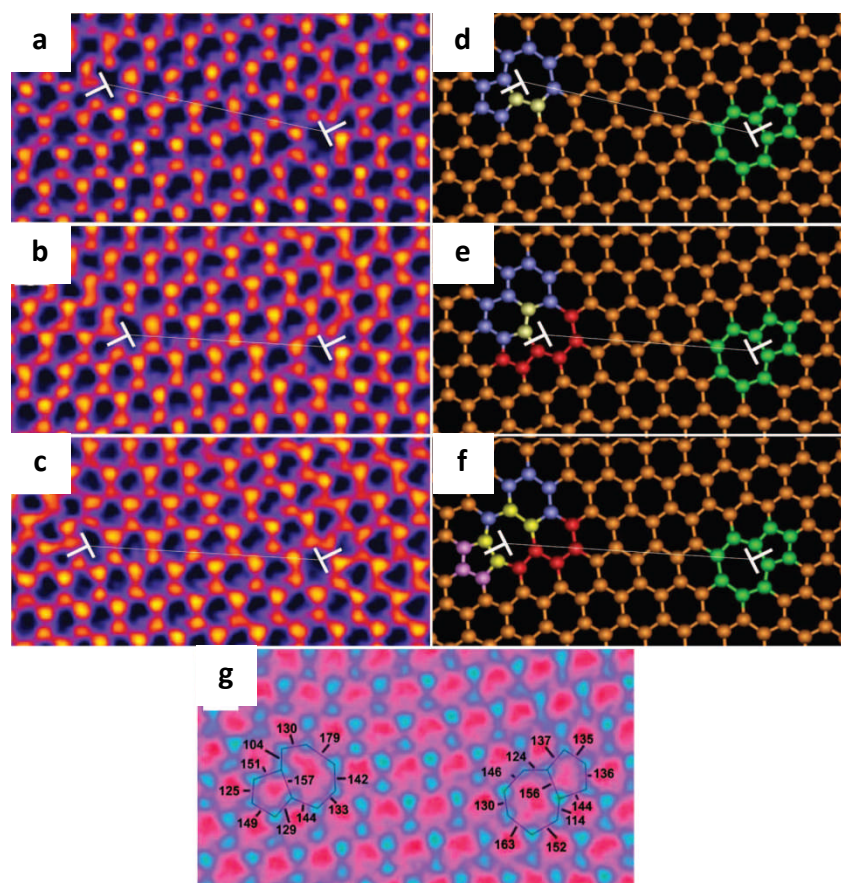


Figure 2.17. (a-c) AC-TEM images of a dislocation pair (white Ts) undergoing a glide (b) and climb (c) migration. (d-f) Atomistic models of (a-c). (g) Bond lengths, in pm, measured for the dislocation cores. Average bulk C-C bond length was 141 ± 10 pm. Reprinted with permission from [271]. Copyright American Association for the Advancement of Science 2012.

2.6.4 Grain Boundaries

Even with the best synthesis techniques, grain boundaries in graphene are unavoidable for sheets fabricated on a scale suitable for industrial application. Yet these structures have been shown to affect the characteristics of graphene, such as leading to local doping and scattering,^{54,268,272} resistance to fracture,²⁷³ and weak localisation.²⁷⁴

It is possible to rapidly distinguish between different grains (sometimes referred to as domains) in the TEM by using dark-field (DF) TEM, where individual crystal orientations are isolated by using an aperture to select the appropriate diffraction spot. This method

has been used to map relative graphene grain orientations and grain densities, and is particularly useful when quantifying and contrasting different CVD graphene growth conditions for optimising grain size.^{275–277} A DF-TEM image, and accompanying diffraction pattern, of polycrystalline graphene are shown in Figure 2.18a,b.²⁷⁶

By employing aberration corrected imaging, such as AC-TEM and ADF-STEM, it is possible to directly resolve the atomic configuration of the grain boundary. In Figure 2.18c ADF-STEM images from ref. [276] clearly show the alternating pentagon-heptagon chain expected from a grain boundary in graphene,⁵⁴ and the angular mismatch between the orientation of the hexagonal lattice on the left side from that on the right. The real-time observation of grain boundary migration is achievable by AC-TEM; by exploiting the propensity for SW bond rotations at electron irradiation energies of 80 kV it is possible to induce changes in grain boundaries at an appreciable rate, and thus it is possible to witness the collapse of isolated nanometre scale grain boundary loop structures,²⁷⁸ such as that shown in Figure 2.18d, to pristine lattice with no angular misorientation.²⁷⁹

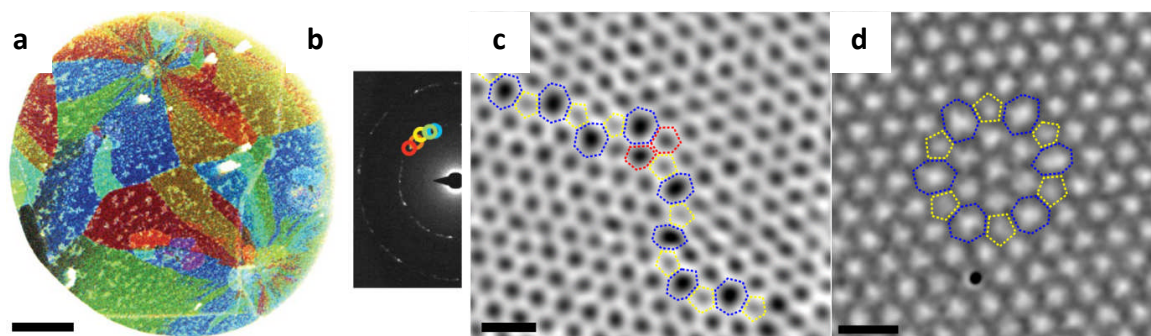


Figure 2.18. (a) False colour dark-field TEM image of multiple graphene grain orientations. Scale bar is 500 nm. (b) The diffraction pattern of the polycrystalline graphene in (a), with the coloured circles corresponding to the selected aperture used to highlight the same coloured grain in (a). (c) Low pass ADF-STEM images of a grain boundary, with colour highlights of yellow, red and blue indicating 5-, 6- and 7- membered rings. The grains are rotated by 27° to one another. Scale bar is 0.5 nm. (a-c) are reprinted with permission from ref. [276]. Copyright Nature Publishing Group 2011. (d) AC-TEM of a nanometre scale grain boundary loop, with a core of seven 6-membered rings rotated by 30° with respect to the bulk lattice. Scale bar is 0.5 nm. Reprinted with permission from ref. [266].

Combining TEM measurements of graphene grains with electrical characterisation, it was found that grain boundaries in few-layer graphene appear to exhibit two distinct configurations; the atomically bonded arrangement seen in ref. [276] (Figure 2.18c), or an interlayer overlap. Tsen *et al.* fabricated electrical devices patterned to cross grain boundaries, as determined by prior DF-TEM characterisation.²⁸⁰ For cases where there was well stitched atomic bonding along the grain boundaries then minimal increases in resistivity were found, however for cases with significant gaps between grains, due to the grains growing in a non-polygon shape, there was a significant increase in resistance. Overlapping grain boundaries did not exhibit such a degradation of performance.

2.6.5 Edges

A great deal of interest has been vested in the study of graphene edges, in particular their effect on graphene nanoribbons; structures that exhibit modified electronic properties to that of bulk graphene.²⁸¹ The edges of graphene terminate in three different ways, known as zigzag, armchair and reconstructed zigzag (or “reczag”). Figure 2.19a-c shows smoothed AC-TEM images of the zigzag, armchair and reconstructed zigzag configuration, respectively, with annotated images, atomistic models and multislice TEM image simulations which corroborate these structures. The armchair and zigzag configurations result from terminating graphene along the appropriate lattice line, without any reconstruction. AC-TEM imaging,^{282–284} and supporting calculations,^{285,286} have demonstrated that the formation of a reconstructed zigzag state is of lower energy than the metastable zigzag configuration. It is possible to capture the formation of dangling, single bonded carbon atoms projecting from the graphene edge; these are known as Klein edges,²⁸⁷ and one is shown in Figure 2.19d (yellow arrow). These protrusions were first observed experimentally by careful AC-TEM inspection of graphene edges by Liu *et al.*,²⁸⁸ and also observed under ADF-STEM by Suenaga *et al.*²⁸⁹ The STEM characterisation also permitted the analysis of the energy-loss near-edge fine structure (ENLES) of the individual carbon atoms of a Klein edge, and indeed that also of a zigzag edge atom, thus demonstrating the application of atomic resolution spectroscopy for delineating between bulk and defective states in graphene.²⁸⁹

The relative energetic stabilities of the three edge structures are not necessarily corroborated by the observed lifetimes of the different edges when observed under the TEM due to the effects of electron irradiation and knock-on damage.^{282,290} Whilst it is

reasonable to assume that the main factor influencing the edge sputtering rate is the coordination of the edge atoms, DFT calculations suggest that the armchair configuration is more stable for long edges, as the kinetic energy from the electron impact can be readily distributed to neighbouring carbons. This does not necessarily apply to holes, however, where zigzag terminations appear to be preferred.^{282,290,291}

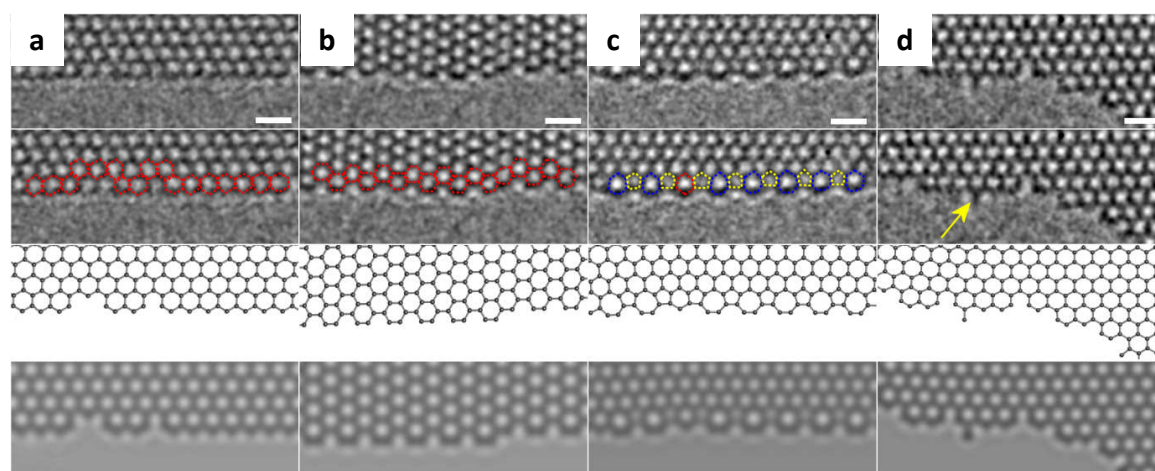


Figure 2.19. Four edge structures: (a) Zigzag edge. (b) Armchair edge. (c) Reconstructed zigzag edge. (d) Klein edge. For each case are shown a smoothed AC-TEM image (top), an annotated AC-TEM image, an atomistic model, and a multislice TEM image simulation (bottom). The annotations represent the number of carbons in each ring; with yellow, red and blue corresponding to 5-, 6- and 7-membered rings. Scale bars correspond to 0.5 nm.

Milling holes in graphene, either by ion/high energy electron bombardment or by radiation induced chemical etching,^{260,291–293} is an effective method for fabricating narrow ribbon structures for TEM study. By further exposing two adjacent holes to the electron beam one can increase their diameter further, effectively narrowing the size of the intermediate constriction between them; in fact it is possible to narrow this graphene ribbon all the way down to a single chain of carbon atoms.^{284,291,294} One can follow the formation of these carbon chains (Figure 2.20a,b) directly from the narrowing ribbon (Figure 2.20c), and are frequently observed as the final stage before the

complete elimination of the constriction as the two holes merge. Rather than a single chain, it is common to observe a double chain structure, as in Figure 2.20b, which may be arise from the splitting of a single zigzag row of 6-membered rings into two carbon chains.²⁹⁴

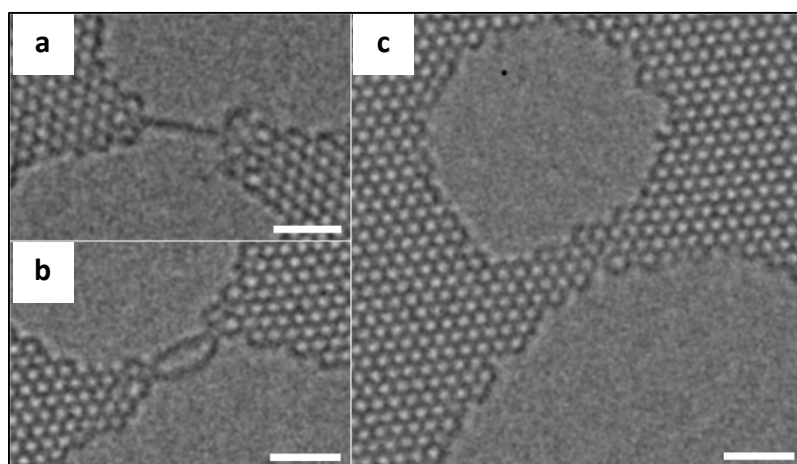


Figure 2.20. Smoothed AC-TEM images of (a) a graphene carbon chain and (b) two adjacent carbon chains. (c) Large field view of an earlier image from the sequence including (b), showing two adjacent holes with a ribbon structure between them. Scale bars are 1 nm.

2.6.6 Multiple Layers

Whilst imaging topological defects in graphene is best done for single layer systems, there exists significant interest in the properties of few-layer graphene due to the distinct electrical properties they exhibit.^{32,112,295} The TEM can be used to reliably characterise both the number of layers and the crystallographic orientation of few-layered samples, making it a good method to corroborate information obtained from other techniques, such as Raman spectroscopy.

2.6.7 Identifying the Number of Layers

There are several techniques for determining the layer count of a graphene sample, most of which do not require the high resolution of an AC-TEM. The most intuitive and straightforward method is by counting the number of fringes at a fold in the graphene; these fringes form at the part of the fold that lies parallel to the beam.^{24,288} A graphene termination with a clean high contrast edge is typically that of a fold rather than an open edge. Figure 2.21a shows an example of a fold, with the four dark fringes characteristic of four-layered graphene. It is possible for this to present a misleading picture as a complex folded structure may lead to multiple sets of fringes.

By just obtaining an electron diffraction pattern of a graphene sample it is possible to confirm the presence of a monolayer or few-layer graphene, although not to quantitatively determine the number of layers in the later case. There are two distinct phenomena that one observes in the monolayer case; firstly the intensity of the diffraction peaks remains approximately constant with increased tilt angle, before steadily decreasing at high angles (Figure 2.21d). This is clearly distinct from the few-layer case, where the intensity can be seen to undergo a series of oscillations with distinct minima and maxima (Figure 2.21e). This is due to the inherent two-dimensionality of monolayer graphene; with its single crystal layer there is only the zero order Laue zone, with no higher order zones associated with further layers.²⁴ Consider a 3D graphical representation of the reciprocal space of monolayer and bilayer graphene, from ref. [296], as shown in Figure 2.21b,c. The reciprocal space for monolayer graphene is a hexagonal array of orthogonally oriented rods, which exhibit periodic attenuations when additional layer contributions, for instance bilayer, are added. The bisecting blue

sheet denotes the diffraction plane, with diffraction patterns for the two planes shown in the Figure 2.21b,c inserts. The action of tilting the sample causes the diffraction plane to rotate with respect to the rods, and thus occasionally pass between the gaps for the multi-layer case, yielding the variation of intensity shown in Figure 2.21e.

In addition to this method, a second monolayer graphene signature is the identification of the angstrom scale corrugations that allow it to be stable. Such a corrugated sample yields a cone shaped reciprocal space (Figure 2.21g), as opposed to rods (Figure 2.21b), which leads to a characteristic Gaussian broadening of the diffraction spots with increased tilt angle (Figure 2.21h). This phenomenon is observed to a more limited degree in the bilayer case as well (Figure 2.21h), but any corrugations appear to be quenched by the presence of further graphene layers.²⁹⁶

By employing focussed electron beam sputtering of the graphene sheet at a high current density it is possible to open up holes. It has been demonstrated that for few-layer graphene samples that these holes open up sequentially layer by layer with continued irradiation, such that one can directly image a part of each individual layer.^{262,297} Figure 2.22a,b shows a tri-layer example, with the region irradiated until vacuum was visible, with each sequential layer consisting of a larger window to the layers preceding it.

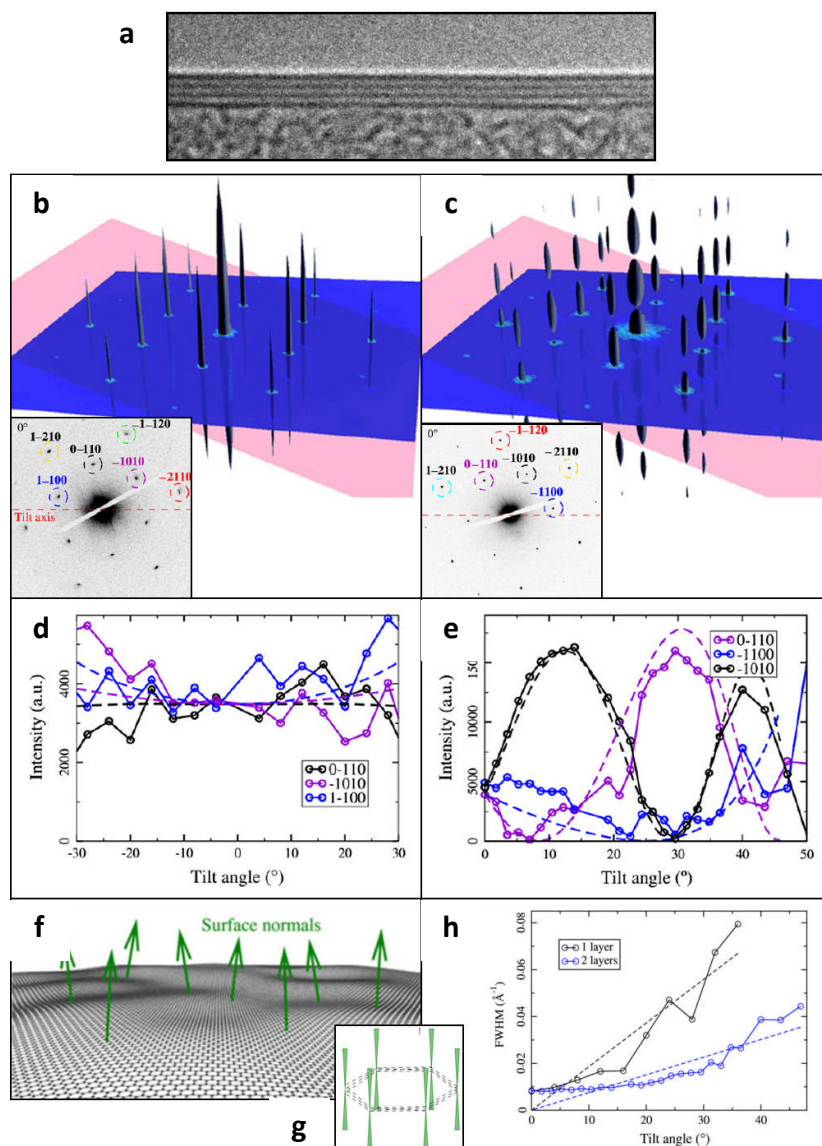


Figure 2.21. (a) HR-TEM image of a folded edge in graphene, showing four dark fringes characteristic of four layer graphene. (b,c) 3D reciprocal space plots of monolayer and bilayer graphene, respectively. The continuous rods for monolayer graphene are rendered periodic by the addition of further layers. Inset diffraction patterns are taken at the blue plane (0° tilt), whilst the grey indicates the effect of sample tilt. (d,e) Plots of diffraction peak intensities with increasing tilt angle for mono- and bilayer, respectively, with the crystal planes colour coded and labelled as in the diffraction patterns of (b,c). (f) Graphic illustrating the surface roughness of a monolayer graphene sheet, and the resulting reciprocal space representation of the range of surface normals in (g). (h) Plot showing the increase in full-width half-maximum (FWHM) of the diffraction spots with tilt angle for both mono and bilayer graphene. (b-h) are reprinted with permission from ref. [296]. Copyright Elsevier 2007.

Atomic resolution imaging by AC-TEM allows for the direct comparison of imaged interference patterns exhibited by few-layered films with that of simulations.^{263,297}

Different layer counts each offer distinct interference patterns, particularly at lower layer counts. Figure 2.22c presents image simulations of an increasing number of graphene layers from 1 to 9 for a -5 nm defocus. These images show a clear flip from black atom contrast to white atom contrast when the layer count is increased from one to two, and when further increased to three the previous hexagonal appearance is replaced by a triangular pattern with alternating contrast. The image simulations for the even numbered (4, 6 and 8) layers share strong similarities to the two layer case, with the hexagonal pattern and white atom contrast. This is opposed to the odd numbered (5, 7 and 9) layers, which display a decreasing resemblance to the triangular interference of the trilayer, and instead tend steadily toward a more hexagonal pattern akin to the even numbered cases. The convergence can be attributed to the decreasing effect of the single '+1' odd layer to the overall interference pattern for higher numbers of layers. The simulated patterns for the 1, 2 and 3 layer cases compare favourably to the AC-TEM image in Figure 2.22a.

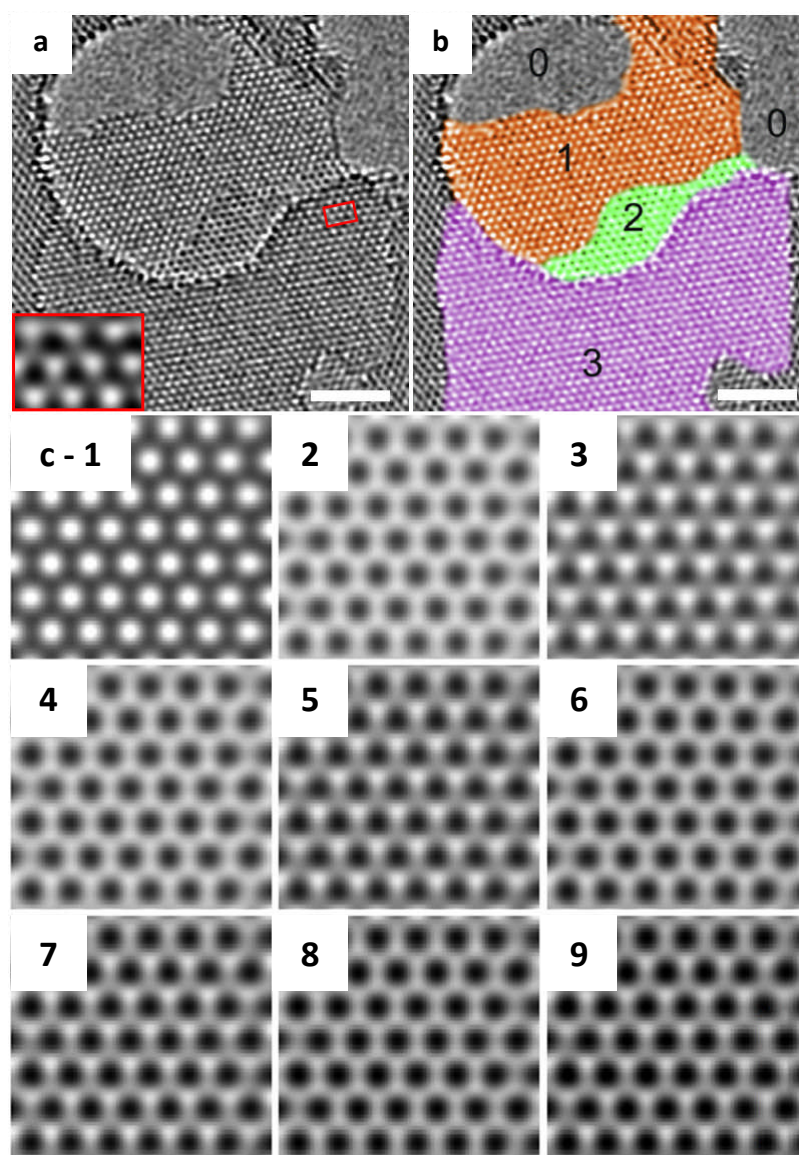


Figure 2.22. (a) AC-TEM image of an electron beam etch hole in few-layer graphene. Insert is a magnified shot from the red boxed region, showing the triangular pattern characteristic of trilayer graphene. (b) Colour coded and labelled overlay of (a), showing single, bi- and trilayer graphene. Scale bars are 2 nm. (c) Image simulations for 1-9 graphene layers at -5 nm defocus. Reprinted from [297]. Copyright Institute of Physics 2010.

2.6.8 Stacking Configuration

Multiple layers of graphene exhibit several permutations of stacking configuration, much like its parent graphite structure. The most common is ABA Bernal stacking; however there are also AAA, ABC and turbostratic configurations. Identification of these

structures can be accomplished in TEM by either analysis of the diffraction spectrum or from scrutinising the contributions to the moiré interference pattern directly by AC-TEM.²⁹⁸

Selected area electron diffraction (SAED) spectra of graphene can readily delineate between Bernal stacking and a crystallographic rotational fault, as an extra set of hexagonally distributed spots can be observed at the same lattice spacing which correspond to the mismatched crystal. Figure 2.23b shows a fast Fourier transform (FFT) power spectrum of Figure 2.23a, which demonstrates a 30° rotational misalignment between the two sets of hexagonally distributed spots. The FFT is calculated from the real space image; however it is equivalent to what would be observed in the diffraction plane of the TEM by using SAED.

Figure 2.23a is an AC-TEM image of a back folded bilayer of graphene, and demonstrates a pronounced moiré pattern. By employing selective Fourier filtering it is possible to reconstruct a real space image containing just the lattice information of each rotation (Figure 2.23e,h). The moiré pattern arises from the relative alignment of carbon atoms between the layers; the carbon rings of the rotated graphene layers are predominantly out of sync, however periodically they match up. The areas of black contrast correspond to rings of carbon atoms that are perfectly aligned between the layers, with lighter contrast regions containing less well aligned rings. Figure 2.23i-k show a comparison of an AC-TEM image with an image simulation of a pair of rotationally misaligned sheets.²⁹⁹ By using the careful comparison of experimental AC-TEM images with multislice simulations, it is possible to infer a great deal of the structure of few-layer systems, such as distinguishing rhombohedral (ABC) stacking from Bernal.³⁰⁰

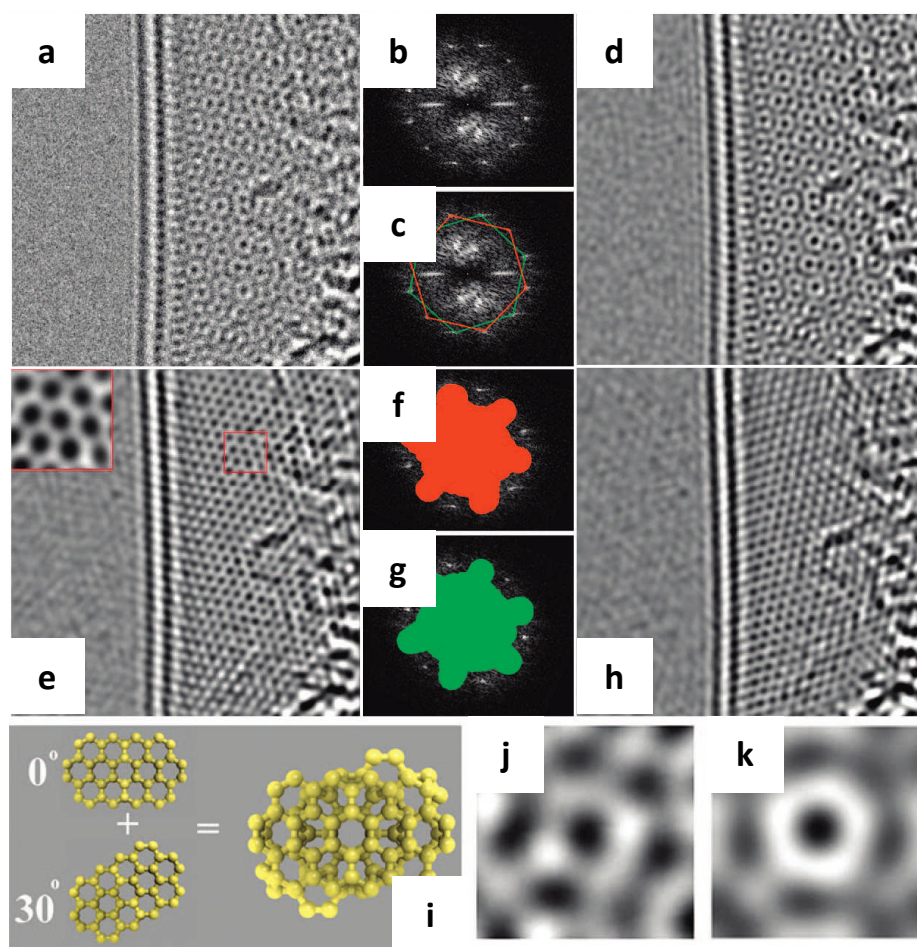


Figure 2.23. (a) AC-TEM image of a back folded bilayer showing a moiré pattern. (b) Fast Fourier transform (FFT) of the (a), showing two sets of diffraction spots, corresponding to the two sets of rotationally misaligned sheets. (c) Annotated FFT showing the two sets of spots. (d) A real space image reconstructed from both sets of diffraction spots, using the masks shown in both (f) and (g). (e) Reconstructed image from the FFT mask shown in (f). Insert shows a magnified region denoted by the red box. (f,g) Coloured masks indicate the inclusive filter frequency domains for panels (e) and (h), respectively, and combined for panel (d). (h) Reconstructed real space image from the frequency domain masked in (g). (i) Atomistic models showing the sum of two rotated graphene sheets yielding a regular superstructure. (j) AC-TEM image and (k) Multislice image simulation of the superstructure, with the dark contrast spot corresponding to the centre of the aligned 6-membered rings (arrows). Reprinted with permission from [299]. Copyright American Chemical Society 2008.

2.7 Conclusion

It is still difficult to evaluate the scale of the impact graphene will have on the world beyond the confines of academia. Whilst it is easy to speculate on potential applications, the actual deployment of graphene will require a compelling economic argument to justify switchover costs. However, it is reasonable to assume that the most disruptive uses for graphene will arise in original technologies that exploit the inherent properties of graphene, rather than attempting to deploy it as a replacement for an existing incumbent material. Regardless of the application, the development of graphene requires refining of the synthesis techniques, and subsequently tailoring these to specific technologies as necessary. A roadmap for the implementation of graphene has been suggested recently by Novoselov *et al.*,¹⁴⁶ in which they discuss the prerequisite need for certain benchmark material qualities to be surpassed before graphene may be implemented in particular products, and presents plausible time scales for certain applications. These range to within the decade for chemical exfoliated graphene applications to past 2020 for high quality graphene devices.

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Chapter 3

Methodology

3.1 Introduction

Over the course of this research project several experimental and analytical techniques were employed. Some of these, such as various materials characterisation methods and chemical vapour deposition (CVD), have already been touched upon in the literature review. However, the objective of this chapter is to cover specifically that which has been utilised for this project, rather than to explain the technique in more general terms. For instance, the section on transmission electron microscopy will refrain from discussing the minutiae of how the equipment technically works, or repeat how it has been used to analyse graphene. Rather, it will be limited to covering specifics, such as the microscope models used, and particular experimental nuances, such as sample pre-treatment before loading.

3.2 CVD Synthesis and Transfer

Establishing a chemical vapour deposition facility was the first objective of the project, as this would permit the repeatable synthesis of consistent graphene samples for characterisation. The setup is illustrated in Figure 3.1. The CVD system uses a split furnace, which can be opened up after cooling to allow for the easy replacement of the quartz tube. This was connected to an exhaust outlet on one end and the supply gas

lines on the other. Each line supplies one of argon, methane or hydrogen, with the methane and hydrogen premixed with argon to limit the risk posed from flammability. The gas lines are each controlled by an on-off valve, a pressure regulator and a mass flow controller (MFC), which for the early work discussed in Chapter 4 was of an analogue type. Superior digital MFCs were used later on, including for the liquid catalyst treatment for growing monolayer graphene discussed later and used in Chapter 6 and Chapter 7.

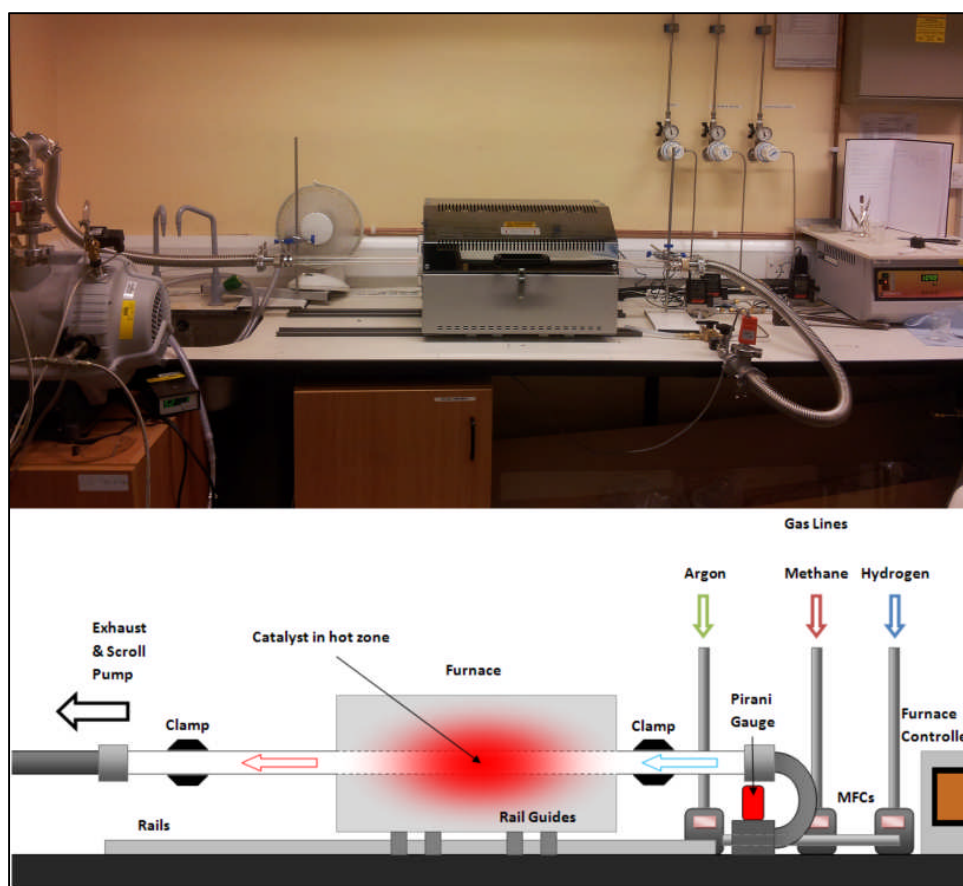


Figure 3.1. A photograph and schematic diagram illustrating the CVD setup used at the time of writing. The scroll pump and digital mass flow controllers (MFCs) were not used for the work outlined in the chapter on the CVD synthesis of FLG, where analogue flow meters were used instead.

3.2.1 Preparation and Transfer of Few-Layered Graphene

By research of the literature (Chapter 2) and careful exploration of the possibility space the following recipe was developed for the growth of few layered graphene (FLG):

1 cm² copper foils (Alfa Aesar, 99.8% purity) were loaded into a quartz tube positioned in the horizontal split-tube furnace. After purging the system with argon gas, 600 sccm of a hydrogen/argon gas mix (25% hydrogen) was introduced to the system. At a temperature of 1000 °C the quartz tube was shifted such that the sample resided in the furnace, where it was annealed and reduced for 30 minutes. A methane/argon gas mixture (20% methane) of flow rate varying from 10 – 50 sccm as desired was then supplied, whilst maintaining the 600 sccm hydrogen gas mix flow. The precursor supply time was changed as required, typically ranging from 1 to 10 minutes. The sample was then removed to ambient temperature by shifting the quartz tube from the furnace, and was left to rapidly cool under a hydrogen and argon atmosphere.

For transfer of graphene from the copper foils a poly-methyl-methacrylate (PMMA) supportive scaffold (8% wt. in anisole, 495k molecular weight) was spin coated on to the graphene surface. A spin speed of 4700 rpm was used for 60 seconds, with the film then cured by heating at 180 °C for 90 seconds. The underlying copper was etched away over night by an iron (III) chloride solution (concentration of 0.1 g mL⁻¹). The graphene/PMMA film was then rinsed in deionised water and transferred to an appropriate substrate, such as a lacey carbon TEM grid or a silicon/silicon dioxide wafer. The PMMA was then subsequently removed by rinsing in solvent, such as warmed acetone or n-methyl-2-pyrrolidone (NMP).

Transfer of the film to a holey silicon nitride TEM grid (Agar Scientific number Y5385) was done by attaching the grid to a lightly sticky pad (Gel-Pak gel-film WF-40-X8-A), which in turn was attached to a glass slide, and using this to “scoop” the film out of the DI water. A further coating of A8 PMMA was applied by drop casting, which acted to relax the graphene film on to the TEM grid, allowing for better adhesion and a better quality transfer of the graphene. This was allowed to dry in air over several hours. The PMMA was then removed by first applying acetone solvent, and then by baking in air for 2 – 3 hours at about 350 °C.

3.2.2 Method for Preparation of Monolayer Graphene

Dr. Wu and Mr. Fan developed a novel liquid catalyst recipe for the growth of high quality monolayer graphene, which was used in the AC-TEM analysis experiments of Chapter 6 and Chapter 7. Graphene was grown on a molten copper sheet (Alfa Aesar, Puratonic 99.999% pure, 0.1 mm thick) of 1 cm², resting on top of a similar sized piece of molybdenum (Alfa Aesar, 99.95% pure, 0.1 mm thick). This was loaded into the quartz tube of the split-tube furnace CVD system, which was subsequently sealed, pumped to vacuum and backfilled with argon. 100 sccm H₂/Ar (20% gas mix) and 200 sccm pure Ar was flowed, and the furnace was ramped to 1090 °C, whereupon the sample was slid into the furnace hot zone and annealed for 30 minutes, after which the CH₄ flow (1% gas mix in Ar) was enabled at 10 sccm and the H₂/Ar flow reduced from 100 to 80 sccm, whilst maintaining the pure argon gas line flow at 200 sccm. These conditions were maintained for 90 minutes to obtain continuous film growth. Following this the CH₄ flow was disabled and the sample immediately removed from the furnace hot zone, allowing for rapid cooling in the H₂ and Ar atmosphere. The sample was subsequently recovered

from the quartz tube once sufficiently cool. A PMMA scaffold (8% wt. in anisole, 495k molecular weight) was spin cast on to the graphene side of the graphene/copper/molybdenum sample at 4700 rpm for 60 seconds, and then cured at 180 °C for 90 seconds. The underlying molybdenum and copper were etched by floating the sample on an Fe(III)Cl_3 and HCl solution for several days, until just a transparent PMMA/graphene film remained suspended on the surface. This was thoroughly cleaned by transferring and floating onto clean DI water several times, then transferred to a 30% HCl solution for 5 minutes, which was found to be critical to allow for thorough decontamination of the graphene and prevent iron aided etching of the graphene,^{1,2} rinsed again in DI water for 30 minutes,³ and subsequently transferred to a holey silicon nitride TEM grid (Agar Scientific Y5385). Once left to dry for about an hour, the sample was baked on a hot plate at 150 °C for 15 minutes to remove water and greatly improve sample adhesion.

3.3 Scanning Electron Microscopy

Graphene samples were regularly characterised by SEM in order to determine the geometry of grain growth, variation in layer count and to identify the degree of damage incurred by the transfer process. Two instruments were utilised for this project, namely the Hitachi S-4300 field-emission gun (FEG) and the Zeiss NVision 40 FIB-SEM (Focussed Ion Beam – SEM dual system). Both instruments were capable of resolving graphene to good resolution with low voltage modes of operation (2-5 kV); however the NVision is a more modern instrument which crucially has an in-lens secondary electron detector that provides much improved contrast when studying thin surface films such as graphene

(see section 2.5.4). As such, where possible work was conducted using the NVision and all published micrographs, including those in this thesis, were obtained with the NVision.

SEM samples were prepared by grounding the graphene/silicon or graphene/copper specimen to a sample stub with silver paste or carbon sticky pads. Whilst the silver paste theoretically provides superior conductivity, to militate against unwanted charging, it was found that the sticky carbon pads were preferable due to not requiring a solvent rinsing stage to recover the graphene specimen from the stub. No appreciable charging effects were encountered with using carbon sticky pads.

3.4 Raman Spectroscopy

Analysing either as grown graphene/copper or transferred graphene/silicon samples by Raman spectroscopy was used to help determine the layer count and the level of defectiveness of the graphene, as discussed in section 2.5.2. This was conducted on the JY Horiba LabRAM ARAMIS confocal Raman spectrometer and accompanying software package, using a 532 nm frequency doubled Nd:YAG laser to provoke excitations. Measurements were taken in a frequency range broad enough to encounter all the salient features in a single readout with the coarse resolution 600 slits per mm grating. As a result spectra were typically taken from 1000 – 2800 cm^{-1} . The exposure time was automatically optimised by the software, and three repeat spectra were captured and averaged to remove noise. In the case of graphene on copper samples the copper background signal needed to be subtracted to provide a clear spectrum, which could either be achieved by fitting a high order polynomial or subtracting a normalised reference spectrum taken from blank copper. Fitting data for the Raman peaks was obtained by using the Lorentzian peak fitter in the Origin software package.

3.5 Atomic Force Microscopy

Determining the stacking profile of FLG grains is difficult using just SEM in isolation. Atomic force microscopy (AFM) provides a sensitive scanning probe method for directly measuring the topology of a graphene film, as discussed in section 2.5.3. Graphene must be transferred to silicon for AFM analysis, as graphene on copper foils was found to be insufficiently rigid or flat to provide usable data. AFM characterisation was performed on the Veeco Park CP AutoProbe SPM in both contact and non-contact mode. It was found that the best results were obtained for scanning fields of $10 \times 10 \mu\text{m}^2$ or below, as larger fields yielded extensive artefacts along the image boundary and limited resolution.

3.6 Transmission Electron Microscopy

Characterisation of CVD synthesised graphene constituted the majority of the project, and was conducted on several instruments. HR-TEM in Chapter 4 was done on a JEOL JEM-4000EX HREM with a lanthanum hexaboride (LaB_6) filament and operated at 80 kV. This instrument was also used to screen TEM samples for graphene quality prior to examination on a more heavily used system. AC-TEM data presented in Chapter 5 was collected by Dr. Warner from a JEOL 2010F at 80 kV, and the higher resolution graphene lattice images were captured with a FEI Titan³ at 80 kV, both of which were based at IFW Dresden.

The atomic resolution AC-TEM data analysed in chapters Chapter 6 and Chapter 7 were captured with the JEOL JEM-2200MCO operating at 80 kV. The image aberration corrector is designed by CEOS, which are able to correct to third order aberration

coefficients using a partially automated software package after an initial rough correction for beam stigmatism. Some figures in Chapter 7 were captured with the additional use of a double Wien Filter monochromator with a 5 μm slit, which filters the FEG source energy width to within a ~ 0.2 MeV envelope, allowing for single atom resolution.

Samples are prepared as outlined in section 3.2, however an additional one to two day 350 °C air bake is performed to thoroughly remove any residue from transfer. Samples to be analysed in the 2200 AC-TEM were subjected to a further pre-clean. The samples were loaded into a vacuum filament heater unit, which was set to approximately 150 °C under vacuum, and left for up to 12 hours. It was found that imaging straight after this treatment greatly decreased sample contamination and permitted unobstructed imaging of the graphene lattice.

3.7 TEM Image Analysis

Various filtering regimes were employed to the captured TEM images to remove noise and enhance contrast. The most straight forward method was a simple nearest-neighbour 3×3 smoothing filter in the ImageJ software package, which was used for Chapter 7. Figure 3.2 illustrates the effect of the two other processing techniques used. The top branch shows the effect of the application of a bandpass filter operation in ImageJ, used in Chapter 5, and the bottom branch shows the effect of manually removing all high frequency contributions, including higher order power spectrum peaks, in order to both remove noise and militate against beam stigmatism effects (used in Chapter 6). False colour schemes have also been used where noted to enhance contrast, and were applied by using colour look up tables (CLUT) available in ImageJ.

Images were calibrated to the correct magnification by measuring the position of the graphene {100} spots in a Fourier transform of the TEM image. The average pixel distance of these was calibrated against the appropriate 0.213 nm lattice spacing.

Geometric phase analysis was employed in Chapter 7 to reveal strain fields about point defect structures.^{4,5} By comparing the relative expansion or contraction of lattice spacings in a TEM image the strain may be inferred. This technique utilises a software plugin for the Gatan Digital Micrograph program called FRWRtools by the Stuttgart Center for Electron Microscopy. Once a TEM image was properly calibrated to the correct scale the plugin was run. Two of the {100} reflections were selected on the Fourier transform by moving the masking circles and a 1 nm resolution with 0 smoothing set. An area of the TEM image was defined to be unstrained and acted as a reference pristine lattice. The strain matrix was defined as symmetric. The strain maps of the four components of the strain tensor (ϵ_{xx} , ϵ_{xy} , ϵ_{rot} , ϵ_{yy}), phase maps and amplitude maps were then calculated from the two selected G-vectors (lattice reflections) by the plugin.

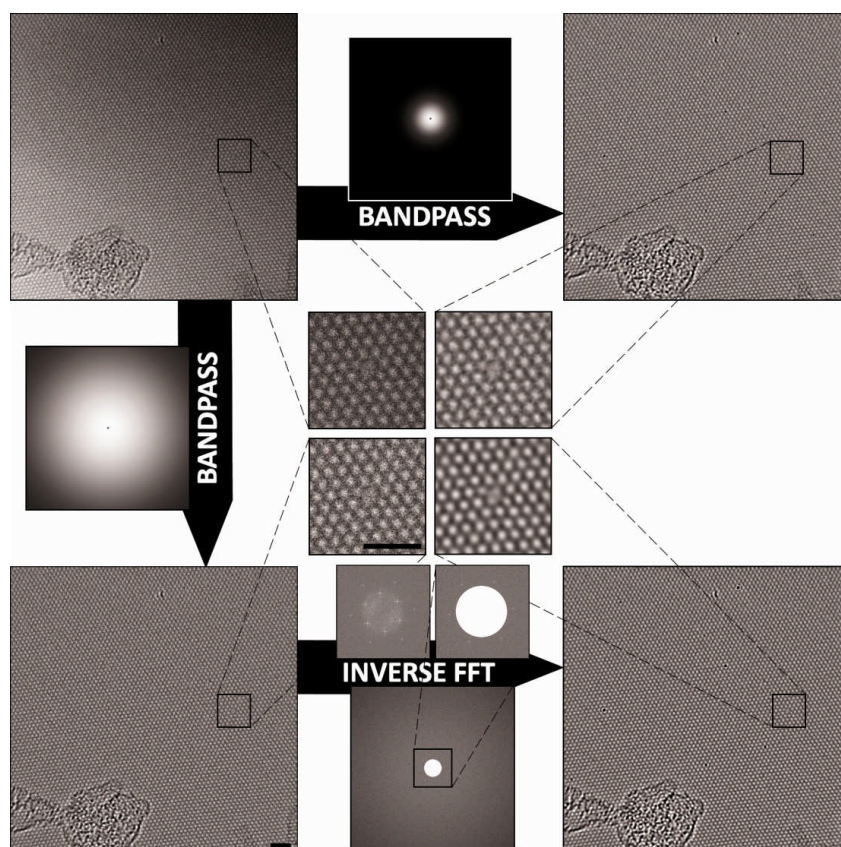


Figure 3.2. A flow chart showing two processing techniques used to analyse TEM images. The top left shows the as-recorded, unprocessed image. The path along the top demonstrates the application of a bandpass filter (FFT mask shown in insert), to remove both the brightness variation and high frequency noise. The path following the left through bottom show the procedure used for images in Chapter 6, where first a high pass filter is applied to remove brightness variation, followed by the application of a positive mask (shown in white in the bottom right FFT insert) to the FFT, to yield a reconstructed image that discards the more astigmatic higher resolution information. The centre shows magnified views of the same divacancy structure for comparison.

3.8 Atomic Modelling and Image Simulation

Atomic models were used for three purposes; illustrative renders, an input for TEM image simulation and an input for density functional theory structural optimisation. These models were prepared in Accelrys Discovery Studio 3.1 and optimised using the in-built Dreiding force field model. Illustrative renders were created from these using

the POVray program. Density functional theory modelling was conducted by Dr. B. Montanari and Prof. N. Harrison at the Rutherford Appleton Laboratory using the CRYSTAL code.

By exporting appropriate atomic models it is possible to generate simulated TEM images with the JEMS application (programmed by Dr P. A. Stadelmann and available at <http://cimewww.epfl.ch/people/stadelmann/home.htm>) and compare them with the experimentally captured image, and thus infer the atomic structure being examined. The atomic models were exported as co-ordinate lists, which were converted to a suitable format for the JEMS program to read by a Python script written by Dr. C. S. Allen. The TEM image simulation works by the multislice method, where it approximates the input crystal as a series of consecutive sub-nanometre slices, such that they obey the weak phase object approximation.^{6,7} The interaction of the electron wave with each slice is combined to provide a model image. With monolayer graphene there is only one slice needed, as it is inherently a weak-phase object. It is possible to adjust the parameters of the simulation to take into account different qualities of alignment and defocus in order to match the simulation to captured experimental data. Typically the parameters are set to match those of the microscope being simulated, with only the defocus spread adjusted, which acts as a limit to the image resolution. Here, simulations were taken for images from the FEI Titan³ and the Jeol 2200MCO, although simulations for the work done on the FEI Titan were approximated to the conditions for the 2200, as no alignment file was available. This was an acceptable approximation, as the simulations were not of high resolution features. The OJ2200 microscope simulation conditions were

set to an accelerating voltage of 80 kV, C_c of 0.591, C_s of -0.005, defocus of 0, energy spread of -0.32 and a lens stability of 0.

3.9 Reference

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Chapter 4

Hexagonal Single Crystal Grains of Few-Layer Graphene on Copper Foils

4.1 Introduction

As discussed in section 2.4.2, studies into the dynamics of chemical vapour deposition (CVD) graphene growth on copper foils have chiefly focussed on monolayer films that develop under vacuum conditions. Under these conditions the copper catalysed deposition of graphene occurs by a surface adsorption process, rather than a surface segregation followed by precipitation process, as in the case of nickel. This is attributed to the low solubility of carbon in copper, and consequently the growth of graphene on copper is expected to be self-limiting and restricted to that of a single monolayer.¹ The growth of graphene by low pressure CVD starts with the nucleation of a large number of grains across the copper surface. These grains form a four-fold symmetry lobe structure and continue to grow with time until they merge together to form a single sheet of polycrystalline graphene.^{2,3}

However, the understanding that copper catalysed CVD graphene was always self limiting to monolayer was overturned by a study that demonstrated an apparent change in growth kinetics when the deposition pressure is raised to atmospheric pressure, with

few-layer graphene formed,⁴ and a further study yielded bilayer graphene growth on copper.⁵ Both of these studies demonstrate that the previously observed self-limiting growth of graphene on copper does not apply under all synthesis conditions, but the details of the time-dependent growth mechanisms of the grains of few layer graphene (FLG) had not been thoroughly investigated. Furthermore, information on the crystallinity of the FLG was lacking, which is vital for understanding the band structure, and ultimately the electrical properties, of graphene films. In work published in 2011,⁶ I investigated the growth of FLG by CVD on copper foils at atmospheric pressure primarily using a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), along with selected area electron diffraction (SAED).

4.2 Results and Discussion

FLG was grown as outlined in the experimental chapter (section 3.2.1). A SEM was used to obtain images of the graphene grains directly on the surface of the copper foils without any processing, demonstrating both the shape and location of the graphene grains. A series of graphene growths on copper foils were conducted, with the methane growth period varied by incremental time intervals of 2, 3, 4, 5, 6, 7 and 10 minutes, using a 20%-methane/argon precursor flow rate of 10 – 15 sccm. Figure 4.1a shows a low magnification SEM image of the copper surface for the 2 minute deposition. The areas of dark contrast are graphene grains that have formed on the bright copper surface. It is apparent from the image that the graphene preferentially nucleates along linear axes, which could be due to the initial graphene nucleation occurring more frequently at step edges, folds or other imperfections in the copper foil which are linear in character. Figure 4.1b - d are images taken at higher magnification, for depositions of

3, 6 and 10 minutes, respectively. The grain shape of the graphene islands can be seen to be hexagonal, with individual grains growing into adjacent grains with time. Figure 4.1e - g show magnified grains for 3, 6 and 10 minutes, respectively, and also show the relative increase in grain size. The hexagonal shape remains for the full range of grain sizes imaged, and is not deformed by growth. Size distribution histograms for the graphene grains were constructed, with the size of the grain defined as the longest distance between two opposite vertices. It was found that a gamma distribution provided a good fit to the distribution of the grain sizes, and could be used to determine their mean size. Figure 4.1h shows a plot of deposition time versus average grain size, which shows a strong linear correlation and a growth rate of approximately 0.5 μm per minute, or an area growth rate of 0.16 μm^2 per minute. Further work was carried out to determine if there was any correlation in the relative angular orientations of the grains, however no noteworthy trends were found.

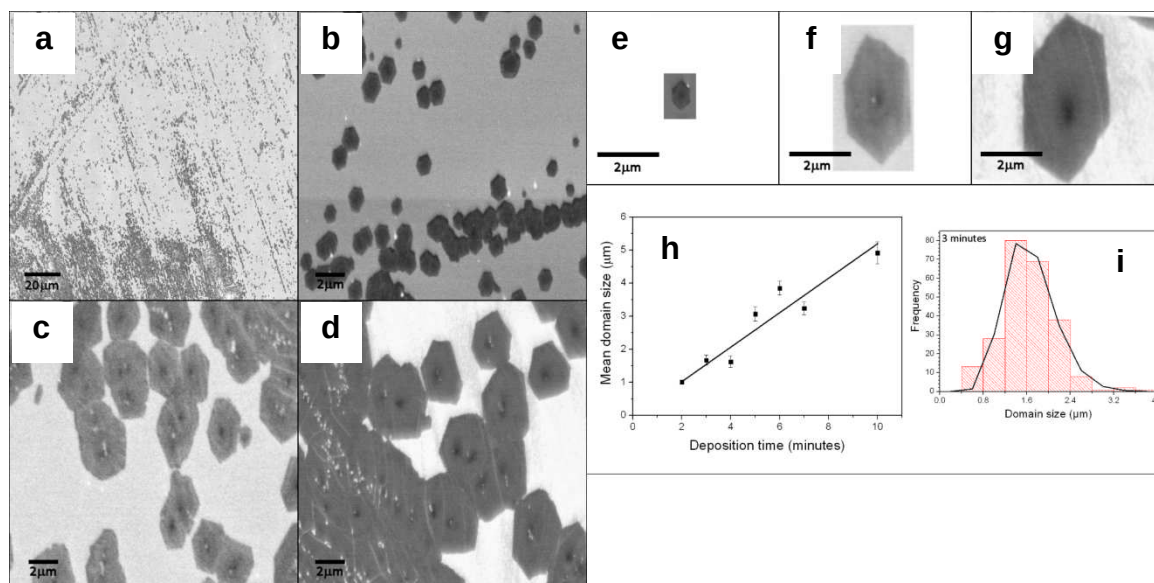


Figure 4.1. (a) A low magnification image from the 2 minute deposition, showing a typical distribution of the graphene grains on the copper foil. (b – d) High magnification images of 3, 6 and 10 minute growths, respectively. (e – g) High magnification, cropped images showing the relative scale of graphene grains for 3, 6 and 10 minutes, respectively. (h) The mean graphene grain size with respect to deposition time, with the mean determined by a gamma distribution of the distribution of grain sizes, as shown for the 3 minute deposition case in (i).

TEM was performed on graphene samples that were exposed to a methane flow of 10 - 15 sccm 20%-methane/argon gas mix precursor, for one and three minutes. Figure 4.2a-c show three typical individual isolated grains from the 1 minute exposure to methane. Each of these is well separated from other grains and enables the structure to be elucidated without the interference of overlapping. The insets in Figure 4.2a-c show their respective SAED patterns taken from the central region of the grain, with care taken to avoid regions that contain back-folded edges. It was found that all SAED patterns could be indexed to single crystals of AB-Bernal stacking, with only six spots of reflection being observed in the inner hexagon of 0.21 nm spacing. The presence of rotational stacking faults that are typical in turbostratic graphite or poor quality flake graphite leads to extra sets of spots appearing at the 0.21 nm lattice spacing in the SAED

patterns, which were not observed in any of the isolated single grains. This demonstrates that the grains are not turbostratic in configuration, but are single well ordered crystals. Contrast from the folded edges of graphene is observed in all three imaged grains in Figure 4.2. The grains are often folded along their edges and no longer display the characteristic hexagonal shape observed in the SEM images. Contrast from the folded edges can be used to reliably characterise the number of graphene layers at that location in the same way that the number of walls in a carbon nanotube can be determined.⁷ Figure 4.2d,e show TEM images of the folded edges from the regions indicated with a red and yellow arrow, respectively, in Figure 4.2a. Figure 4.2d shows six lines of contrast, confirmed by the line profile shown in Figure 4.2j, indicating that there are six layers of graphene in this region. Further along the edge (see Figure 4.2e) there are fewer lines of contrast, which suggests a reduction in the number of graphene layers toward the perimeter of the grain. In Figure 4.2e the transition from four layers of graphene to three is apparent. Figure 4.2f and g show a similar effect of thinning towards the edges for the grain in Figure 4.2b, and Figure 4.2h,i show it for the grain in Figure 4.2c. This effect was observed for all edges and indicates the central part of the grain contains more layers than the outer regions. Thus the number of graphene layers diminishes closer to the graphene grain boundary in a step pyramid type terraced structure.

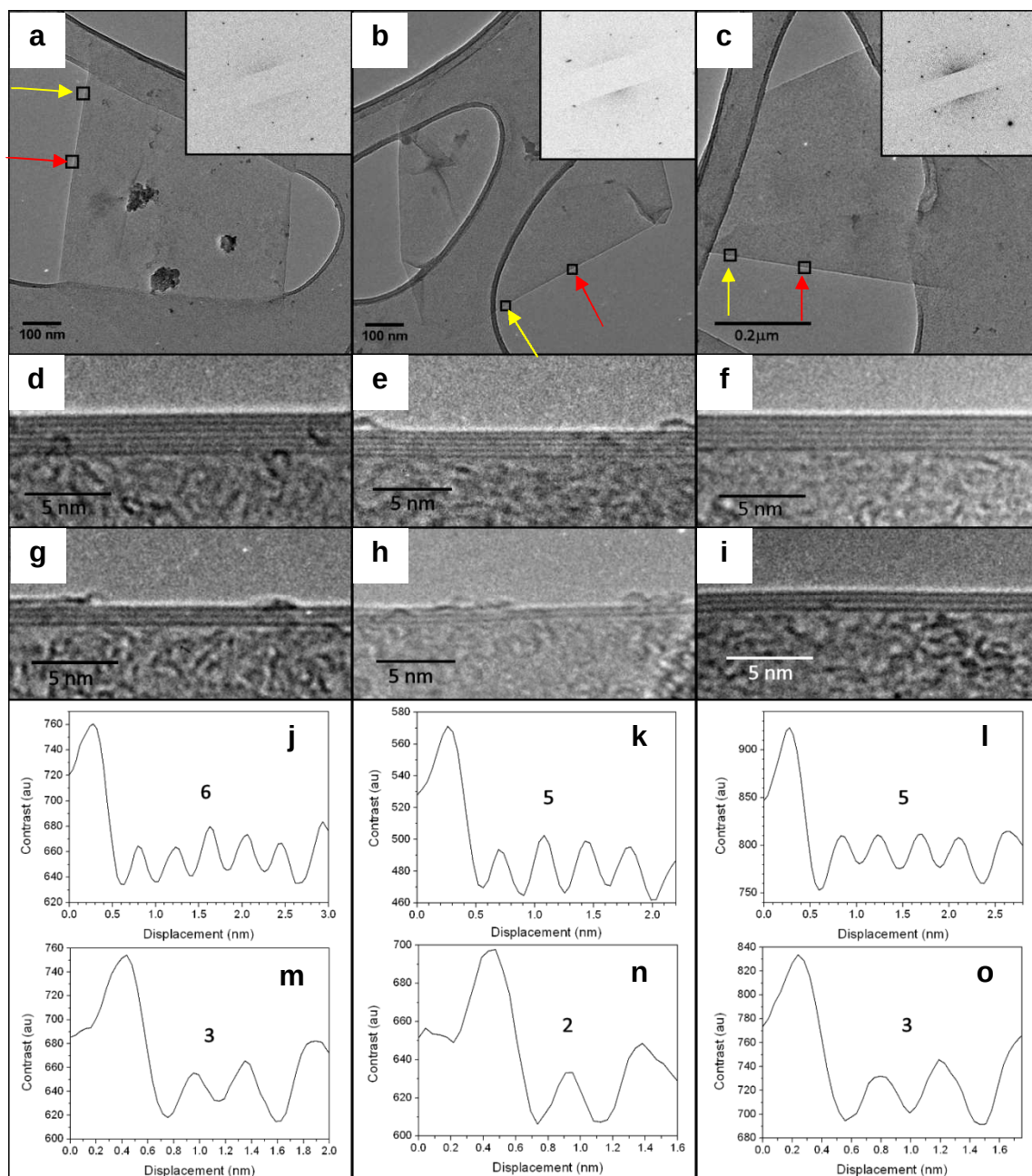


Figure 4.2. (a – c) TEM images of single, isolated grains of few layer graphene. SAED taken from the centre of the grains are shown in the inserts. (d – i) HRTEM images of the folds, from the arrowed regions in (a – c), with (d), (f) and (h) denoted by the red arrows, and (e), (g) and (i) the yellow. (j – o) Intensity profiles taken by a box average across an appropriate section of the folded region shown in (d – i), with (j) corresponding to (d), (k) to (e) etc. The number of minima denotes the layer count, and is shown above the profile.

In order to investigate the thickness of the graphene grains on the copper foil AFM was used. A contact-mode AFM image of the grain from the 3 minute deposition is shown in

Figure 4.3a, with the scanning direction from left to right. Line profiles to measure the height as a function of distance were taken across the two regions indicated with boxes in Figure 4.3a, and are shown in b and c. The total height of the grain with respect to the copper substrate was found to be approximately 4 nm, significantly greater than the 1 - 1.6 nm measured for a monolayer film on silicon dioxide,⁸ suggesting FLG. The interlayer spacing in graphite is approximately 3.35 Å; however one must also take into account the effect of the van der Waals force, the substrate-graphene spacing, wetting and other surface interactions at these high resolutions.⁹ These effects act to increase the apparent thickness of a graphene layer on a generic substrate, however measuring the height of graphene on a graphene substrate is known to give more accurate measurements of between 0.3 – 0.4 nm. Along the left side of the grain, lines of darker contrast are apparent, which coincide with dips in the z-height profile, shown in Figure 4.3b,c. Taking z-height measurements from the peaks of the line profiles suggests an average height difference between the peaks of ~ 0.3 nm, which is in good agreement with the known interlayer spacing for graphite. This supports the TEM evidence in Figure 4.2, where the number of layers of graphene increases towards the central region of the grain. Figure 4.3d shows a sketch representation of a terraced few layer graphene grain on a copper foil, with Figure 4.3e showing an alternative inverted layout that would also generate the observed steps. The thickness of each graphene layer is not drawn to scale relative to the size of the grain for clarity of presentation. In the published work the model shown in Figure 4.3d was assumed, as the carbon precursors require access to the catalytic copper surface in order to form graphene, which is precluded in the case shown in Figure 4.3e due to the obstruction of ascending layers. However, recent studies after publication of these results suggest that the FLG grows as an inverted

pyramid, with mobile carbon species able to intercalate underneath incomplete graphene layers.^{10,11}

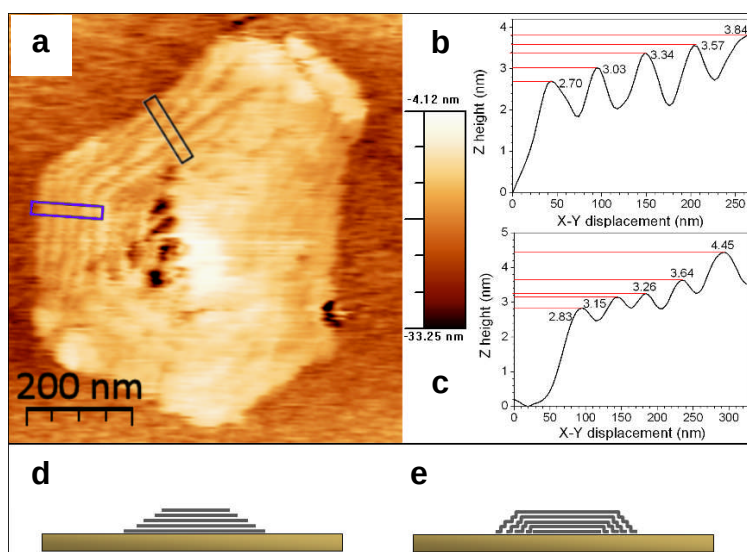


Figure 4.3. (a) A contact mode AFM image of a FLG grain, scanned from left to right. (b,c) Box averaged z-height line profiles shown for the black, (b), and blue, (c), highlighted regions in (a). (d,e) Sketches of the two possible configurations of the terraced few layer graphene grain on copper foil; (d) step-pyramid and (e) inverted.

Figure 4.4a shows a TEM image with individual graphene grains that had nucleated in close proximity to one another, and were beginning to merge together. A number of the edges have folded during the transfer to the TEM grid, illustrated by the highlighted area in Figure 4.4d. Figure 4.4b shows the TEM image of a section of a back-folded edge, indicated with the boxed region in Figure 4.4a. No lines of contrast can be resolved at this edge, as with the cases shown in Figure 4.2, indicating that the thickness of this grain is minimal. In this region four grains have partially merged, leaving a hole in the central region. SAED was used to map the crystallographic orientation of the merged grains. Figure 4.4c shows the SAED patterns for each of the respective numbered regions in Figure 4.4a. Some areas show multiple spots of 0.21 nm spacing in the SAED patterns,

such as 1, 3 and 6, indicating that there are rotational stacking faults within the region measured. This is either due to back-folding of edges, intrinsic rotational stacking faults, overlapping grains or from a boundary region where the two grains meet and have different crystallographic orientations. Since the SAED analysis of individual isolated grains, shown in Figure 4.2, revealed they were single crystals, intrinsic rotational stacking faults can be ruled out and thus one can attribute the presence of multiple spots in some of the SAED patterns to the back-folding of edges, overlapping grains and grain boundaries with disorientation. The relative angles are shown in a polar representation in Figure 4.4d, with the angle of displacement relative to the vertical shown, normalised to 360°. The SAED patterns of regions 2, 4, 5 and 7 - 9 in Figure 4.4c show one set of spots associated with AB-Bernal stacking, further demonstrating the well ordered growth of the grains. The angle does not appear to be maintained across adjacent grains; the apparent equivalence of the rotation of regions 7 and 8 with part of region 1 is likely due to the SAED aperture encompassing the adjacent grain, with one of the other two diffractions in region 1 attributable to its grain. By examination of the TEM images it is often discernible that areas that show multiple diffractions are also at, or close to, areas where the shadow of a folded sheet is visible.

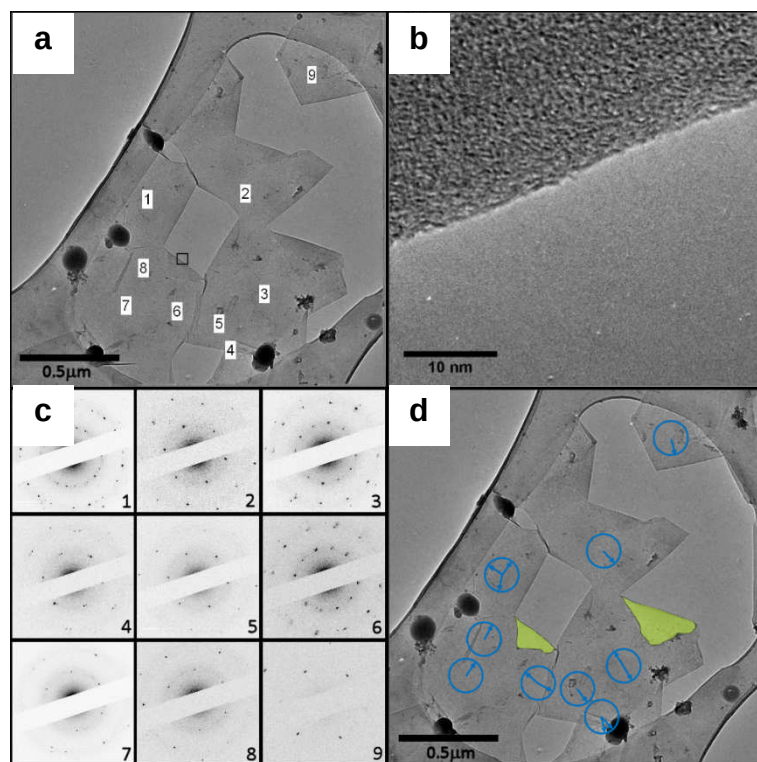


Figure 4.4. (a) TEM images of several graphene grains in the process of merging together. (b) HRTEM taken from the boxed region shown in (a). (c) SAED of the numbered areas in (a). (d) A polar representation of the relative angular rotation of the SAED patterns from the vertical. In addition two areas where the shadow of an underlying fold of graphene can be seen are highlighted.

As shown in the SEM images in Figure 4.1, the size of the graphene grains increases with exposure time to methane, with several merging to form large macroscopic sheets even after 3 minutes. Figure 4.5a shows a TEM image of a large area FLG sheet on a lacey carbon grid formed from 3 minutes of methane exposure. Based upon the growth dynamics revealed from the SEM images in Figure 4.1 and the SAED analysis in Figure 4.2, one expect this sheet to be polycrystalline from the single crystal grains that have merged together. 2D maps of the crystallinity of the sheets were obtained by taking SAED patterns, shown in Figure 4.5b,c, for 18 different regions, labelled in Figure 4.5a. A high proportion of the regions measured, 14 out of the 18, showed single crystal SAED

patterns, but the relative orientation of the single crystals varied substantially. In Figure 4.5d, arrows are used to indicate the relative crystallographic direction as determined from the respective SAED pattern. Regions containing two sets of spots in the SAED pattern were attributed to grain boundaries. For example, the SAED patterns from regions 4 and 6 indicate two single crystal grains with different orientation, and the SAED taken in between, region 5, is a superposition of the two patterns seen in regions 4 and 6, suggesting that the grain boundary passes through there. The orientation of the grains appears to be random and no correlations can be observed. HRTEM images of folded regions (Figure 4.5e,f) demonstrate that there is no appreciable increase in layer number from the shorter growth time case.

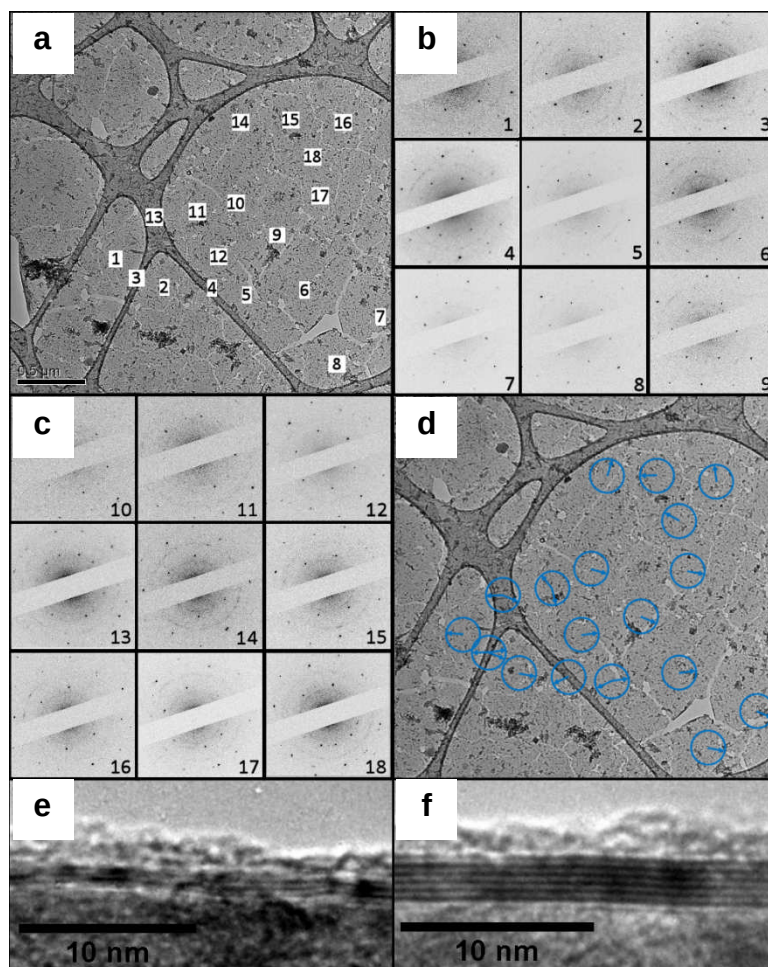


Figure 4.5. (a) A TEM image of a FLG sheet formed after a 3 minute deposition. (b) and (c) show SAED patterns from the appropriately labelled regions in (a). (d) A polar representation of the relative angular rotation of the SAED patterns from the vertical. (e) and (f) HRTEM images of two folded regions.

Raman spectroscopy was used to further characterise the graphene. Figure 4.6 shows representative Raman spectra of graphene grown on copper (2, 4 and 10 minute deposition). The copper foil background signal was subtracted for clarity. The G and 2D peaks, at the blue and black arrows respectively, confirms the presence of graphitic carbon. The weak D peak suggests some disorder, but a D/G ratio of 0.11 - 0.46 is comparable with FLG films prepared using Ni substrates.¹² Analysis of the 2D peak can be used to determine the layer count of graphene, with a monolayer yielding a peak that

can be fitted by a single Lorentzian line shape.¹³ However, this may also be attributable to turbostratic graphene, where the full-width half-maximum (FWHM) of the peak is roughly double that for the monolayer case (FWHM $\sim 50 \text{ cm}^{-1}$), along with an up shift of $\sim 20 \text{ cm}^{-1}$. The 2D peaks shown in Figure 4.6 have a FWHM of $41.9 \pm 0.3 \text{ cm}^{-1}$, $49.0 \pm 0.4 \text{ cm}^{-1}$ and $46.5 \pm 0.5 \text{ cm}^{-1}$, for 2, 4 and 10 minutes respectively, which in the absence of other characterisation techniques would suggest turbostratic graphene has grown on the copper foil. However, the combination of SEM, TEM, AFM and SAED has provided us with in-depth knowledge of the structure of the FLG material synthesised and conclusively rules out the formation of extensive amounts of turbostratic graphene. This indicates that the presence of a broadened, single Lorentzian 2D peak is not always interpretable as corresponding to turbostratic graphene. This agrees with the results of Reina *et al.*, who found the profile of the 2D peak in the Raman from FLG grown by CVD on nickel surfaces also broadens to a single peak. They found that the ratio of the intensity of the G peak, I_G , to the 2D peak, I_{2D} , correlates with the layer number. The ratio of $I_G:I_{2D}$ increases as the number of layers increases, with a value greater than 1 indicative of more than one layer. For three layers of graphene, Reina *et al.*¹² reported a ratio of $I_G:I_{2D} = 1.3$, with a FWHM of 70 cm^{-1} . From Figure 4.6 a ratio $I_G:I_{2D}$ of 1.8, 2.4 and 1.9 are found, which indicates more than 3 layers, however the FWHM of approximately 45 cm^{-1} is substantially less than the 70 cm^{-1} reported by Reina *et al.* This highlights that care is required when relying solely upon Raman spectroscopy to determine the number of layers of CVD grown graphene.

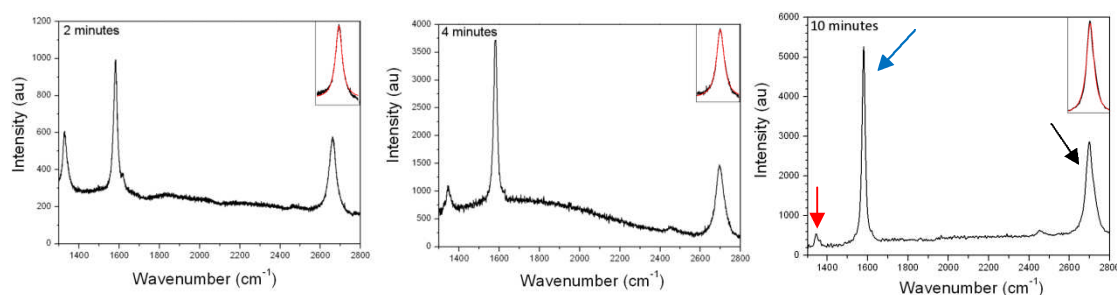


Figure 4.6. Raman spectra for graphene grown on copper foil (2, 4 and 10 minute deposition, precursor flow of 10 – 15 sccm 20%-methane/argon), with the copper signal subtracted, taken with a 532 nm wavelength laser. The red arrow corresponds to the D-peak, and occurs at 1345 cm^{-1} , the blue arrow the G peak, at 1580 cm^{-1} , and the black arrow the 2D peak, at 2700 cm^{-1} . The inserts shows a single Lorentzian (red) fitted to the 2D peaks (black).

The hexagonal shape of the graphene grains are dissimilar to the four lobed structures that have been found elsewhere for graphene grown on copper foil.^{2,3} As mentioned, in the published work of these experiments the assumption was that the subsequent extra graphene layers were growing on top of one another, akin to a step-pyramid. In the light of recent findings to the contrary^{10,11} it would be prudent to discuss their relation to the reported results above.

Work conducted with Re, Ir and Ru have suggested an under-layer growth mechanism occurs in these systems,^{14–16} supporting an under-layer growth scheme for copper catalysts. However, CVD growth on copper relies on the catalytic effect of the metal surface to break down the carbon precursors, thus one would expect the growth to be self-limiting once surface coverage has been achieved, as the catalytic effect is essentially passivated. To resolve these conflicting hypotheses low energy electron microscopy was used by ref. [10] to collect information that is highly sensitive to the surface, which permits the delineation between surface and sub-surface graphene. With this technique ref. [10] were able to determine that graphene growth and nucleation of

subsequent layers must occur from below, in an inverted step pyramid configuration. This would support observations in the SEM images reported here (Figure 4.1); it is notable that nearly every graphene grain has a central spot of high contrast. This is speculated to be an impurity site on the copper, which acts as a nucleation site. With the concentric plateaus that are observed it is logical to conclude that the subsequent layers also nucleate from this site; a reasoning that is only possible in the under-layer growth scheme. It is speculated that due to the weak coupling between the graphene π -orbitals and the copper 4s shell that it is possible for carbon radical groups from the decomposed methane to migrate beneath the already grown graphene sheet, and thus nucleate at the same nucleation site. Decoupling of the already grown sheet should be relatively low-energy, particularly as it would only need to be at the areas where subsequent layers are growing. Very recent work supports this conclusion, in which isotopic labelling of the carbon was employed in order to follow the course of the growth.¹¹

4.3 Conclusion

In summary, single crystal grains of few-layer graphene were grown by atmospheric pressure chemical vapour deposition on a copper catalyst. The individual grains were verified to be AB-Bernal stacked crystals by SAED, and formed into a characteristic hexagonal shape, likely stemming from the crystal symmetry of graphene. Subsequent graphene layers appeared to grow in terraces from the centre of the grain, as demonstrated by both contact-mode AFM and HRTEM. The absence of self-limited monolayer graphene growth demonstrates a different growth mechanism is possible on

a copper catalyst under high precursor supply conditions, which while resulting in few-layer graphene, still maintains high quality crystallinity within the grain.

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4.4 Reference

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AC-TEM Analysis of Few-Layer Graphene: Inter-Grain Connectivity and Out-of-Plane Distortions

5.1 Introduction

Understanding few-layer graphene (FLG) is important due to its potential employment in conductive films, with the higher layer counts offering lower resistivities at the cost of impaired light transmission. Furthermore, bilayer and FLG offer distinct dispersion relations to that of monolayer graphene, with the capability of inducing a band gap in bilayer films.^{1,2} In this chapter are presented two studies by aberration corrected transmission electron microscopy (AC-TEM) of FLG. Discussed in the first section is the identification of different FLG inter-grain stitching, and in the second the effect of an out-of-plane perturbation on the surrounding FLG structure.

5.2 Delineating Grain Intersection Type in Few-Layer Graphene

5.2.1 Introduction

Graphene films synthesised by chemical vapour deposition (CVD) are of a polycrystalline nature, with multiple small graphene grains growing to merge into a continuous film.³ AC-TEM allows for the detailed study of the atomic structure of graphene,⁴ and can be combined with the analysis and filtering of 2D fast Fourier transforms (FFT) to generate reconstructed images that can be used to elucidate the stacking configuration of the graphene layers.⁵ Understanding the atomic structure of polycrystalline CVD graphene may assist in the further development of the field;^{6–8} for instance the use of graphene grain boundaries may allow for the engineering of the band structure,⁹ and electronic devices have shown increased resistivities for inter-grain electronic transport when compared to intra-grain measurements, with weak localisation also observed in the inter-grain case.¹⁰

As shown schematically in Figure 5.1, there are two primary ways one can envisage two separate graphene grains being connected; either by direct atomic bonding at the interface of the two graphene sheets to create a discrete atomic grain boundary (Figure 5.1a), or by one sheet overlapping another to form a bilayer boundary region that is not atomically discrete and relies on interlayer van der Waals forces to hold the two grains together (Figure 5.1b). These shall be referred to as the atomic interface and the overlap interface, respectively. Investigations of monolayer graphene grain boundaries reported the existence of atomically bonded discrete interfaces.^{11,12} These grain boundaries were found to consist of pentagonal, hexagonal and heptagonal carbon rings connected in a chain, allowing for two graphene grains of different lattice directions to bond together.

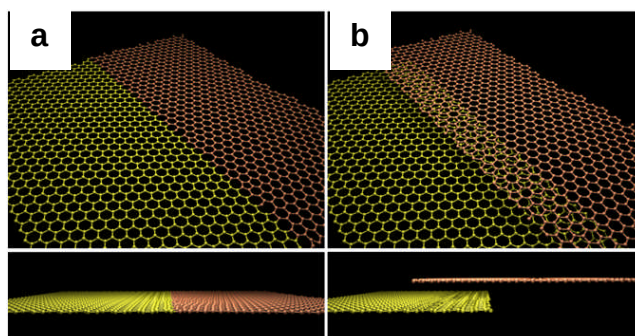


Figure 5.1. Schematic illustrations of the two primary ways of connecting graphene sheets. (a) 3D perspective view of atomic bonding at the interface and a side view of the atomic interface below. (b) 3D perspective view showing the graphene sheet on the right overlapping on top of the graphene sheet on the left (i.e., overlap interface), with a side view of the overlapping interface below.

Hexagonal single crystal grains of FLG can be produced on the surface of copper foils using atmospheric pressure CVD.¹³ In the cases where the FLG grains merged together to form a polycrystalline film, 2D mapping of the FLG grain's crystallographic orientations, using selected area electron diffraction (SAED), showed random orientations. Some regions of the polycrystalline FLG film showed multiple reflections in the SAED patterns (i.e., at least two graphene lattices with some arbitrary rotation), and it is unclear whether this is due to contributions from two single crystals with different orientations or from a region that contains rotational stacking faults. SAED is limited in its spatial resolution, and as such other techniques are required to gain information about the origin of the multiple reflections in the SAED patterns and thus the true nature of the grain boundaries in these films. With this in mind I investigated the atomic structure of the grain boundaries in between FLG grains using AC-TEM at an accelerating voltage of 80 kV.

5.2.2 Results and Discussion

FLG samples were grown using CVD and transferred onto holey silicon nitride (Si_3N_4 , but abbreviated to SiN) membrane TEM grids for electron microscopy characterisation (see section 3.2.1). Scanning electron microscopy (SEM) imaging of the SiN membrane TEM grid was conducted after FLG transfer in order to confirm successful adhesion of the film and to provide insight into the degree of folding and distortion induced from the process. Figure 5.2a demonstrates that the majority of the holes in the SiN membrane are not covered by the FLG. This is attributed to the small grain size ($\sim 1\text{ }\mu\text{m}$) of the FLG obtained under the used growth conditions; as these are smaller than the membrane holes one could expect that the adhesion between adjacent grains may not always be sufficient to allow for them to bridge the hole. However, as can be seen in Figure 5.2b,c, some holes in the SiN membrane are covered by FLG, permitting TEM inspection.

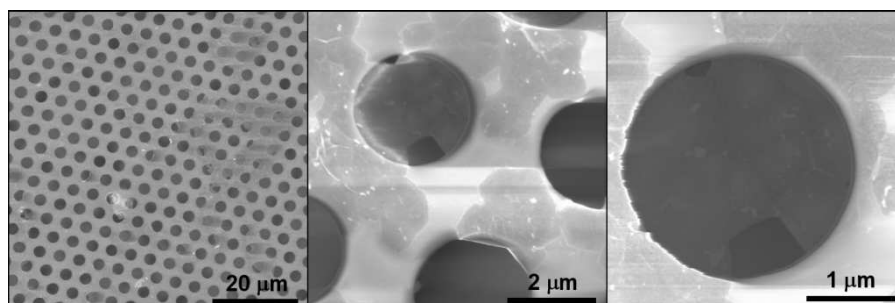


Figure 5.2. SEM images of a holey silicon nitride membrane TEM grid after graphene transfer. Graphene coverage of the viewing holes was only evident in a limited number of cases.

Figure 5.3a shows a TEM image of a region of the sample where two FLG grains have merged together. Inspection of this area using AC-TEM with a magnification high enough to observe the atomic structure enabled the layer stacking orientations to be tracked across this region. Regions with pure AB-Bernal stacking gave rise to a hexagonal lattice structure, whilst regions containing rotational stacking faults produced moiré patterns.

Figure 5.3b-f show five examples of AC-TEM images taken from the five regions marked with boxes in Figure 5.3a. The respective 2D fast Fourier transform (FFT) is shown as an inset in each image. The six fold crystal symmetry of graphene results in the 2D FFT having a set of six hexagonally distributed spots with 0.21 nm lattice spacing in the first ring. The orientation of the spots in the FFT is directly related to the arm-chair direction of the graphene lattice.¹⁴ A rotational stacking fault in the few layer graphene adds another six spots to this inner ring, due to the differing rotational alignments of the graphene lattices. If the rotational stacking fault is intrinsic to the layer order (i.e., not from a back-fold) then this is likely to be a turbostratic configuration. The FFT spots from regions 1 and 2 (Figure 5.3b,c) share the same direction, as do regions 4 and 5 (Figure 5.3e,f). Region 3, where the moiré pattern is observed in the real space image (Figure 5.3d), exhibits a superposition of the rotations seen in region 1-2 and region 4-5, which when compared with the location shown in Figure 5.3a suggests that region 3 bestrides a boundary between two graphene grains of different crystal orientations. The typical scale of the turbostratic region between these two grains was found to be of the order of 100 nm by scanning the region for observable moiré patterns using AC-TEM. This indicates that the grain boundary is not necessarily atomically defined.

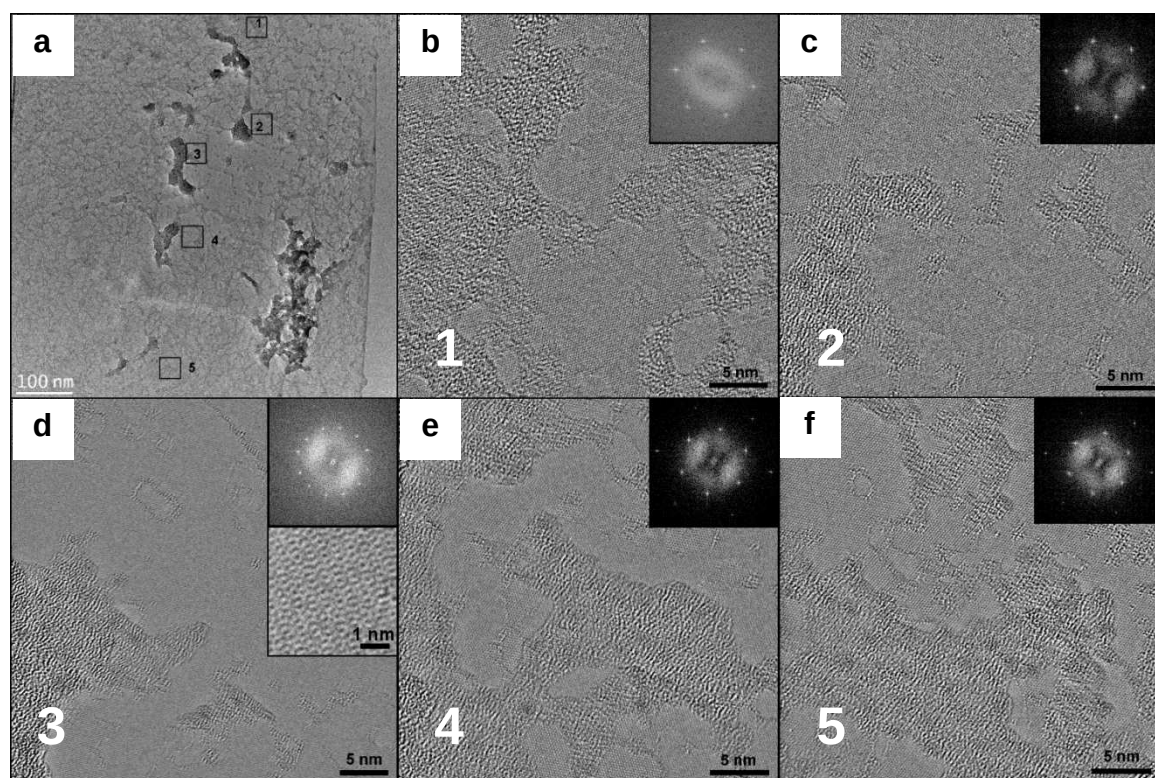


Figure 5.3. (a) Low magnification TEM image of a region of FLG, with the 2D FFT taken from the numbered boxed regions. (b - f) TEM images from the appropriately labelled boxed regions in (a); inserts show the 2D FFT pattern. Additional insert for (d) shows the moiré interference pattern that can be observed at high magnification in area 3.

Even though the moiré pattern, and thus the boundary region, between two FLG grains is on the order of 100 nm, it was possible to find regions on the extremities of this boundary that exhibited sharp transitions from AB stacking to moiré patterns. As was discussed in Figure 5.1, there are two possible ways that the graphene layers can connect. In order to evaluate whether AC-TEM can distinguish between these two interfaces I conducted AC-TEM image simulations to examine their resulting contrast profiles. These used the multislice method and the JEMS software package, with microscope conditions approximated to that of the JEOL 2200 (see section 3.8). A comparison of the differences between the two would enable the reliable identification of the boundary type.

Figure 5.4a shows a top view of an incomplete sheet of graphene (yellow) residing on 3 sheets of graphene with AB-Bernal stacking (gray), with a lattice direction mismatch of approximately 23° between the two. This is representative of the connectivity shown in Figure 5.1b, the overlap interface, where one graphene sheet with non-AB orientation overlaps another set of AB stacked FLG sheets. AC-TEM multi-slice image simulations are shown in Figure 5.4b-d for increasing levels of defocus (5, 10 and 40 nm, respectively). The moiré interference pattern originating from the rotational stacking fault from the incomplete layer is visible in the top half of the images, whilst the hexagonal pattern expected from AB-Bernal FLG can be found on the bottom. A negative mask filter was applied to the FFT of Figure 5.4d and inverted to reconstruct an image without the respective contribution of one of the two lattices, as shown in Figure 5.4e,f, with the masks shown in the insets. Figure 5.4e shows a rotated hexagonal pattern along the top half, and thus is the incomplete layer contribution, whilst Figure 5.4f yields a continuous lattice stretching across the image, and can be concluded to be the AB-Bernal contribution. It was apparent that the contrast of the boundary increased concomitantly with the defocus, as did the boundary breadth, which can be readily identified qualitatively by inspection of Figure 5.4b-d. Figure 5.4g shows a portion of a reconstructed image generated by removing all of the periodic lattice components from Figure 5.4d. Figure 5.4h shows an intensity box profile taken from the region indicated with a red box, with pixel values along the x-axis summed to give one average gray value and then plotted as a function of the distance in the y-axis. The minimum gray value in Figure 5.4h is 179, with a maximum at 197, thus giving a total difference of 18 gray scale units across the profile.

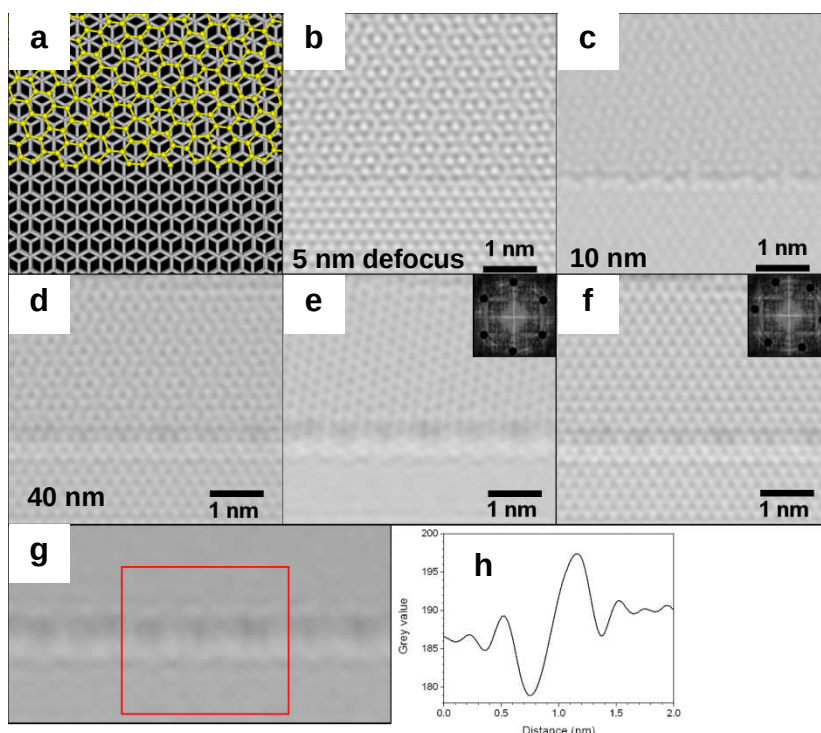


Figure 5.4. (a) Top-down view of the graphene overlap interface used in the simulation, showing the underlying AB Bernal stacked graphene (gray) and a rotationally mismatched upper layer across part of the structure (yellow). (b – d) Multislice image simulations of (a) at 5 nm, 10 nm and 40 nm defocus, respectively, taken in the region of the sheets termination. (e – f) Reconstructed images from the FFT negative masks, shown in the respective inserts, taken from the 40 nm defocus simulation. (g) A close up of the boundary of a reconstructed image from both FFT negative masks of the 40 nm defocus simulation. (h) A box profile taken vertically of the red region in (g).

Figure 5.5a illustrates a top-down view of an atomically bonded interface between two graphene lattices of different orientations (yellow), on top of 3 graphene layers with AB-Bernal stacking (gray). This is the representative of the connectivity shown in Figure 5.1a; the atomic interface. The bottom half of the top graphene layer adopts AB stacking with the underlying FLG. Image simulations (Figure 5.5b-d) for defocus values of 5, 10 and 40 nm, respectively, show a similar moiré pattern on top of a hexagonal base as in Figure 5.4, and this is further demonstrated in the reconstructions shown in Figure 5.5e,f. The principle difference between the two cases lies in the behaviour of the

boundary. Figure 5.5g shows a portion of a reconstructed image of Figure 5.5d after all the periodic lattice structure was removed by an FFT mask. Figure 5.5h shows an intensity box profile, taken from the red box region in Figure 5.5g. Variation in gray values of 182 – 185 units gives a difference of 3 units over the box plot range, with no discernible boundary edge seen.

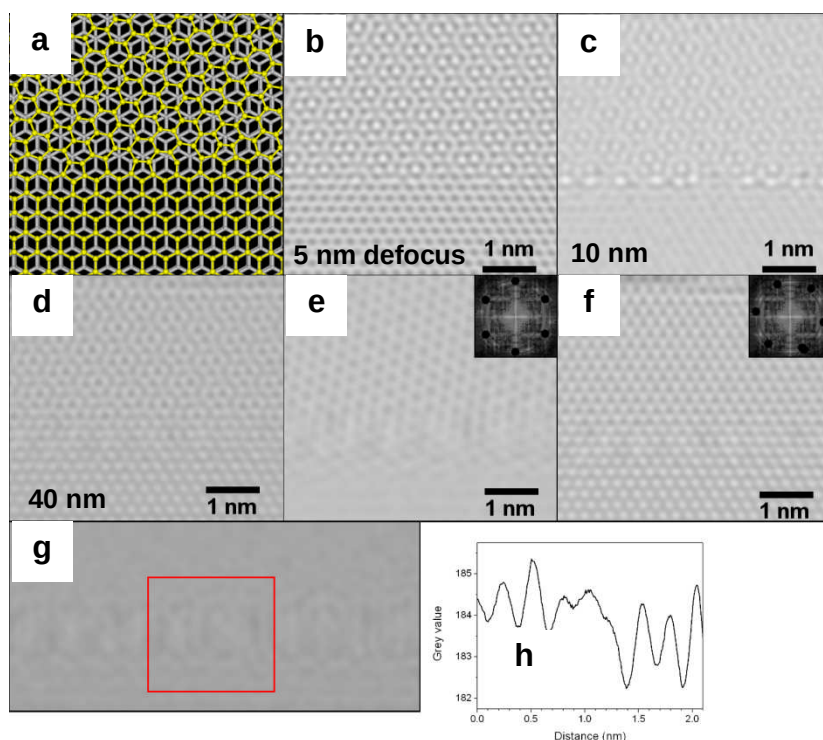


Figure 5.5. (a) A top-down model of an atomically bonded interface between an AB Bernal layer and a rotationally mismatched partial single layer (yellow), on top of AB Bernal graphene (gray). (b – d) Multislice simulations of (a) at 5 nm, 10 nm and 40 nm defocus, respectively, taken in the region of the graphene interface. (e – f) Reconstructed images from the FFT negative masks, shown in the respective inserts, taken from the 40 nm defocus simulation. (g) A close up of the boundary of a reconstructed image from both FFT negative masks of the 40 nm defocus simulation. (h) A box profile taken vertically of the red region in (g).

Comparing the intensity profiles presented in Figure 5.5h with Figure 5.4h reveals a significant difference between the two types of connectivity. It is apparent that the principle identifier for differentiating between an overlapping, incomplete graphene

sheet and an atomically bonded graphene interface is the level of contrast of the boundary. Specifically, in the case of an atomic bonding interface between two graphene sheets it was noted that there was negligible contrast at the boundary. However for the overlap interface it was found that there was a significant contrast change in the region of the edge and that also the breadth of the boundary was found to increase with defocus; an effect not observed for the atomically bonded interface.

Utilising this information it was possible to identify the two types of graphene interfaces with AC-TEM. Figure 5.6 shows a high magnification AC-TEM image of an atomic interface between two graphene sheets of different lattice rotations. In Figure 5.6a a moiré interference pattern can be seen on the left of the image, indicating the presence of a rotational stacking fault, and the hexagonal patterning on the right shows AB-Bernal stacked FLG. Further analysis by applying a FFT was performed, yielding the expected sets of hexagonal spots. In the insert for Figure 5.6a the FFT shows two sets of hexagonal spots at 0.21 nm lattice spacing, confirming the presence of a rotational stacking fault. Figure 5.6b,c show the reconstructed images from the inclusive masks shown in the lower left inserts. The high magnification images located at the top right of Figure 5.6a-c are taken from each of the boxed regions and are used to highlight the change in the real space image across the boundary. From these inserts it can be confirmed that the boundary is of an atomic interface type, due to the expected lack of contrast along the edge. Variation of the defocus yielded no change in the contrast of the interface.

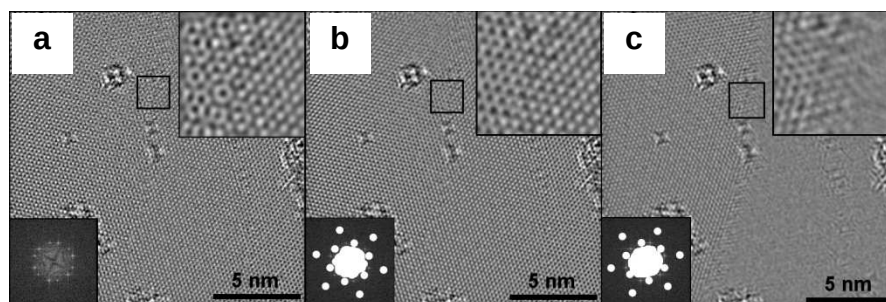


Figure 5.6. (a) AC-TEM image of a graphene interface taken at a low defocus, with inserts showing the FFT (lower left) and a magnified view of the boxed region (upper right). (b) and (c) both show images reconstructed from the frequency of particular grains selected by the positive masks shown in the lower left of each.

Figure 5.7 shows a further example of an AC-TEM image taken from another area, with a similar boundary region showing moiré patterns on one side and AB-Bernal stacked FLG on the other. However, this region demonstrates both an atomically bonded interface and an overlapping region, and as such can be used to directly compare the two. In the lower left (yellow) of Figure 5.7a the moiré interference associated with turbostratic graphene is evident, which arises from the graphene layer shown by the application of the positive mask used in Figure 5.7b. Reconstruction of the FFT positive mask in Figure 5.7d shows the underlying AB stacked FLG, with the remaining set of diffraction spots, shown in Figure 5.7c, accounted for by graphene about the periphery (red). The texturing of the FLG sheet in this area is due to the sputtering from the 80 kV electron beam during the extensive periods of imaging.^{15,16} However, this was not observed to affect the graphene atomic interface. The edge from the sheet giving rise to the central moiré pattern can be seen to have negligible contrast variation, in comparison to the remainder of the graphene edges around the perimeter; these lead to the reconstructed graphene planes in Figure 5.7c and the second moiré patterns at the bottom right and top left in Figure 5.7a, which exhibit a strong contrast and a broad extent when imaged

under a defocus of approximately 40 nm. Thus the central boundary can be concluded to be an atomically bonded interface, whereas the higher contrast boundaries about the periphery are of the overlap interface type. Figure 5.7c also illustrates a feature that was found for all boundaries studied; that elimination of both the constituent graphene lattice contributions to the image by FFT reconstruction does not lead to the entire removal of the contrast from the edge. The likely reason for the edge still being visible is that it is comprised of various defects; randomly orientated pentagons, hexagons and heptagons in the case of the atomic bonding interface and electron beam irradiation damaged edges in the case of the incomplete sheet. Since these defects would not likely be aligned with either of the two lattice directions the reconstruction from the FFT mask would not lead to their removal, and thus they would be expected to remain. (i) and (ii) are box averaged intensity profiles across the appropriately annotated boxed regions in panels b and c.

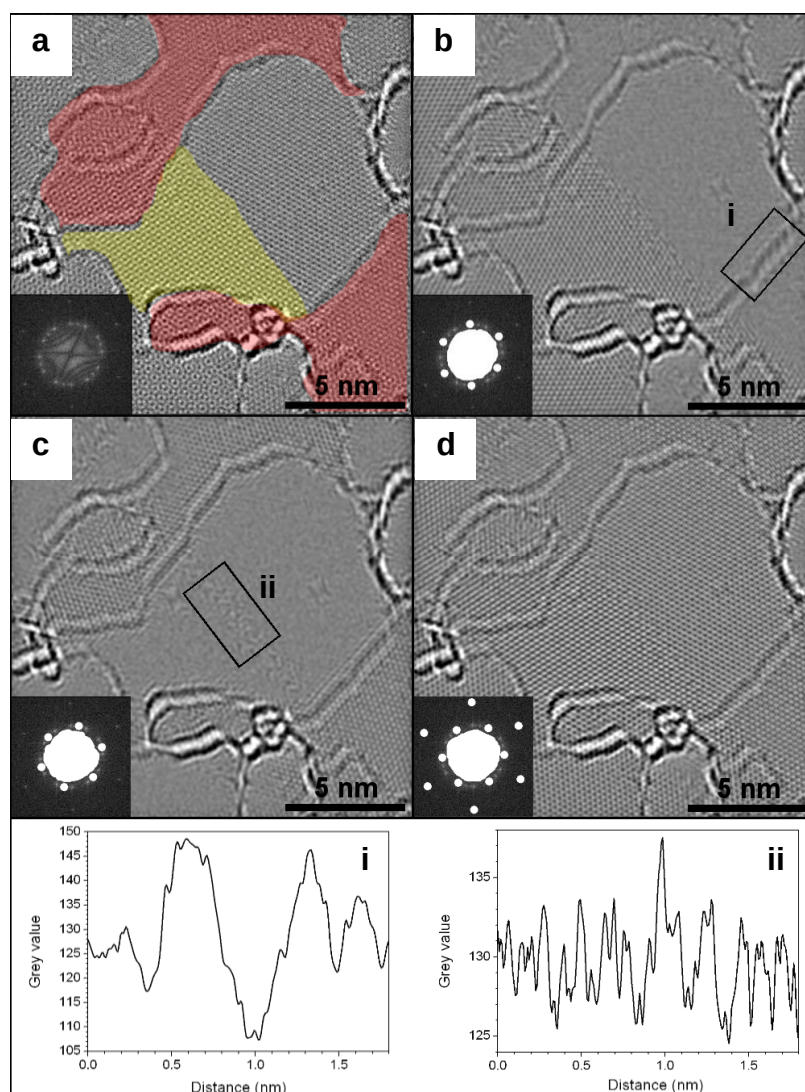


Figure 5.7. An HRTEM image of several graphene sheets overlaying one another. The image was taken at a defocus of approximately 40 nm. The lower left insert shows an FFT taken from the image. (b – d) are reconstructed images from the frequency grains selected in the inserts. (i) and (ii) are box averaged intensity profiles across the appropriately labelled boxed regions in (b) and (c).

The image simulations demonstrated a marked increase in contrast for the overlapping graphene edges when the magnitude of the defocus was increased. Figure 5.8a shows another overlap interface, with the moiré pattern visible on the right. A subsequent image was taken with increased defocus, with the extra contrast emphasising the edge. Comparing this to the reconstructed image from the negative mask FFT (Figure 5.8c) one

finds that they correlate well, as shown by the overlay in Figure 5.8d. The boundary is rough, with an approximate variation of between 0.5 – 1 nm from the average line. This differs to the comparably smooth and straight boundaries seen for the atomic interfaces shown in Figure 5.6 and Figure 5.7. The roughness could be attributed to the action of incident electrons from the electron beam.¹⁵ Figure 5.8f shows a further image taken at a similar defocus to Figure 5.8b (Figure 5.8e is a magnified and rotated image of the appropriate region from b), and shows some change in the profile of the boundary due to electron beam sputtering, in particular along the area of the boundary denoted by the red line. No such variation was observed for the atomic interfaces in Figure 5.6 and Figure 5.7. Variations in the susceptibility of electron beam induced sputtering have been observed for intrinsic graphene edges compared to folded graphene edges due to the presence of unsaturated atoms terminated intrinsic graphene edges.¹⁷

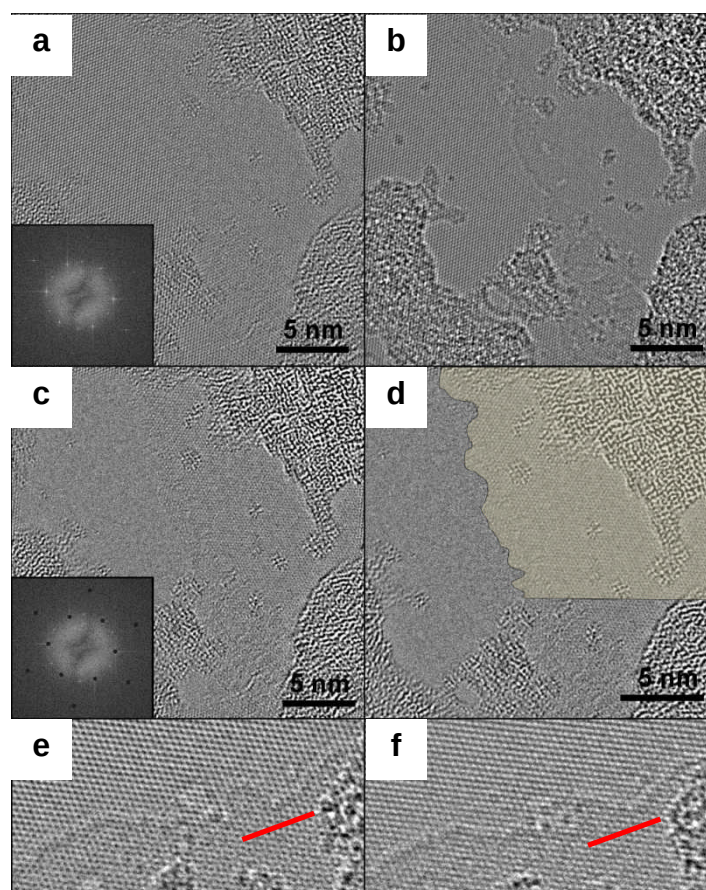


Figure 5.8. (a) A low defocus AC-TEM image of a region containing an overlap interface; the insert shows the FFT. (b) The same region as (a), taken under high defocus. (c) Reconstructed image from the negative mask shown in the insert, showing the partial sheet on the right of the image which generated the moiré pattern in (a). (d) An overlay of the edge, taken from (b), matched on to (c). (e) Magnified and rotated image taken from the box in (b). (f) Same region as (e) taken after a 10 second exposure to the electron beam.

The presence of these two distinct interface types is contingent on the system being of several layers. The atomic interface, much as for monolayer graphene, occurs when two graphene sheets in the same plane grow into one another. The inevitable rotational mismatch of the lattice directions between the two grains is resolved by the formation of five and seven member carbon rings along the boundary. The nature of the overlap interface is more complex. The models in Figure 5.1 and Figure 5.4 show a sheet of graphene that is overlaying an AB ordered graphene structure, with a rotational

mismatch, and that terminates part way. As discussed in Chapter 4, FLG grown on copper by CVD should not grow in a turbostratic configuration, thus the rotational mismatch of the boundary cannot be explained by incomplete turbostratic layers growing on top of the underlying graphene structure. It is possible that under certain circumstances when two adjacent FLG grains grow into one another this overlap may be observed. For atomic interfaces to form it would require that the graphene sheets from the adjacent grains be suitably aligned in the axis perpendicular to the sheet, thus if one of the grains was thicker than its neighbour it is possible that the sheets on top may continue to grow across the adjacent grain, with the crystal structure of these higher sheets matching the original seed grain rather than that of the neighbour. This is illustrated schematically in Figure 5.9.

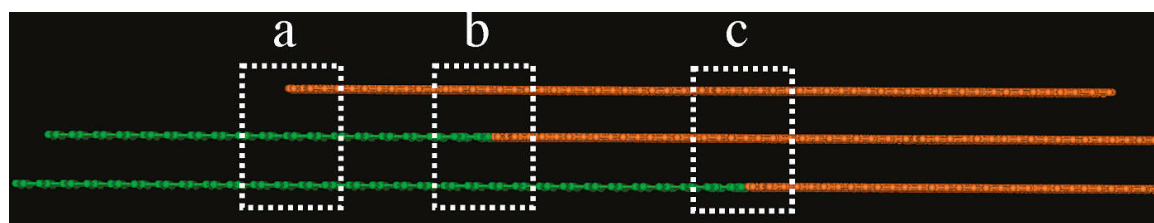


Figure 5.9. Schematic illustration showing the side view of the two neighbouring FLG grains intersecting (green, bilayer; orange, trilayer). Region (a) shows the top layer of the trilayer graphene grain (orange) overlapping onto the bilayer graphene grain (green), which in AC-Tem would result in a moiré pattern on the right and hexagonal structure typical of AB-Bernal graphite on the left. Region (b) shows an atomically bonded interface in the middle, which would result in a moiré pattern on both the left and right side. Region (c) shows an atomically bonded interface in the bottom layer, which would result in moiré pattern on the left and hexagonal structure on the right.

5.2.3 Conclusion

Graphene grain boundaries and the interconnection between FLG sheets are important considerations when working to optimise electronic and mechanical properties. The

ability to identify grain boundaries, and differentiating them from isolated sheet edges, is potentially important for electronic device fabrication. The mechanical strength of polycrystalline 2D films of FLG could be improved by reducing the number of overlapping sheets at the interfaces between individual FLG grains, as only van der Waals forces provide the adhesion, in contrast to atomically bonded grains that have stronger covalent bond attachments. Image simulations and AC-TEM imaging demonstrate that there are two discernible types of graphene boundary in the FLG system, where one is the case of the termination of a graphene layer on top of another, and the second the case of an atomically bonded graphene – graphene interface between two sheets of different lattice directions. It is possible to differentiate between the two graphene boundaries by observing the variation in contrast over the cross-section of the boundary, with the size of the cross-section increasing concomitantly with the defocus for the overlapping graphene layer case, and with little discernible edge contrast for the atomic graphene interface scenario. The presented images and observations illustrate the complexity of the FLG system, with both atomic grain boundaries and small regions of turbostratic graphene, originating from overlap at grain intersections, in an otherwise well ordered AB-Bernal stacked graphitic system.

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5.3 Characterising Out-of-Plane Distortions in a Few-Layer Graphene Sheet

5.3.1 Introduction

An unavoidable consequence of CVD growth is the attachment of the graphene to the surface of the metal catalyst, such as nickel or copper, which must then be removed in order for the graphene to be isolated and transferred to a desired substrate. A transfer method that is widely used is to apply poly(methyl methacrylate) (PMMA) as a supporting scaffold for the graphene to adhere to, whilst the underlying metal catalyst is etched.^{19–21} The PMMA-graphene film can then be transferred to an appropriate substrate, where the PMMA is removed. The nature of the transfer procedure tends to lead to the graphene film being partly cracked²¹ and folded,^{5,22–24} arising from the flexible nature of the PMMA-graphene thin film at transfer or from the relaxation and adhesion of the graphene to the new substrate being imperfect. The energetics of the graphene fold system have been found to be dependent on a combination of the van-der Waals forces between the overlapping sheets and the stress in the sheets from the bend, with folds along armchair or zigzag directions being energetically preferable.²³ Understanding the atomic structure of defects that form at creases and pleats in graphene layers that develop from the transfer process could be important for future electronic and mechanical applications, where the effects of such defects could be deleterious to their performance.^{25,26} I show that a crease termination in a FLG system acts to induce rotational faults between the layers, or turbostratic stacking, in the region nearby. The stacking configuration is known to significantly affect the electronic properties of FLG,^{27,28} such as theoretical calculations demonstrating dependence of the

Fermi velocity on the rotational angle between layers,²⁹ and the opening of a band gap due to electronic interactions in ABC configured trilayer graphene systems.³⁰

5.3.2 Results and Discussion

Creasing in the graphene system is evident even before transfer. Figure 5.10a shows a tilted SEM image of as grown FLG on copper foil, with the micron sized white creases clearly visible. The folds likely occur during the cooling down from 1000 °C, with the differing thermal expansion coefficients of graphene to copper leading to the formation of the creases. The transfer process is expected to lead to further creasing due to the flexible nature of the graphene, even when backed with a polymer scaffold. Figure 5.10c demonstrates this to be so, with a FLG film transferred to a holey silicon nitride TEM grid showing multiple creases. From the SEM images it is evident that the creases all have terminations; it is almost impossible for the typically micron sized creases to form complete folds along the centimetre scale of the complete graphene film. An exception to this is the case where a crease forms with one end terminating at the film edge. A number of creases appear to terminate in the same region, as can be seen in the areas about the red arrows in Figure 5.10a,b.

To study the folds and terminations in more detail FLG was grown by atmospheric CVD on copper and transferred by the use of a supporting PMMA layer to a TEM compatible substrate. Figure 5.10d shows an AC-TEM image of a crease running across a region of FLG, low magnification images of which are in Figure 5.10e,f. The crease diverges from a pinch approximately 500 nm into the film and extends away to the edge, seen on the left of Figure 5.10e.

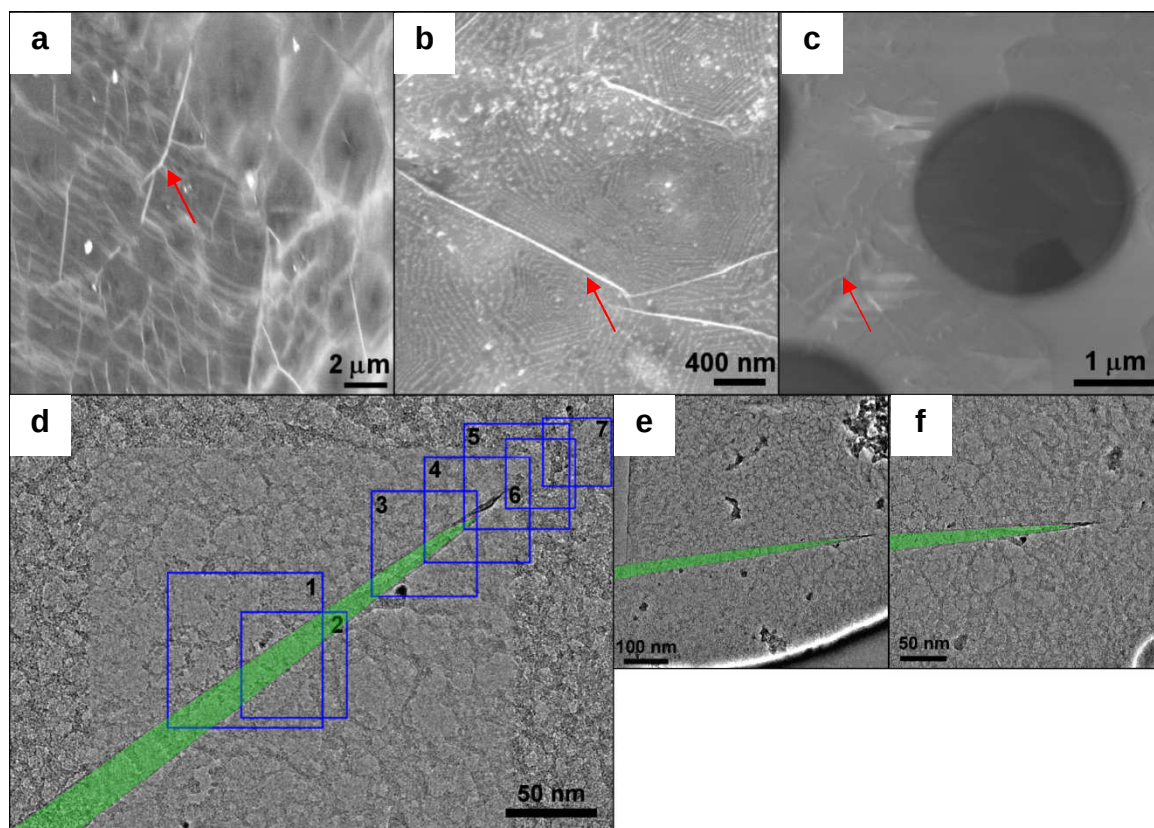


Figure 5.10. SEM images of (a) FLG as grown on copper, (b) FLG transferred to silicon dioxide, (c) FLG transferred to a holey silicon nitride TEM grid (tilted at 54°). White crease marks (red arrows) are clearly visible in both (a) and (b), and the creasing in (c) is most marked on the left of the hole. (d) TEM image of a crease leading to a single pinch at the top right. The crease is highlighted in green. The numbered blue boxes denote appropriately designated high magnification regions that are analysed further later. (e,f) Low magnification images of the region of the crease, again highlighted in green.

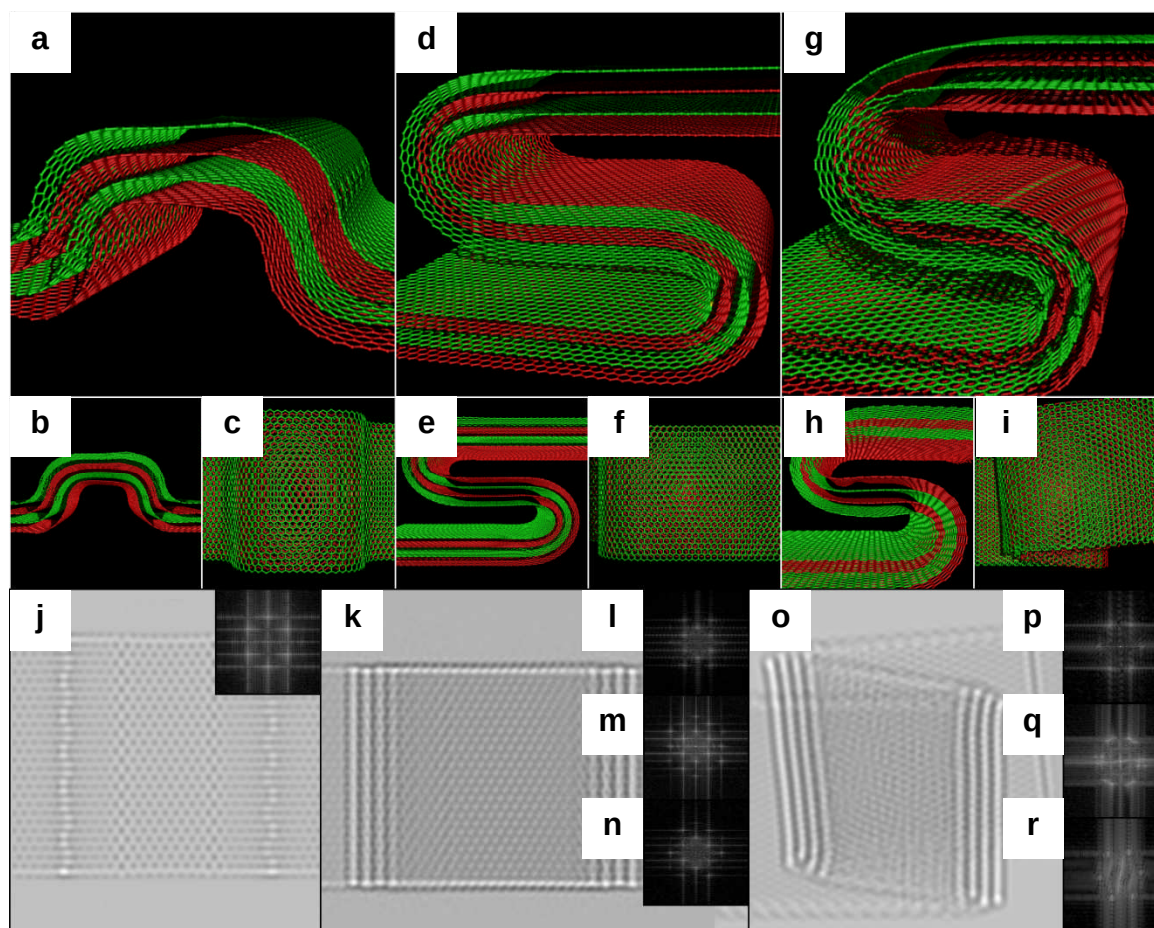


Figure 5.11. (a-i) Atomistic models of three types of crease, with a-c showing an upward buckle in the FLG, d-f showing an overlapping back fold and g-i showing a skewed overlapping back fold; a skew of -10° for the bottom layer and 15° for the top with respect to the zigzag direction orthogonal to the middle sheets edge. (j,k,o) Multislice TEM simulations of the buckle (j), overlap (k) and skewed overlap (o) taken at 7 nm defocus. The inset of j shows an FFT taken from the central region of the simulation. (l-n) shows FFTs taken from the left, centre and right parts respectively of the simulations in k. (p-r) shows FFTs similarly for o.

To better understand this non-trivial system, it is useful to first investigate some schemes that could conceivably describe a FLG crease by modelling and TEM simulation. In Figure 5.11a-i atomistic models are demonstrated for three different conceivable types of four layer graphene crease. The first set (Figure 5.11a-c) shows a simple upward buckle, the second (Figure 5.11d-f) an overlapping back fold and the final (Figure 5.11g-i) a skewed back fold, with a rotation between the layers of the fold. Figure 5.11j,k,o show

multislice TEM image simulations (see section 3.8) performed at 7 nm defocus on supercells large enough to fully include the model. The buckle model does not yield the two sets of four interference lines along the fold edges that are observed in the other two simulations; these interference fringes require a complete fold, whereas the buckle model produces a pair of single blurred bands along the steepest regions of the deformation. The inset to Figure 5.11j shows a 2D fast Fourier transform (FFT) taken from the central area of the crease, showing a single set of six spots at 0.21 nm spacing in a hexagonal configuration, resulting from the six fold symmetry of the graphene lattice. The back fold model shown in Figure 5.11d-f yields a pair of interference fringe sets in the simulation, with the FFTs shown displaying a single set of spots with no rotational variation across the crease region. The model illustrated in Figure 5.11g-i is skewed such that the bottom layers are rotated by -10° with respect to the middle sheets, and the top layers by 15° . The FFTs to the left and right of the fold, Figure 5.11p and r, show a 25° and a 20° rotation from the vertical, with the central region exhibiting a group of blurred spots from approximately 19° to 27° , which likely arises due to the superposition of the two sheets plus a further angle for the intermediate sheet. Unfortunately the simulation resolution is insufficient to adequately delineate this.

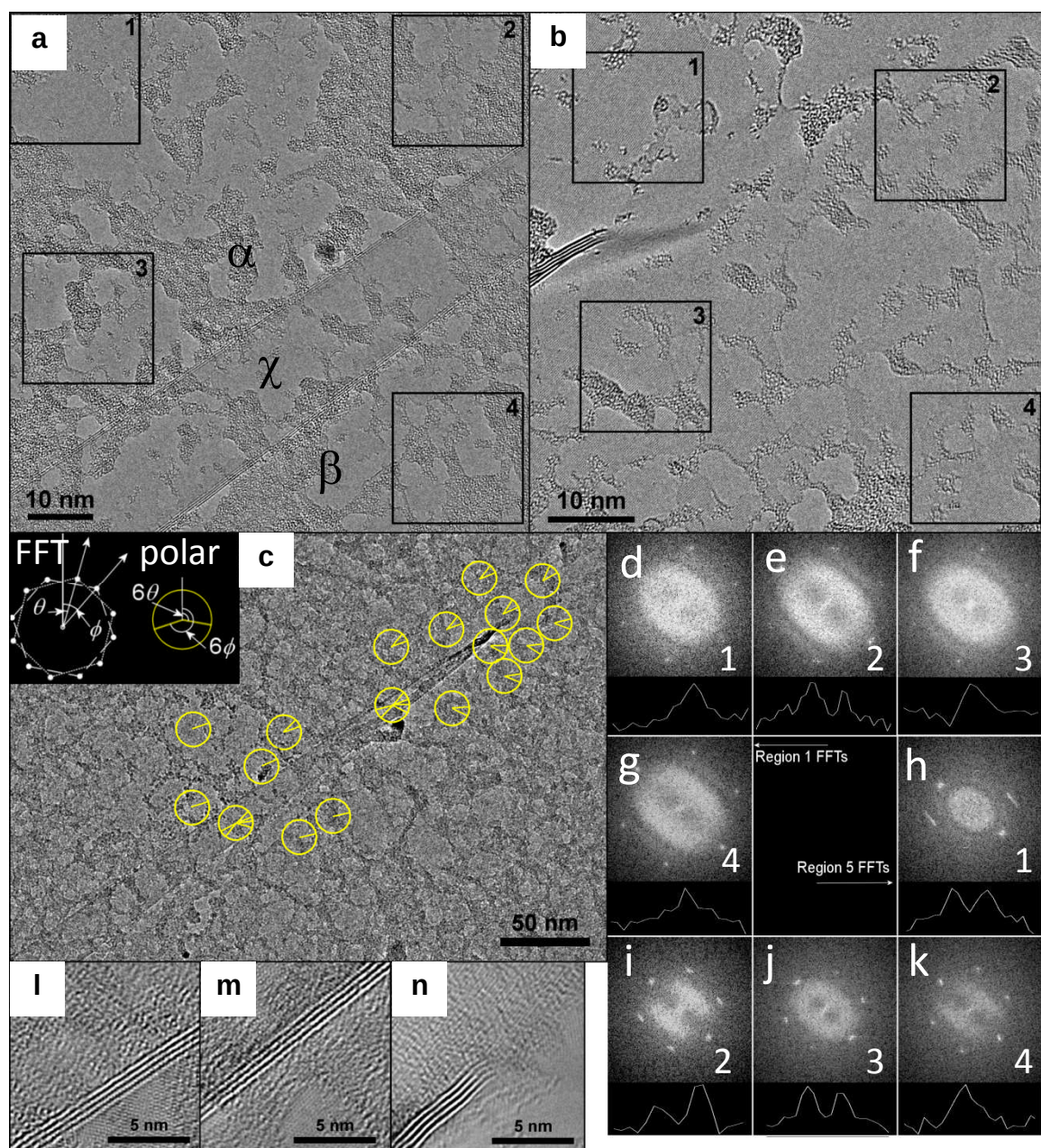


Figure 5.12. (a,b) TEM image of region 1 and 5, respectively, as defined in Figure 5.10d. Boxed regions denote areas from which a FFT was taken. The Greek letter labels in panel a are used to refer to a particular side of the fold structure. (c) A polar representation (see insert) map of the relative angular rotation of the FFT patterns from the vertical, with the angle normalised to 360°. (d – g) FFTs taken from the corresponding numbered boxes in a, (h – k) FFTs taken from the numbered boxes in b. Inserts for d-k show intensity line profiles taken across the FFT spots. (l – n) Magnified images from region 1 (l, m) and 5 (n) showing the interference fringes arising from the folding of the graphene.

Figure 5.12a and b show representative AC-TEM images taken from the crease, here corresponding to regions 1 and 5, as defined in Figure 5.10d. Figure 5.12c shows a polar map (see insert) of the angle of rotation of the hexagonal spot patterns obtained by FFTs at various locations about the crease, with the rotation vector normalised such that a 60° rotation of spots from the FFT vertical axis corresponds to a 360° rotation in the graphic. FFTs taken from the numbered boxed regions in Figure 5.12a and b are shown in Figure 5.12d–k, with Figure 5.12d–g taken from boxes 1–4 in Figure 5.12a and Figure 5.12h–k boxes 1–4 from b. Figure 5.12d,f,g show the characteristic set of six spots at 0.21 nm spacing expected for AB-Bernal stacked graphene, however there is a notable splitting of the spots evident in the FFT shown in Figure 5.12e, which can be seen from Figure 5.12a to originate from a region nearer to the central pinch of the fold. The majority of FFTs from Figure 5.12b, nearer still to the central pinch, demonstrate similar splitting in showing two sets of six spots. This second set of spots originates from the presence of a rotational stacking fault between the graphene layers, with the angle between the spots corresponding to the angle of rotation between the sheets.¹⁴ The stretching of some spots into lines, particularly noticeable in Figure 5.12h, coincides with a distortion of the graphene sheet such that it is no longer normal to the direction of the electron beam. This arises due to the non-perpendicular perspective leading to apparent contraction of lattice spacing in this region; akin to the curved edges of carbon nanotubes.³¹ Figure 5.12a shows two sets of four interference fringes (high magnification for the top set shown in Figure 5.12l and the bottom set in Figure 5.12m) tapering to a single set of four fringes in Figure 5.12b before terminating (high magnification in Figure 5.12n). This result demonstrates that the FLG is four layers thick at the crease.

It is interesting to note that the FFTs in Figure 5.12d-g, and also in Figure 5.12h-j, show a variation in the diameter of the Thon ring signal from the amorphous carbon. Since these variations are encountered in the same image it cannot be due to any shift in the defocus, suggesting that these variations may originate from a displacement in the z-axis of the graphene, which is possible considering the scale of the crease and the effect it would have on the surrounding graphene.

Angle from (°)	α_a	α_b	β_a	β_b	χ_a	χ_b	χ_c	χ_d	χ_e	χ_f
vertical	11.5±0.2	6.0±0.3	13.3±0.3	19.1±0.2	6.9±0.5	11.3±0.3	14.4±0.3	18.8±0.5	36.6±0.2	41.2±0.5
α_a	0	-5.5±0.4	1.8±0.4	7.6±0.3	-4.6±0.5	-0.2±0.4	2.9±0.4	7.3±0.5	25.1±0.3	29.7±0.5

Table 5.1. The mean of measured FFT rotations on the left (α), right (β) and central (χ) part of the crease. α_a and β_a denote the FFT spots that are present before splitting.

The map of the relative angles of rotation of the FFT spots shown in Figure 5.12c demonstrates a splitting of the spots from FFTs taken from either side of the crease within approximately 200 nm of the pinch node. There was no further correlation found between distance from the pinch node and the scale of the rotational misalignment. To further characterise the fold it becomes necessary to introduce a notation denoting the different areas of the crease. In Figure 5.12a the labels α , β and χ are shown in the top left, bottom right and central region of the crease, respectively, and shall be referred to when describing FFT angles on different sides of the crease folds. The mean rotation of the spots clockwise from the vertical was found to be $\alpha_a = (11.5 \pm 0.2)^\circ$ and $\beta_a = (13.3 \pm 0.3)^\circ$ for the top left and bottom right side of the crease, respectively, further from the crease end and before the FFT spot splitting. Nearer the pinch we see splitting of the FFT spots, leading to an extra set of spots appearing at $\alpha_b = (6.0 \pm 0.3)^\circ$ for the left and $\beta_b = (19.1 \pm 0.2)^\circ$ for the right side. These values are summarised in Table

5.1. The appearance of the second spot set proximal to the pinch node suggests that the strain in the FLG film about this area is sufficient to induce a shifting in between the layers, resulting in a rotational fault. Some theoretical work has suggested that the translational energy between mutually rotated layers leads to a reduction in the sliding energy between the two layers.³² As such, it could be that the overall energetics of the system are made more favourable by the incorporation of this rotational stacking fault, as it would allow for the layers to more freely move across one another to relieve the strain caused by the pinch. FFTs taken further from the pinch node show no such splitting, with the action of the bulk graphene negating the localised strain of the pinch, thus inhibiting the formation of a stacking fault.

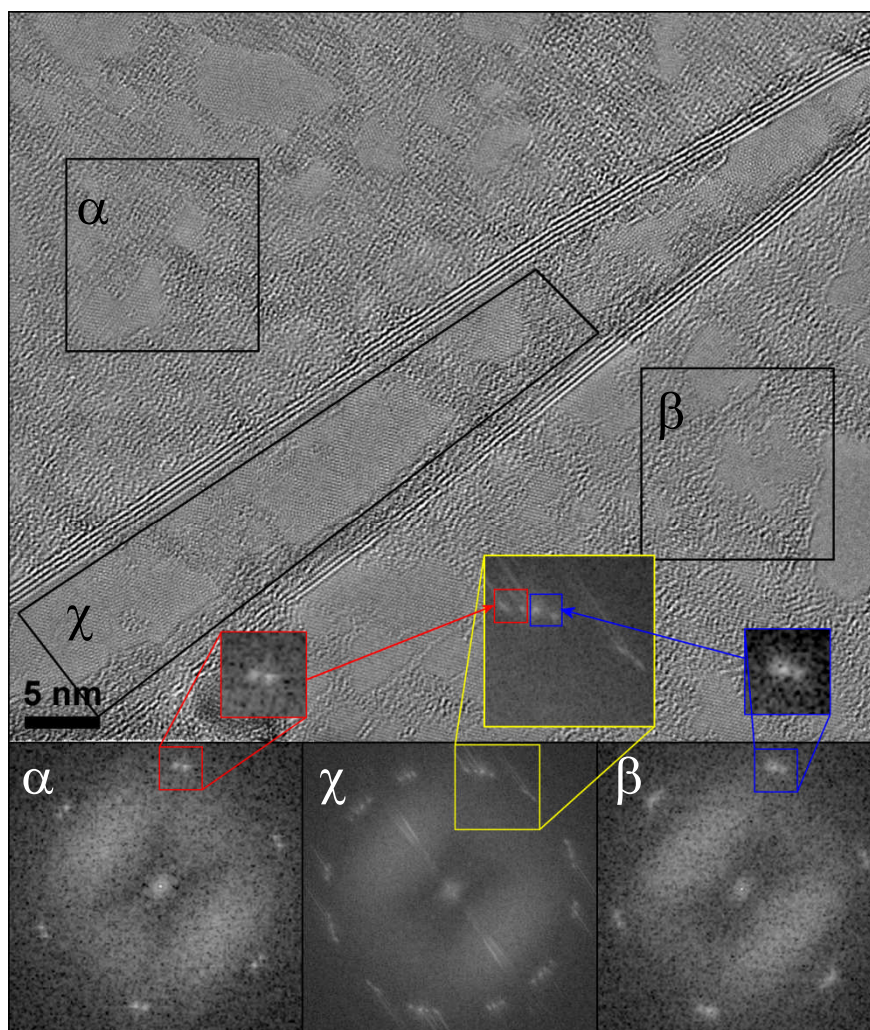


Figure 5.13. An AC-TEM image taken from region 3 (figure 1d). The highlighted areas have corresponding FFT patterns shown underneath, showing two sets, six sets and two sets of hexagonal spots for α , β and χ , respectively. Four of the spot sets in χ correspond to the same rotation as the sets seen in α and β .

Figure 5.13 shows an image taken from region 3, with FFT patterns extracted from the boxed areas. The patterns in α and β both show rotations in agreement with the averages stated in Table 1, however the area in between the two interference fringes, χ , is of interest in characterising the nature of the fold type. The FFT shows six sets of hexagonal spots, suggesting that there are six rotational configurations in the actual crease region, more than the two in the regions either side. However, these are not all stacking faults in a single set of FLG; rather it is more likely that they are three FLG

sheets which each have a single rotational stacking fault, in a configuration similar to the skewed back fold model shown in Figure 5.11g. This is supported both by four of the FFT spots corresponding with good agreement to rotations found in the regions either side of the fold region (see Table 1), and by the remaining two spot sets having an average rotation of $\chi_e = (36.6 \pm 0.2)^\circ$ and $\chi_f = (41.2 \pm 0.5)^\circ$ from the vertical, which when subtracted by the rotations of the misaligned sheets to the top left of the fold (α_a and α_b) yields values of $(30.6 \pm 0.4)^\circ$ and $(29.7 \pm 0.5)^\circ$. This would be in good agreement with the fold being along a zigzag axis in the sheets. Research demonstrating that folds along the armchair and zigzag directions are energetically more favourable support this.²³

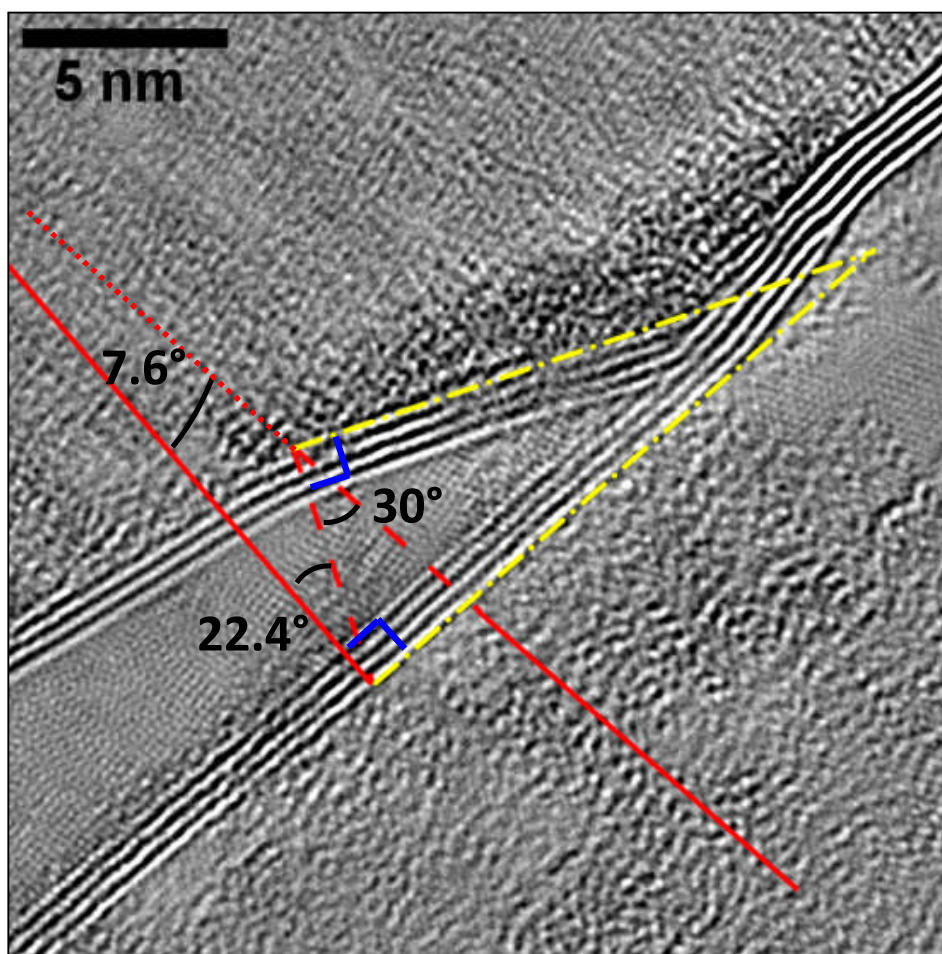


Figure 5.14. An AC-TEM image from region 4 including annotations showing the observed rotations in the FLG system across the skewed back fold, with both a 30° and a 22.4° fold, leading to an overall skew of 7.6° across the crease. The yellow dashed lines are orthogonal to the appropriate red lines describing the FLG orientation, and can be seen to correlate with the interference fringes originating from the folds in the AC-TEM image.

As mentioned, the observed results support the skewed back fold model shown in Figure 5.11g. This accounts for the fold induced interference fringes along either side of the crease, the change in relative rotation of the sheets before and after the fold and the multiple sets of FFT spots observed in the central area of the crease. Finally, the unique FFT spots in the crease region have a relative rotation of 30° to the spots corresponding to the graphene outside the crease, strongly supporting a zigzag fold. On either side of the crease the angle of the induced rotational stacking fault was found to be $(5.5 \pm 0.4)^\circ$

for the α side and $(5.8 \pm 0.4)^\circ$ for the β side, suggesting that the same rotational stacking fault propagates through the fold rather than the fold causing discrete defects on either side, which is further supported by the observation of FFT spots with corresponding rotations in region χ , as demonstrated in Figure 5.13. The overall skew of the fold, calculated from the mean difference between the FFT angles for regions α and β , was $(7.6 \pm 0.3)^\circ$. These angles are superimposed on an AC-TEM image of the converging crease in Figure 5.14, showing the correspondence between angles calculated by FFT and the strong distortion leading to the crease node. The red lines represent the relative orientation of the FLG across the crease, with the additional yellow lines taken normal to them at the folds. These can be seen to closely match the imaged folds as it converges toward the end of the crease, with a measured angle of 23.1° extracted from the AC-TEM image comparing well to the expected angle of 22.4° .

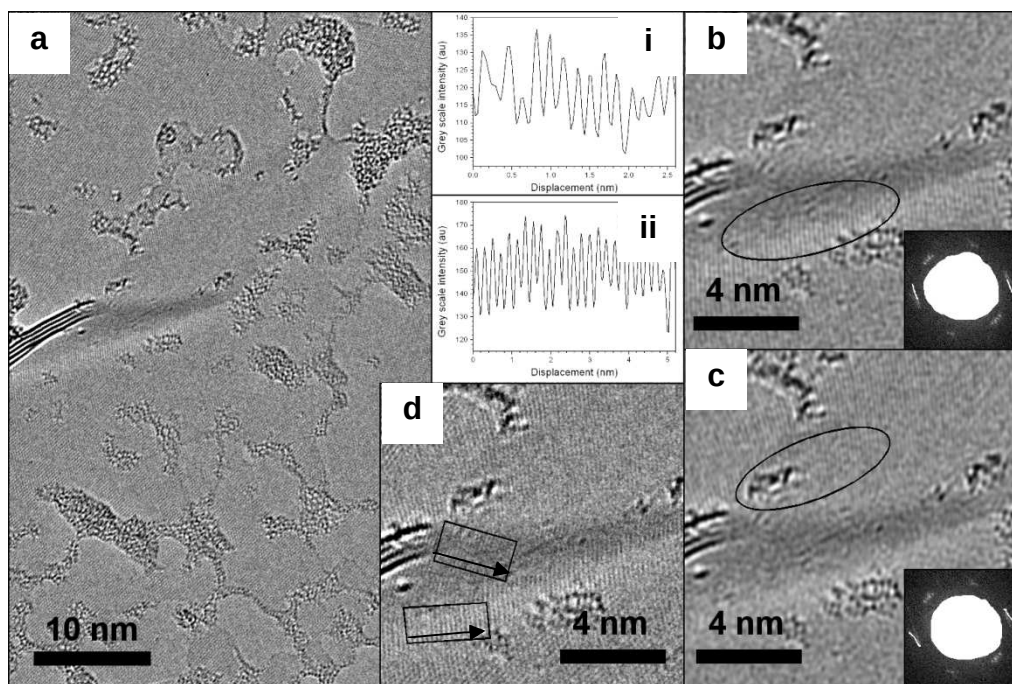


Figure 5.15. (a) AC-TEM image taken from region 5. (b,c) Reconstructed FFT images (FFT positive masks shown in the inserts) of a, showing bending in the graphene lattice lines over and around the shaded region near the fold fringes (circled). (d) A magnified image of the region at the termination of the interference fringes. Box averaged intensity plots are shown, taken from regions labelled i and ii. The arrows correspond to the positive x axis direction.

The low magnification TEM image of the fold in Figure 5.10 shows the fold end part way through the graphene film. An AC-TEM image of the termination of the fold is displayed in Figure 5.15a, showing a pronounced band of shadowing to the bottom right of the interference fringes. Reconstruction of positive masked FFTs taken from the area (Figure 5.15b and c), which selects a specific lattice orientation to display, show the lines of the graphene lattice bending across the shadowed area. The box averaged intensity profiles are taken from the corresponding labelled boxes in the high magnification insert to Figure 5.15a, from the shadow (i) and the light fringe (ii), with the arrow indicating the x-axis direction. The boxes were selected so as to be orthogonal to the direction of the lattice lines, such that measurements of the full width half maxima of the peaks from

the profiles would yield characteristic lattice distances for the regions. The light fringe lattice spacing was found to be 0.21 nm and 0.17 nm for the dark fringe. It is postulated that the change in contrast is similar to a thickness effect, with the out of plane distortion of the graphene being severe enough to lead to a pronounced apparent reduction in the graphene lattice parameter, and hence the darker contrast.³³ The strong warping of the graphene in this region would be due to the presence of the fold termination, much as a similar fold in a simple sheet of paper would yield.³⁴ This result is further supported by the streaking evident in the FFT shown in Figure 5.12h, akin to in carbon nanotubes, and the variation of the diameter of the Thon rings in the FFTs taken from different regions of the same image.

5.3.3 Conclusion

The structure of a FLG crease has been characterised by AC-TEM imaging and simulation. The crease has been shown to be back folded on itself, converging from a shallow skew to one with a 30° fold direction and with a combined skew across the fold of 7.6°. In the high strain region around the end pinch of the FLG crease severe out of plane distortions were observed, corroborated by direct lattice imaging and measurements, FFT spot stretching and the observation of pseudo-thickness originating contrast. The most important observation for consideration with regards to graphene in applications, however, is the strain induced stacking faults that have been demonstrated to occur near to the fold pinch. Such stacking faults could have a notable effect on the capabilities of FLG based devices, and illustrates the importance of the fold inducing transfer step when incorporating CVD graphene grown on copper into a device. Understanding the behaviour of folds in graphene is of importance as part of the wider

area of study of graphene defects, where their macroscopic effect in electrical devices, and also mechanical systems, will be of interest.

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Spatial Control of Defect Creation in Graphene at the Nanoscale

6.1 Introduction

Defects in graphene not only modify its properties¹⁻⁸ but also extend its functionality by providing sites for chemical reactions, which enables intentional doping at specific points. Electron and ion beam irradiation have been successful in generating defects in carbon nanostructures, such as fullerenes, nanotubes, peapods, and more recently graphene.⁹⁻¹² For ion beam irradiation, defects are sporadically formed over a wide area of graphene with lack of nanoscale spatial control and in-situ monitoring at the atomic level. Alternatively, electron beam irradiation within an aberration corrected transmission electron microscope (AC-TEM) allows for in-situ atomic level monitoring without having to remove the sample from vacuum or subject it to further characterisation methods.

Electron beam irradiation of graphene well above its knock-on damage (KOD) threshold of ~ 86 keV within an AC-TEM generates defects that can be subsequently imaged, with the electron beam accelerating voltage reduced to below the KOD threshold after defect creation to minimise further beam damage.¹³⁻¹⁶ However, this approach exposes a large

amount of the graphene to electrons with energy above the KOD threshold, and limiting defect creation to one specific location is nearly impossible. Efforts to control defect creation in graphene within a specified nanoscale region using a focussed electron beam in a TEM have been limited to the creation of nano-pores or small holes in the graphene.^{17,18} In this case the energy of the electron beam was above the KOD threshold and it is likely that many other wide-spread smaller vacancies are also formed throughout the graphene sample. Scanning transmission electron microscopy (STEM) has also been used to create vacancies in a carbon nanotube by the use of an intensely focussed electron beam above the KOD threshold, but again it is likely that many other smaller defects such as monovacancies were also created within the sample.¹⁹ A key challenge in this area of graphene research is the ability to induce defects only within the specified area of interest and then be able to image the structure without creating further defects.

In this chapter I show that it is possible to have nanoscale control of defect creation in monolayer chemical vapour deposition (CVD) graphene with minimal contamination. The electron beam irradiation potential is set to 80 kV within an AC-TEM, which is just below graphene's theoretical KOD threshold. However, substantially increasing the electron beam current density (BCD) resulted in the localised sputtering of graphene, even below the KOD threshold of 80 kV. By careful control of the electron BCD, defect creation can be confined to within a $10 \times 10 \text{ nm}^2$ region of graphene and the average level of complexity controlled by the exposure time.

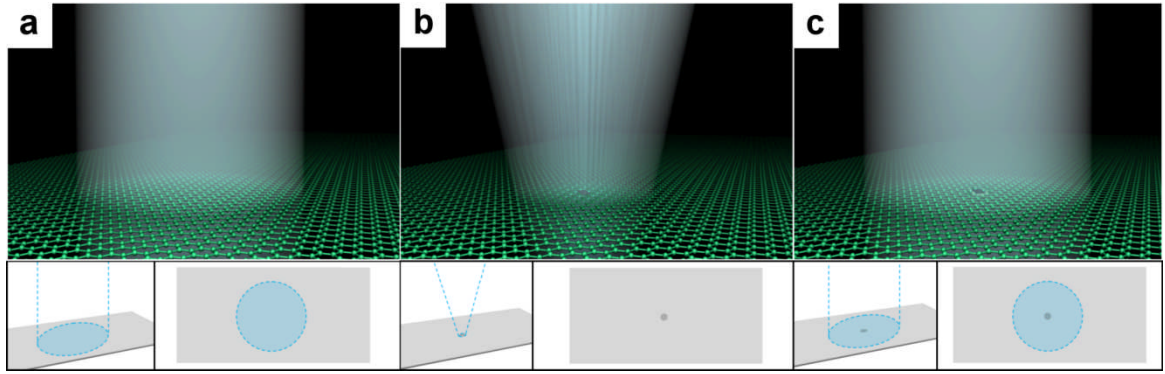


Figure 6.1. Schematic illustrating the beam profile used in the three principle stages; (a) a broad beam used to image graphene before defect formation (typical beam current density $\sim 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$), (b) a focussed probe with a high current density used to form defects ($\sim 10^8 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$), (c) a broad beam used to image graphene after defect formation ($\sim 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$).

6.2 Results and Discussion

Graphene was synthesised by a novel atmospheric pressure liquid catalyst CVD method (section 3.2.2).²⁰ Figure 6.1 illustrates the concept of our nanoscale control of defect creation; the beam is set to normal imaging conditions with uniform illumination at a BCD $\sim 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$ (Figure 6.1a). No defects in graphene were created under these conditions, consistent with previous reports.^{14,21} A reference image is taken of the pristine graphene lattice. Next the beam is focussed to a BCD $\sim 10^8 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$ within a 10 nm diameter spot to create defects (Figure 6.1b). The exposure time is varied as desired and then the beam is expanded back to the original conditions for imaging (Figure 6.1c). An image is subsequently taken of the created defects, typically within 30 – 60 seconds. This delay was due to the need to re-adjust the focus and two fold astigmatism.

Defects were created in a clean area of pristine graphene only when the BCD reached $\sim 10^8 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$. Analysis of the spatial profile of the electron beam showed a non-

uniform BCD when focussed, with over half the total beam current contained within a zone of approximately 10 nm diameter (see Appendix C). It is within the 10 nm hot-spot that the BCD reaches $\sim 10^8 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$, and results in the created defects being confined to this region. After focussing the probe, a predetermined time was allowed to elapse before the beam was defocused to image the specimen.

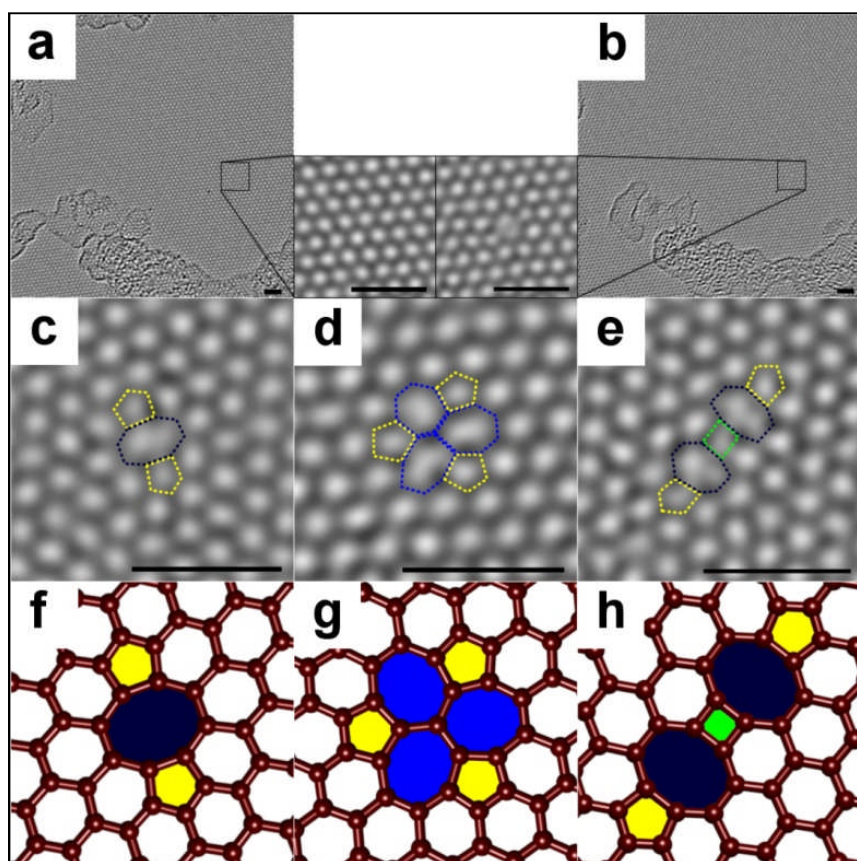


Figure 6.2. (a) AC-TEM image of a pristine graphene sheet before 30 s exposure to a focussed electron beam. (b) Divacancy formed in exposure area directly after irradiation. Inserts show magnified images of highlighted areas in (a) and (b). (c-e) AC-TEM images of three different 30 s exposures, resulting in (c) a divacancy, (d) a divacancy having undergone a single SW bond rotation, (e) two linked divacancies along the armchair direction. (f-h) Atomic models corresponding to the TEM images (c-e). The colour scheme (dashed line annotations and model filling colour) denotes the number of carbons in the respective carbon ring, such that green, yellow, blue and dark blue represent 4-, 5-, 7- and 8-membered carbon rings, respectively. Scale bars represent 1 nm.

Manipulating the exposure time to the focussed beam gives a degree of control over the average complexity of the defects that are formed, as demonstrated in Figure 6.2 and Figure 6.3. Figure 6.2a shows an AC-TEM image of a pristine graphene sheet before a 30 second exposure, Figure 6.2b directly after, with a single divacancy in the exposed area. AC-TEM images from three 30 second exposures in different pristine regions are shown in Figure 6.2c-e. The divacancy structures observed have two adjacent atoms removed from the lattice, and in the case of Figure 6.2d the divacancy has undergone a single Stone-Wales (SW) transformation.²² In Figure 6.2e two divacancy defects are joined, forming an extended defect along the armchair lattice direction. Monovacancies were observed less frequently due to the high energy of the monovacancy configuration, which leaves one carbon atom in an unsaturated state with only two bonds (see Chapter 7), and is thus unstable with respect to the more energetically favourable divacancy structure when under electron beam irradiation.¹⁵

Figure 6.3 shows that extending the exposure time from 30 to 60 or 120 seconds resulted in the formation of larger defect structures. Shown for 60 seconds are three linked divacancies along the armchair direction (Figure 6.3a), a divacancy plus a SW rotation (Figure 6.3b, similar to that shown in Figure 6.2d), and a complex defect structure along the zig-zag lattice direction, containing a dislocation pair and vacancies (Figure 6.3c). Atomic models of the defect structures in Figure 6.3a-c are presented in Figure 6.3d-f, respectively.

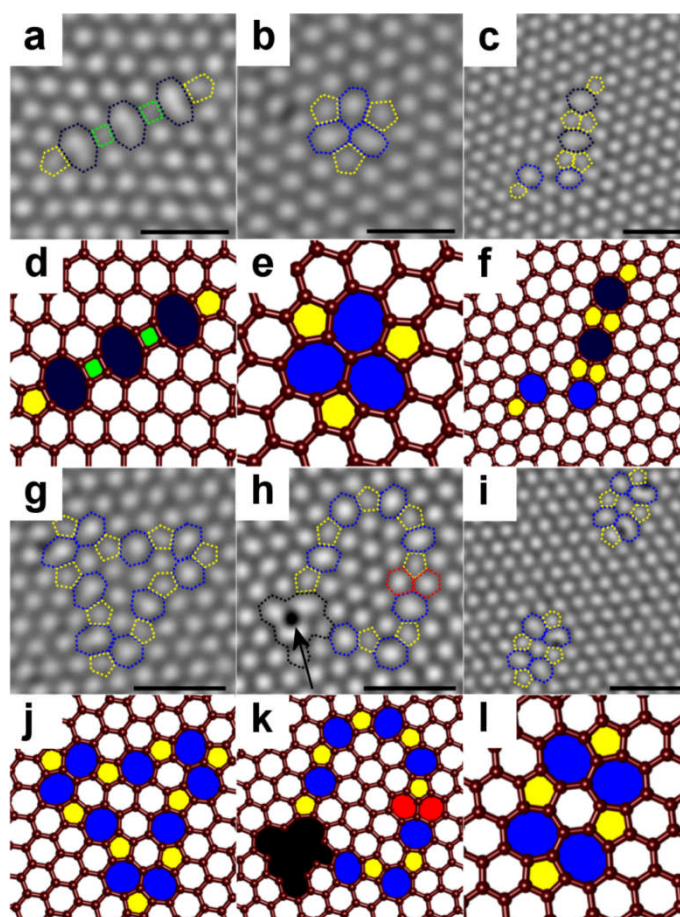


Figure 6.3. (a-c) AC-TEM images of defects formed after 60 s of focussed electron beam irradiation: (a) Three linked divacancies. (b) A divacancy after a SW transformation. (c) Defects clustered around one of a pair of dislocations. (d-f) Atomic models of the defects presented in (a-c), respectively. (g-i) Annotated AC-TEM images of defects formed after 120 s of focussed electron beam irradiation: (g) An enclosed, rotationally misaligned core of six hexagons, surrounded by a complete loop of pentagons and heptagons. (h) A larger, partially completed loop, isolating several rotated hexagons. A gap in the loop, filled by two hexagonal rings, is highlighted in red. The arrow marks an adatom, which inhibits direct interpretation of the area bordered in black due to localised lattice distortion arising from the adatom. (i) Two divacancy defects, each having been transformed via two SW rotations, leading to a single isolated, rotated hexagon. (j-l) Atomic models corresponding to the defect structures in (g-i). Scale bars represent 1 nm. The colour scheme (dashed line annotations and model filling colour) denotes the number of carbons in the respective carbon ring, such that green, yellow, blue and dark blue represent 4-, 5-, 7- and 8-membered carbon rings, respectively.

Increasing the exposure to the focussed electron beam to 120 seconds allowed for the creation of defects of further complexity (Figure 6.3g-l). Figure 6.3g shows six hexagons surrounded by a complete loop of pentagon-heptagon pairs. The central hexagons are rotationally misaligned by 30° with respect to the bulk graphene lattice, with the loop acting to screen this misaligned core from the rest of the lattice. Whilst this low energy vacancy configuration has been hypothesised,¹⁶ to the best of our knowledge this structure has not been directly observed before. Another set of rotationally misaligned hexagons are similarly enclosed in a nest of alternating pentagons and heptagons (Figure 6.3h). However, in this image the structure of the loop is incomplete and two hexagons complete the circuit. Within a small area, denoted by the black border in Figure 6.3h, it is difficult to clearly resolve the lattice structure to determine the bonding configuration due to the presence of an adatom (marked by an arrow), which is likely sorbed at the more reactive defect site.⁵ The defects in Figure 6.3g,h originate from multiple divacancy structures, akin to those illustrated by Figure 6.3i. In this case two divacancy structures have each transformed through two SW rotations, leading to a single hexagon that is rotated by 30° with respect to the rest of the lattice. Several of these divacancy structures can form into the more complex configurations shown in Figure 6.3g,h.¹⁶ Figure 6.3j-l present atomic models of the defect structures in Figure 6.3g-i respectively.

This ability to control the average complexity of defects created by adjusting the exposure time is summarised in Figure 6.4, which characterises the defect structures directly after creation. Figure 6.4e shows a linear plot of atoms lost per nm^2 as a function of total dose, the gradient of which was used to calculate a sputtering cross-section of 1.35×10^{-2} barn. The complexity of the defects has been parameterised by

assigning a value of one both to every non-6-membered ring and to rotationally misaligned 6-membered rings present in the irradiated area (examples are shown in Appendix F). An exception to this are the isolated divacancies, which can freely oscillate between three stable configurations via SW rotations on a short time scale, even under imaging doses (Appendix D), and thus were assigned a value of 6. Representative annotated AC-TEM images, with accompanying atomic models, are also shown, with the complex closed loop structures only found at exposure times of 120 s. However, these longer exposure times do not guarantee the formation of these higher level defects, but are a necessary prerequisite. Simpler single divacancy defects are still observed to form during some 120 s exposures. Exposure times beyond 120 seconds often led to holes opening up within the graphene sheet due to etching from impurities, hence the limit of 120 s exposure times. It was found that holes opened up even in regions of graphene that had not been directly exposed to the electron beam, but were close by and next to contamination. This indicates that the hole opening process is not always driven by electron beam induced sputtering and that an e-beam mediated chemical etching method may not provide sufficient spatial control for defect creation.

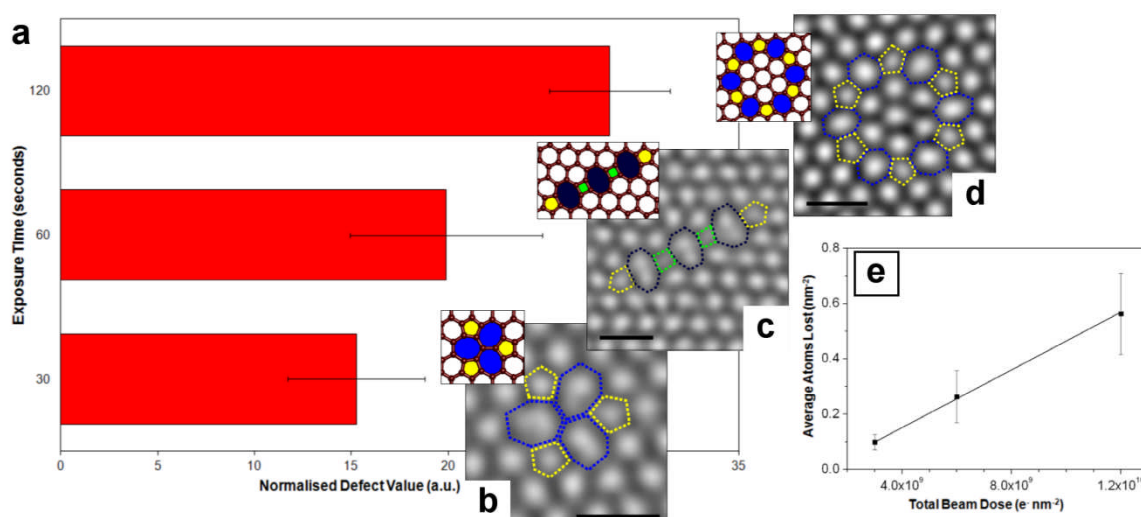


Figure 6.4. (a) A bar chart parameterising the effect of exposure time on defect complexity, defined here as the number of non-6-membered carbon rings plus any rotationally mismatched 6-membered rings in the irradiated area, parameterised as the normalised defect value (NDV). Error bars are the calculated standard error. (b-d) Representative AC-TEM images for each exposure time (30, 60 and 120 s, respectively), along with atomic models; (b) has a NDV of 6, (c) NDV = 7, (d) NDV = 19 (7 rotated rings + 12 non-6-membered rings). The colour scheme (dashed line annotations and model filling colour) denotes the number of carbons in the respective carbon ring, such that green, yellow, blue and dark blue represent 4-, 5-, 7- and 8-membered carbon rings, respectively. Scale bars are 0.5 nm. (e) The average number of atoms lost per nm² as a function of total beam dose (e⁻ nm⁻²), yielding from the gradient a sputtering cross section of 1.35x10⁻² barn. Error bars are the calculated standard error.

The stability of the defects created by irradiation was examined. Figure 6.5a-c shows the evolution and relaxation of a large defect configuration, shown earlier in Figure 6.3g, to a near pristine lattice under normal imaging conditions. This defect configuration has been shown to have a low formation energy, and as such would be expected to be stable.¹⁶ This is supported to a degree by the observations, where the defect was observed for six minutes under imaging BCD conditions, before a set of three SW rotations (atoms and bonds that rotate are highlighted in gold Figure 6.5d) causes it to collapse to an energetically less stable state. Over the course of a further five minutes of

imaging the defect was observed to relax into a less disordered state, with the image series concluding with the defect reduced to two monovacancies in a graphene lattice. Given that the initial defect is formed from a combination of three divacancies, the presence of these residual vacancies is expected, and it is likely further observation would show the quenching of these residual monovacancies by additional mobile surface adatoms.

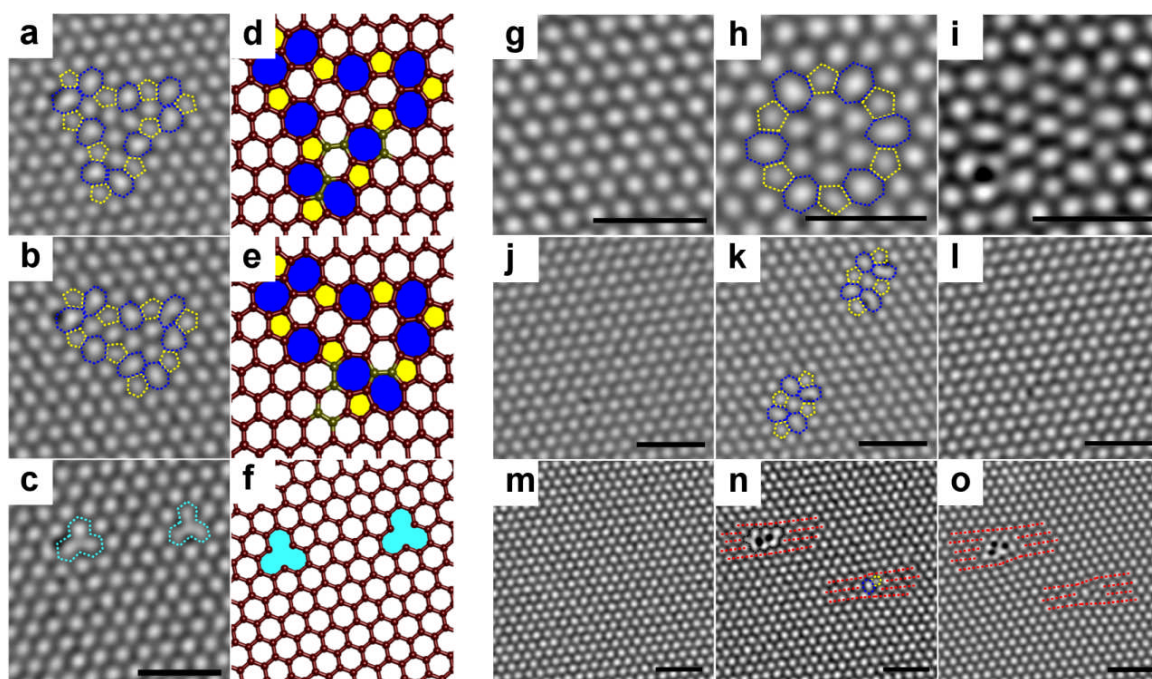


Figure 6.5. (a-c) AC-TEM images and (d-f) accompanying atomic models, showing the near complete relaxation of a complex defect structure, observed under imaging BCD. After 360 s the structure changes to that shown in (b); the atoms and bonds that undergo a SW rotation are highlighted in gold in (d), with resulting positions highlighted in gold in (e). (c) The final image of the series, 660 seconds after initial observations, shows the defect reduced to two monovacancies (light blue, also highlighted in (f)). AC-TEM image (g) before and (h) after a 120 s high BCD exposure. (i) The same defect after 900 s of exposure to an imaging BCD, showing no change in configuration. (j) Pristine region of graphene lattice before focussed irradiation. (k) Two divacancy defects formed after 120 s high BCD exposure. (l) Quenching of the two divacancy defects back to pristine lattice after 480 s without irradiation (beam blanked). (m) Pristine graphene lattice before irradiation. (n) Creation of dislocations by 120 s exposure to high BCD irradiation. (o) Stability of two dislocation defects, with surrounding lattice planes highlighted in red, after 600 s without irradiation. The colour scheme (dashed line annotations and model filling colour) denotes the number of carbons in the respective carbon ring, such that yellow and blue represent 5- and 7-membered carbon rings, respectively. Scale bars are 1 nm.

Although some defects relaxed to pristine graphene following exposure to the imaging beam, others were observed to be resilient to continued irradiation at a BCD $\sim 10^5 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$. Figure 6.5g-i show a closed loop defect that was stable for a prolonged period of time under normal imaging conditions, with Figure 6.5 before, Figure 6.5h

after 120 s of focussed irradiation, and Figure 6.5i after a further 780 seconds of imaging exposure. The defect did not change for over 900 seconds of exposure to imaging doses of irradiation. These defects, consisting of a closed loop of pentagon-heptagon pairs, have been proposed to occur intrinsically with low formation energies.²³ Kurasch *et al.* showed that these closed-looped structures can unwind under higher BCDs of $10^7 e^- \text{nm}^{-2} \text{s}^{-1}$.²⁴ Divacancy defects were found to be less stable and susceptible to quenching by adatoms on the surface (see Chapter 7). Figure 6.5j-l show the creation of two divacancy defects by focussed irradiation from a pristine lattice. Following the recording of the image in Figure 6.5k, the electron beam was blanked; preventing irradiation of the specimen, for 480 s. Subsequent images recorded from same region (Figure 6.5l) showed the defects were quenched back to a pristine lattice, suggesting that defect annealing can occur in the absence of the electron beam. Created dislocations, such as the pair shown in Figure 6.5m-o, were found to be predominantly stable against annihilation. From these observations it can be concluded that quenching of simple divacancy defects can occur without electron beam irradiation. However, for the relaxation of more complex, closed loop defects it is necessary to provide an initialising SW rotation to destabilise the defect, causing a cascade of further rotations culminating in a pristine lattice, with vacancy quenching also subsequently occurring in cases such as shown in Figure 6.5c. The energy for this initialising SW rotation must come from the electron beam, as the thermal energy contribution alone is insufficient,²⁵ thus these defects are expected to remain stable when not subject to irradiation.

The creation of vacancy defects at 80 kV, albeit under irradiation at higher BCD than normally used for imaging, implies that it is still possible to induce limited sputtering in

graphene. Work conducted on an 80 kV AC-STEM system (see Appendix E) demonstrated that 80 kV electron beam irradiation of a single carbon atom at high doses of $\sim 2.54 \times 10^{10} \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$, which is two orders of magnitude more than achieved using the focused TEM probe, does not lead to a sputtering event. This initially puzzling result suggests that the sub-threshold sputtering process does not depend on the dose received by a single carbon atom, but relies on an area of the sample to be irradiated. Chemical etching by surface contamination can be eliminated as the cause of the reported defects, as it does not produce defects at defined locations in a clean area of graphene, as demonstrated by AC-STEM data showing holes opening in the graphene areas away from the focus point of irradiation but near sources of iron contamination (see Figure 6.6). Furthermore, chemical etching typically produces holes rather than the defect structures observed here; holes in these experiments were only observed for exposure times in excess of 120 s. Meyer *et al.* studied the electron beam dependent cross-section for sputtering in graphene using a BCD of at most $10^6 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$, and at 80 kV they did not observe a single defect for a total dose of up to $10^{10} \text{ e}^- \text{ nm}^{-2}$.²⁶ A cross-section of 1.35×10^{-2} barn for a BCD $\sim 10^8 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$ was measured in our experiments, which is more than two orders of magnitude larger than the calculated value of 7×10^{-5} barn reported in ref. [26]. This confirms that standard knock-on sputtering cannot be the mechanism in our observations.

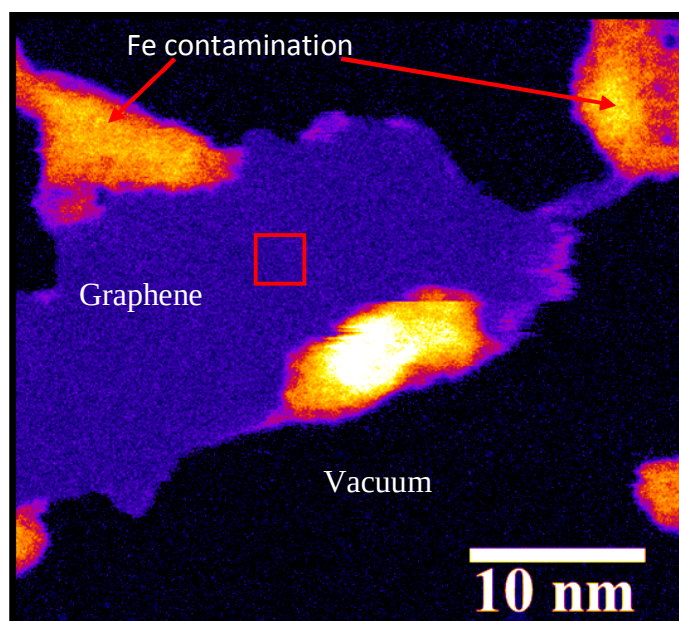


Figure 6.6. False colour angular dark field STEM image of graphene after 30 minutes of continual electron beam irradiation in the region shown by the red box. Holes (dark) have opened up around the graphene (blue) that was imaged. Contamination, identified as Fe by electron energy loss spectroscopy (EELS), appears as the bright regions.

There are two possible explanations for the BCD dependent cross-section within the irradiated area, specifically; lowering of the sputtering threshold due to weakening of the chemical bonds from ionisation/plasmon excitations, or an increase in the out-of-plane atomic vibrations in graphene that provide additional momentum to enable an 80 keV electron to sputter a carbon atom. Calculations show that the threshold for sputtering has to be reduced by only $\sim 10\%$ from 22 to 19.7 eV to achieve our experimentally observed cross-section (see Figure 6.7). One can discount electron beam heating effects as graphene is an excellent thermal conductor; as such calculations show negligible overall temperature rise would be expected in our sample (see discussion and graphics in Appendix G),²⁷ consistent with calculations on carbon nanotube heating.²⁸ Crucially, thermal conduction in graphene occurs via efficient phonon modes and a small contribution from free electrons.^{29,30} Under continual irradiation there may be some

depletion of electrons within the irradiated area, due to their involvement in thermal conduction, that could weaken the sp^2 bonds and lower the threshold for sputtering. However, given that the major contributor to thermal conduction in graphene arises from phonon propagation, it seems more likely that the excitation of phonon modes provides an increase in the out-of-plane velocity component that leads to our observed sputtering. Recent work has shown that flexural phonon modes play an essential role in thermal conductance in suspended graphene.³¹ Graphene also has unusual and strong coupling between plasmons and phonons.^{32,33} Thus, an inelastic collision may trigger a flexural phonon mode either directly or through plasmon coupling that causes a temporary increase in the out-of-plane motion of surrounding atoms, and if a subsequent elastic collision were to occur with one of these atoms then sputtering may result. For low beam current densities the probability of this occurring reduces due to the short lifetime of either the plasmon or phonon mode. The behaviour of flexural phonon modes in graphene follows a quadratic dispersion relationship and thus the density of states and its dependence on temperature are different to the Debye model.³⁴ Focussed electron beam irradiation may change the distribution of occupied phonon modes with an increased proportion of flexural modes at the expense of in-plane modes, whilst not changing the overall temperature of the system. Direct evidence of phonon excitations in graphene from electron beam irradiation has been reported in ref. [14]. Explanations of variations in the sputtering-cross section with BCD are known to be challenging and further investigation is required to gain deeper insight into this phenomenon.³⁵

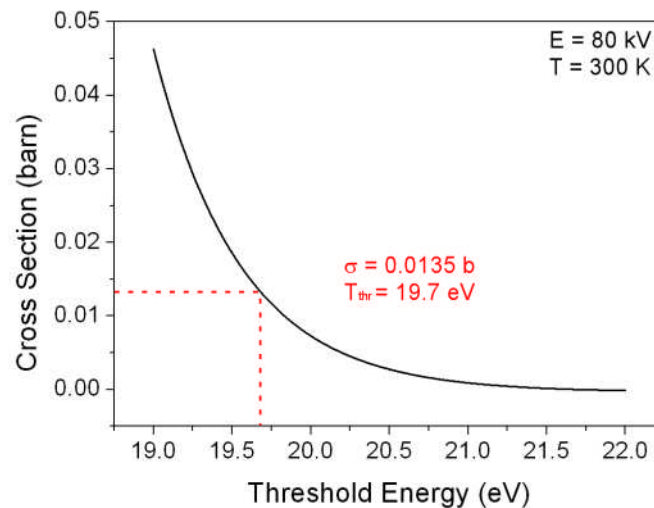


Figure 6.7. A plot showing the dependence of sputtering cross section on mean square velocity, calculated with 80 keV incident electrons. Marked is the expected mean square velocity at 300 K.

6.3 Conclusion

The ability to create defects in a controlled area, ($10 \times 10 \text{ nm}^2$), with variable complexity, opens up the possibility for enhanced engineering of graphene. The introduction of the focussed, high current density electron beam perturbs the system and leads to changes in the sputtering cross-section. Whilst some structures are observed to simply revert back to a defect free lattice, instances of beam induced defects that are stable have also been observed. These latter, stable defects could provide the necessary reaction points for controlled functionalisation, as they would likely be less susceptible to annealing during processing. Also shown are that dislocation pairs, known to induce strain in the lattice of graphene, can be created by sputtering along the zig-zag lattice direction.³⁶ These results provide important foundations regarding which defects are stable enough to persist in graphene and thus be useful for future studies.

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Chapter 7

AC-TEM Characterisation of Point Defects in Monolayer Graphene

7.1 Introduction

By employing the selective defect creation technique outlined in Chapter 6 the generation of particular structures for study was rendered significantly more efficient. Rather than relying on happening upon intrinsic defects in the graphene sample, it was possible to deploy an appropriate dose and generate defects for study. In this chapter studies of two categories of defects are discussed; the behaviour of vacancy defects quenched by residual iron atom contamination and the structure of isolated monovacancy defects.

7.2 The Dynamics of Single Iron Atoms in Graphene Vacancies

7.2.1 Introduction

Manipulating the novel properties of graphene,¹ such as carrier concentration^{2,3} or magnetism,⁴⁻⁶ by utilising defects is an area of research with important ramifications in the deployment of graphene for devices. Impurities, such as metals, often reside on the

surface of graphene but they can also be incorporated into the lattice to form a substitutional or interstitial dopant structure. The magnetic moment of transition metal atoms incorporated into a graphene sheet through covalent bonds to the surrounding C atoms in a mono or divacancy have been theoretically modelled, with some metals (Cr, Mn) showing paramagnetic moments and others (Zn, Pt) being diamagnetic.⁶ Fe exhibits a paramagnetic moment when substituting two carbon atoms in a divacancy interstitial configuration but not when directly substituting a single carbon atom in a monovacancy arrangement.⁶ This conclusion is supported by studies of Fe implanted graphite that show paramagnetism.^{7,8}

Available methods for the introduction of defects or dopants into graphene with fine spatial control are challenging and limited, but are likely to play an important role in the manipulation of graphene properties. Recent work has shown that focussed electron beam irradiation at an accelerating voltage of 80 kV results in vacancy formation in graphene with $10 \times 10 \text{ nm}^2$ spatial control.⁹ The increased chemical reactivity of these created defect sites offers the possibility of trapping adatoms residing on the surface.

Aberration corrected transmission electron microscopy (AC-TEM), operated at accelerating voltages of 80 kV and below, allows the study of the behaviours of single atom point defects in a graphene sheet.¹⁰⁻¹³ These include metal substitutions and interstitials, and their evolution over time under controlled electron irradiation. Previous work in this area has used high resolution (HR-) TEM to study the diffusion of metals on graphene sheets,¹⁴⁻¹⁶ and vacancy quenching by metal atoms in graphene and carbon nanotubes.^{17,18} Scanning TEM (STEM) combined with electron energy loss spectroscopy (EELS) has also been employed to investigate metal-graphene interactions and has

provided information on extended plasmon resonances surrounding Si atoms in graphene and the oxidation resistance of Fe atoms incorporated into the graphene lattice.^{19–23} However, direct observation of the incorporation and migration of covalently bonded metal atoms in graphene, which would provide insights into the strain and stability, has yet to be observed.

For this chapter vacancy defects in graphene are created in a defined spatial region using the focused 80 kV electron beam irradiation technique discussed in Chapter 6.⁹ I then studied the dynamics of the mechanisms by which mobile Fe atoms are trapped by vacancies through covalent bonding to the graphene lattice and the resulting strain induced in these structures.

Graphene was synthesised by a liquid Cu catalyst chemical vapour deposition (CVD) method (section 3.2.2),²⁴ and transferred to Si₃N₄ TEM grids using a PMMA polymer supporting scaffold. An important stage in this process is the removal of residual FeCl₃ used to etch the Cu by using an HCl rinse. To maximise the possibility that a Fe atom will be trapped within created vacancy structures the HCl rinse duration was reduced, leaving more Fe residue on the graphene surface. The nature of the metals observed by AC-TEM was confirmed as Fe using annular dark field STEM combined with EELS (Figure 7.2). Hybrid exchange density functional theory (DFT) calculations (the B3LYP functional)^{25–27} were performed using the CRYSTAL code by collaborators at the Rutherford Appleton Laboratory (Dr. B. Montanari and Prof. N. Harrison).²⁸ The numerical approximations adopted, and the double valence with polarisation local Gaussian basis set, are described by them elsewhere.²⁹ The Fe basis set was that used in previous studies of inorganic materials³⁰ enhanced with a diffused sp-function at 0.2 a₀⁻².

Defects were represented in a periodic 10 x 10 supercell of the graphene primitive unit cell within the Brillouin zone of which the eigensolutions were sampled on a Pack-Monhurst grid of shrinking factor 4 yielding 10 symmetry irreducible k-points.

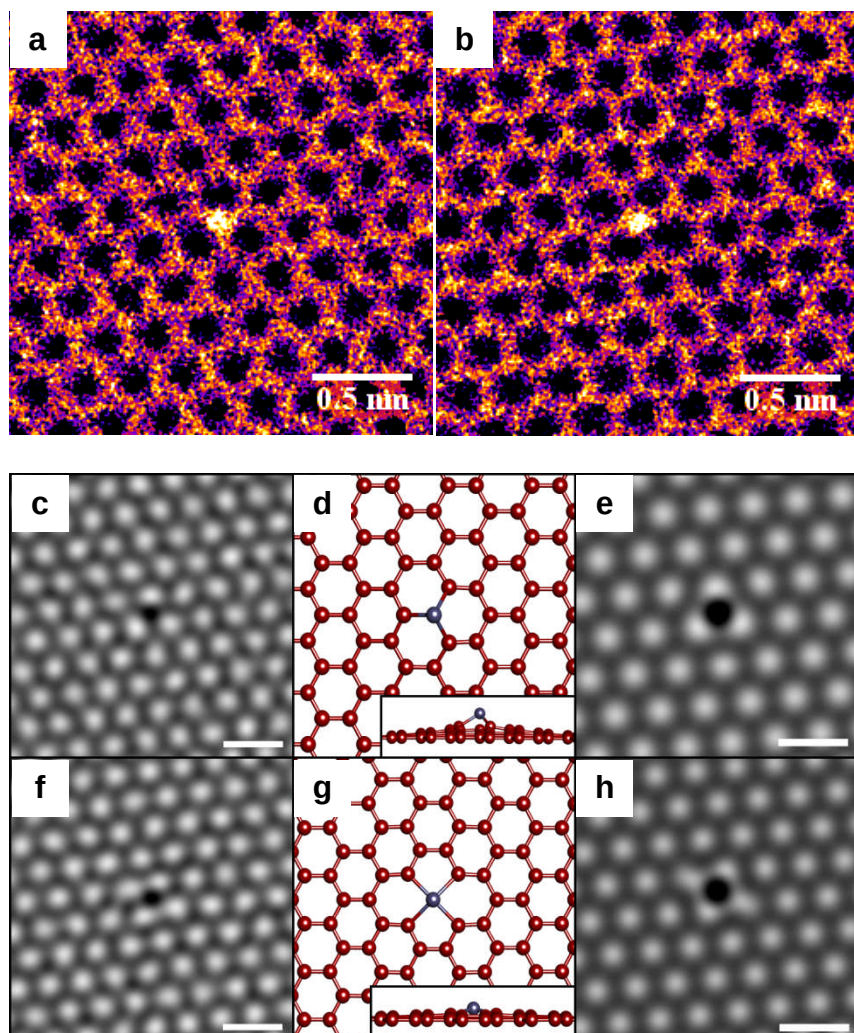


Figure 7.1. False colour AC-TEM images of (a) A Fe substitutional defect in a graphene monovacancy (Fe@MV) (b) A Fe interstitial defect occupying a divacancy (Fe@DV). (c) Smoothed AC-TEM image of the Fe@MV shown in (a), (d) DFT optimisation of the Fe@MV structure (the insert shows a side view), and (e) a multi-slice TEM image simulation of the system. (f-h) Similar to (c-e), but for Fe@DV. Scale bars denote 0.5 nm.

7.2.2 Results and Discussion

Initially discussed here are the two most frequently observed atomic configurations for single Fe atoms in a graphene lattice. Figure 7.1a,b show raw AC-TEM images (rendered with a fire colour look-up table (CLUT) scale applied to enhance visual contrast), of the two Fe atom point defect configurations. Figure 7.1a demonstrates the substitutional configuration, with a Fe atom occupying a monovacancy in the graphene sheet; this is referred to as Fe@MV, as in ref. [6]. Figure 7.1b shows the interstitial configuration, where a Fe atom resides in a graphene divacancy, replacing two C atoms, and is referred to as Fe@DV. A smoothed AC-TEM image of the Fe@MV is shown in Figure 7.1c. DFT calculations for the Fe@MV structure yield the relaxed geometry shown in Figure 7.1d, and by applying a multislice image simulation (see section 3.7) to this Figure 7.1e is produced, showing strong agreement with the AC-TEM image in Figure 7.1c. A smoothed AC-TEM image, the DFT relaxed geometry and AC-TEM image simulation for the Fe@DV are shown in Figure 7.1f-h. These image simulations demonstrate excellent agreement with the observed structures.

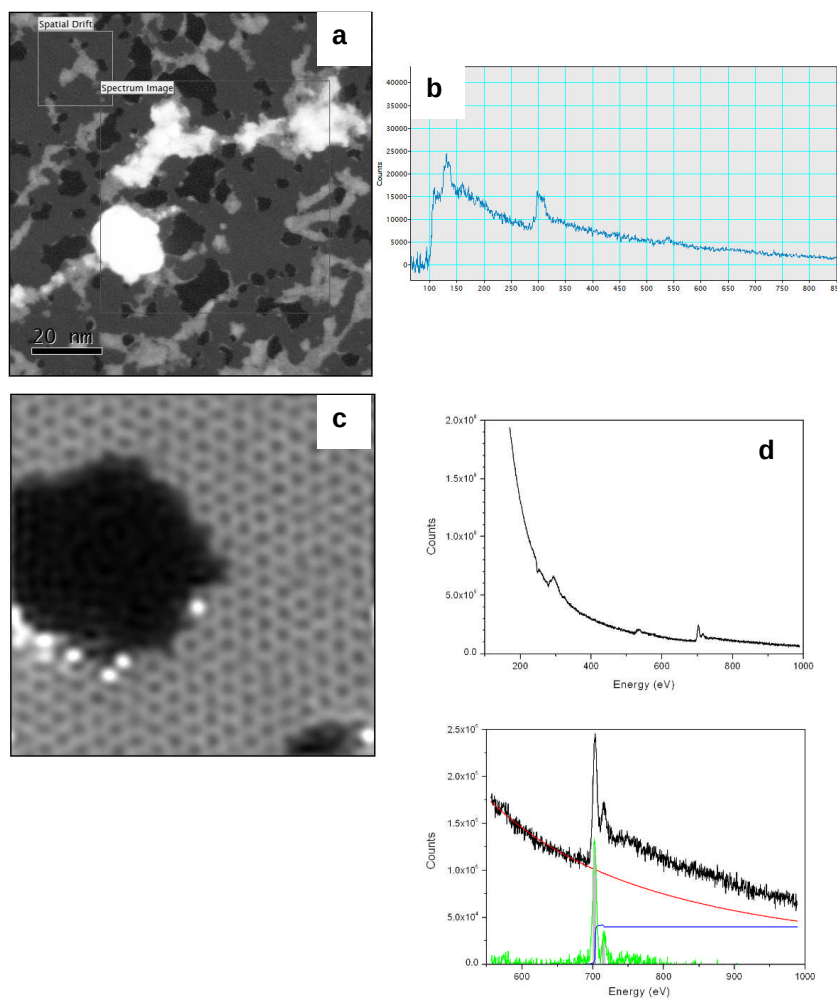


Figure 7.2. (a) ADF-STEM image graphene region analysed by EELS. (b) Electron energy loss spectrum showing L₂₃ losses characteristic of Si and K edge of C. (c) ADF-STEM image of graphene, with a hole whose periphery comprises residual contaminant (white). (d) EELS from the white contrast region of (c), showing peak signatures for the Fe L_{2,3} edge.

To categorically identify the contaminant as Fe it was necessary to combine EELS analysis of the sample with further additional experiments. The EELS data, shown in Figure 7.2, identifies the presence of Si and C as well as Fe in the sample. It is speculated that the Si originated from the quartz tube of the CVD furnace, and the Fe from the FeCl₃ etchant solution. In order to distinguish between Si and Fe doped defects a second graphene transfer method, specifically an electrochemical bubbling transfer method in NaOH solution,^{31,32} was used to prepare graphene TEM samples that were not exposed

to sources of Fe contamination. It can be inferred that dopant defects imaged by TEM in the electrochemically transferred samples were highly likely be Si (i.e., Si@MV or Si@DV), as no sources of Fe were present, and thus can provide a suitable reference for comparison to the dopant defects imaged in the FeCl₃ transferred samples.

Box averaged intensity profiles of equivalent contrast level TEM images were used to distinguish between Fe and Si dopants that were in the substitution (@MV) configuration, as shown in Figure 7.3. Multislice image simulations were employed to compare predicted variations in contrast for Si and Fe substitutions, which suggest contrast ratios of 1.83 for Fe:C and 1.47 for Si:C are to be expected. Image simulations for Na substitutions showed a low ratio of 1.25, which is sufficiently small as to be difficult to resolve in an AC-TEM image and can thus be ruled out from consideration in instances of substitutions observed for bubbling transferred samples.

Graphene transferred by the bubbling method in NaOH yielded significantly fewer instances of doped defects, however two separate instances of stable adatom substitution were found. One of the image series consisted of 15 frames and the other of 5 frames, and gave contrast ratios of 1.48 ± 0.17 and 1.5 ± 0.2 . For graphene transferred by FeCl₃ etchant solution three instances of an adatom substitution were measured; 1.68 ± 0.23 (12 frames), 2.1 ± 0.2 (6 frames) and 1.98 ± 0.22 (16 frames). The consistency of the contrast increase for the FeCl₃ transferred samples gives us confidence in identifying these defects as containing Fe.

Figure 7.3a shows an AC-TEM image of a Si dopant (Si@MV) with a high contrast ratio (1.73) from an electrochemically transferred sample. Figure 7.3b,c show AC-TEM images of Fe dopants from the FeCl₃ transferred samples with a high contrast ratio. By

calculating box averaged intensity profiles (an example box is shown in Figure 7.3b) it is possible to compare the intensity of the dopant atom with the mean intensity of the graphene C atoms (Figure 7.3d-f). Figure 7.3g-i use a CLUT to enhance the difference in contrast between the adatoms and the graphene, as well as the difference between the Si and Fe dopants, with the Fe markedly more red.

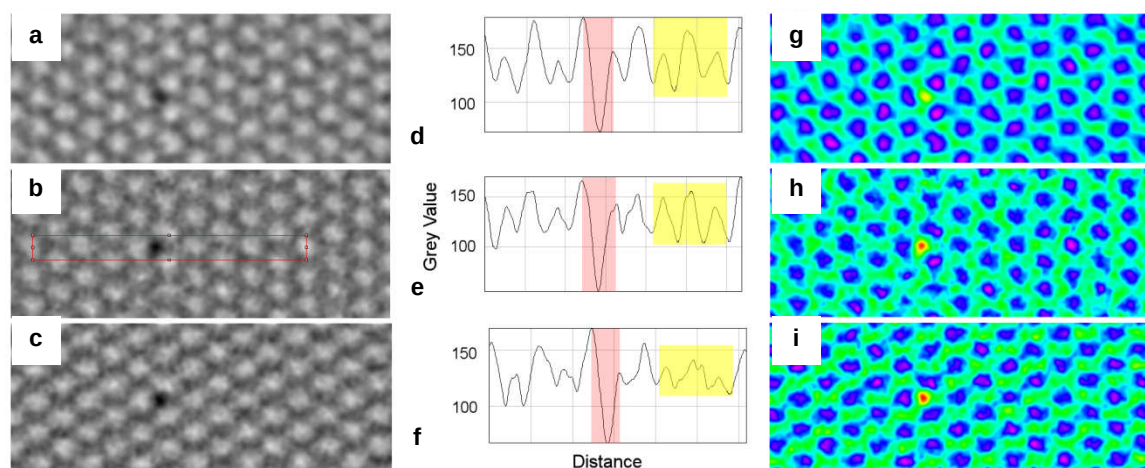


Figure 7.3. AC-TEM images of (a) Si and (b,c) Fe atoms in graphene. (d-f) The box intensity profiles (a representative box averaging region is shown in panel b), with the red highlighted regions corresponding to the impurity dopant and the yellow highlighted region corresponding to carbon atom contrast. (g-i) 'Spectrum' colour look-up table (CLUT) applied to the AC-TEM images shown in (a-c), respectively, demonstrating the higher contrast (red) for the impurity atom.

Because of the controlled defect creation procedure used, it is possible to image the graphene lattice prior to Fe atom incorporation. Theoretical modelling studies of Fe adatoms on a graphene surface predict a migration barrier of $< 1\text{eV}$, suggesting the Fe atoms are relatively mobile on the surface of graphene when irradiated,^{33,34} thus allowing for surface adatoms to stochastically occupy created vacancies. Figure 7.4a shows an AC-TEM image of a vacancy created in the lattice by focussed electron beam irradiation, and Figure 7.4b an image of the same region taken several seconds later,

showing an interstitial Fe atom bonded to 4 adjacent C atoms in the Fe@DV configuration. The position of the atoms in the DFT optimised geometries of the defect structure shown in Figure 7.4a and b are recorded and used to generate a 2D displacement map from their difference (Figure 7.4c), with interpolation used to fill between the shown data points. Figure 7.4d shows a created divacancy and several seconds later (Figure 7.4e) the divacancy has been filled with both a C and a Fe atom to form a Fe@MV structure. A displacement map is shown Figure 7.4f of the difference between the atomic positions of the DFT optimised structures. Both 2D displacement maps show appreciable strain arising from the Fe atom incorporation. The displacement maps show atom displacements in the vicinity about the Fe adatom of up to 0.5 Å. This observed vacancy quenching phenomena allows us to rule out the dark contrast spot originating from functionalisation of a carbon atom with a methyl or other functional group, as suggested in ref. [35].

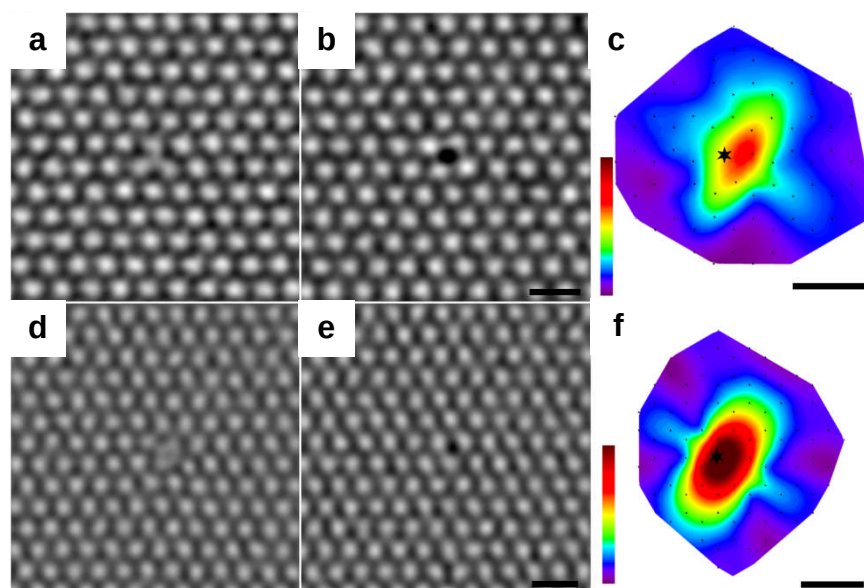


Figure 7.4. (a) Smoothed AC-TEM image of a monovacancy in graphene created by focussed electron beam irradiation. (b) Smoothed image taken a few seconds after (a) showing a Fe atom in the interstitial Fe@DV configuration. (c) Displacement map obtained from the difference of DFT optimised monovacancy and Fe@DV structures. (d) Smoothed AC-TEM image of a divacancy created by focussed electron beam irradiation. (e) Image taken 10 seconds after (d) showing a Fe atom in the substitutional Fe@MV configuration. (f) Displacement map obtained from DFT calculated DV and Fe@MV structures. The displacement map colour LUT scale is from purple; 0 Å, to red; 0.5 Å displacement. Image scale bars are 0.5 nm.

Real time monitoring of the Fe atoms reveals they were not fixed in the MV or DV positions, but swap atomic positions and configurations. Figure 7.5 shows the migration of a Fe atom between each of the four possible permutations. Figure 7.5a,b show the Fe atom moving one atomic step in the Fe@MV configuration at different graphene sub-lattice sites, and Figure 7.5c,d show corresponding atomic models. In Figure 7.5e,f a rotation of the Fe@DV position is observed between the two frames, with the Fe atom changing lattice site, as illustrated in the atomic models shown in Figure 7.5g,h. The Fe atom was also observed to change bonding configuration, switching between the Fe@DV and Fe@MV, or from Fe@MV to Fe@DV. This implies that the Fe atom changes coordination from four C atoms in a Fe@DV to three C atoms in the Fe@MV. Figure

7.5i,j show a Fe@DV to Fe@MV transition and Figure 7.5m,n show a Fe@MV to Fe@DV transition with respective atomic models in Figure 7.5k,l and o,p. Theoretical models suggest that driving this migration by thermal activation is prohibitively expensive at room temperature,⁶ therefore an additional energy contribution from electron irradiation is important. Theory would also suggest that this transition is associated with a concomitant switching of magnetic moments, since Fe@DV has a predicted paramagnetic moment, whereas Fe@MV does not.⁶

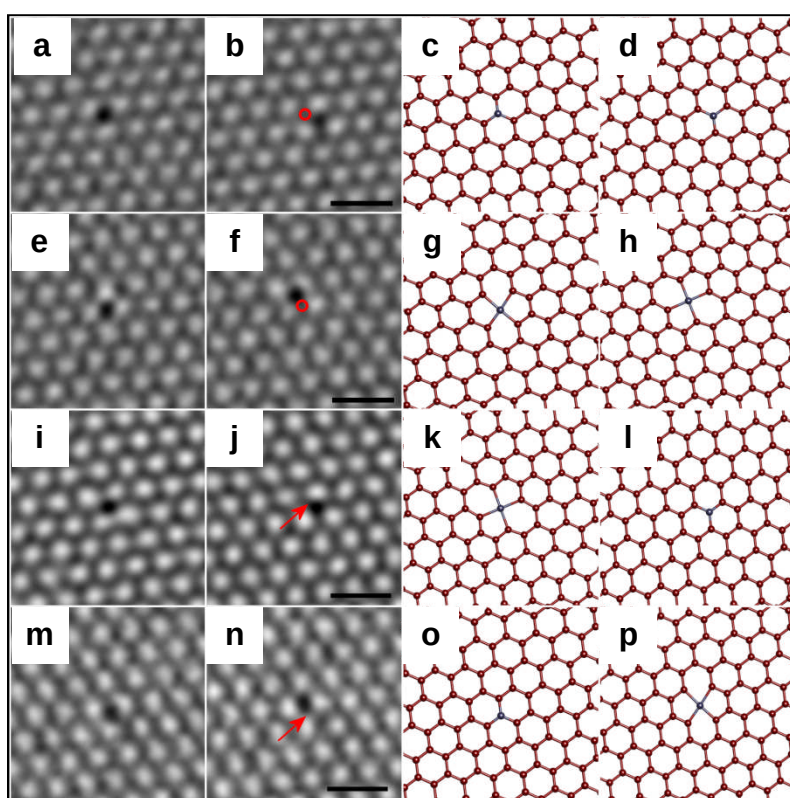


Figure 7.5. AC-TEM images showing the mobility of the Fe defect atom; shifting between adjacent MV sites (a,b), changing DV sites (e,f), switching between DV to MV sites (i,j), and moving from a MV to a DV site (m,n). Corresponding atomistic models are shown in the adjacent panels. Red annotations (circles or arrows) show the location of the defect atom in the previous frame.

The migration of metal defects chemically bonded in graphene has been discussed previously in the wider literature, before atomic resolution AC-TEM images such as

those shown here were available. In particular, the conventional HR-TEM work by Gan *et al.*¹⁴ on the migration of Au atoms incorporated into graphene prompted a number of further theoretical investigations.^{36,37} In ref. [36] molecular dynamics simulations were employed to elucidate plausible pathways for the migration of an Au interstitial atom occupying a divacancy, with the lowest energy pathways involving an out-of-plane translation of either the Au or an adjacent C. In ref. [37] the migration of the Au adatom substitution was modelled in a similar manner to that of the graphene monovacancy,³⁸ with an intermediate pentagon configuration and the Au pushed out of plane. These results, in conjunction with the imaging data presented here, suggest that migration is likely to occur as a result of radiation induced diffusion;³⁹ in which the effect of electron beam irradiation on C atoms surrounding the Fe adatom indirectly facilitates the migration of the Fe. In both references [36] and [37] the possibility of a more direct, out-of-plane event involving the metal atom is also discussed, but it should be noted that, due to mass of the Fe atom, it is less likely that the Fe would be significantly perturbed by the 80 kV electron beam. For comparison, the maximum energy transferred in an 80 kV elastic electron-atom collision with a C atom is $E_{Cmax} = 15.8$ eV, and with Fe $E_{Femax} = 3.4$ eV; thus there is markedly less energy available for any subsequent reconfiguration for the Fe atom case.

In Figure 7.6 atomistic models are presented that schematically illustrate the suggested plausible steps in a Fe-vacancy complex migration for each of the four defect permutations observed. In Figure 7.6a-c the steps for a lattice switch, or Fe@MV to Fe@MV, are shown, with an electron to carbon collision imparting energy below the threshold for knock-on displacement to the yellow highlighted C atom, adjacent to the

blue Fe substitutional. This sub-threshold collision energy ensures that rather than being ejected, the C remains bonded to the Fe atom in an out-of-plane top site. The Fe atom then follows a migration pathway similar to that of a mobile atom in a MV migration,³⁸ with the displaced carbon atom occupying the new vacated MV site after the Fe has completed the migration. The sputtering cross-section for simple outright ejection at 80 kV, at least for a pristine lattice, is unfavourable.⁴⁰ For the Fe@DV migration (Figure 7.6d-f) a C atom is displaced into a top site position, initially forming a tri-vacancy complex, which the Fe atom subsequently occupies in a similar way to Pt observed in sputtering experiments,¹⁸ before switching to a more stable DV interstitial position, with the C atom occupying the residual vacancy position. DFT optimisation found that this Fe occupied tri-vacancy (Fe@TV) structure's energy is 4.9 eV higher than the initial Fe@DV configuration, which is beneath the maximum energy of 15.8 eV that can be transferred in an 80 kV electron-carbon collision. The Fe@DV to Fe@MV switch proposed in Figure 7.6g-i can be simply explained by the incorporation of a surface C atom into the graphene lattice. However, it is possible that this switch is facilitated by either an electron collision perturbing the C from the top site or a displacement of the Fe. In Figure 7.6h a suggested intermediate C top site configuration is illustrated, which resembles a five-coordinate Fe-porphyrin structure,⁴¹ that is stable,⁴² and which exists as a transitional step. The opposite switch (Figure 7.6j-l) requires a collision event with an adjacent C atom that moves it into an out-of-plane position, opening up a DV that the Fe moves to occupy. The now surplus C atom either remains in the top site position on the Fe, or it may be displaced by a subsequent electron collision. The top site configuration of carbon on Fe@DV was modelled to have an energy 3.8 eV higher than that of the

initial Fe@MV configuration, which is again beneath the maximum energy transfer from the 80 kV electron beam.

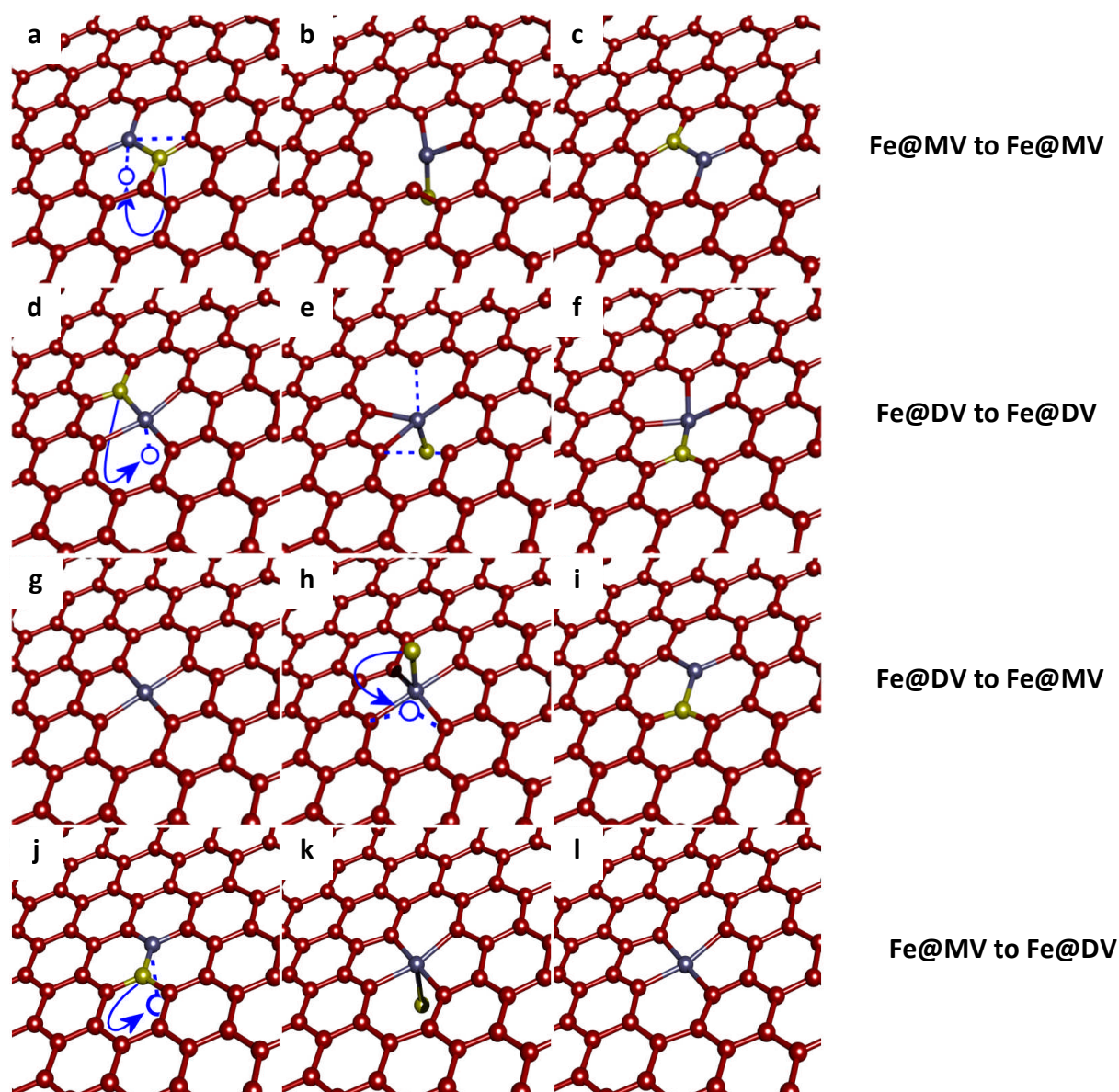


Figure 7.6. Atomistic schematics illustrating the four observed types of Fe-vacancy complex migration. Fe@MV to Fe@MV: (a-c) Electron collision leads to partial ejection of C (yellow highlight) and repositioning of Fe (grey blue) into the adjacent MV position. The displaced C then occupies the previous Fe lattice site. Fe@DV to Fe@DV: (d-f) C displacement creates a transitional tri-vacancy occupied by the Fe, with the displaced C in a top site. Fe@DV to Fe@MV: (g-i) A mobile surface C is localised on the top site of the Fe adatom. This C atom is subsequently perturbed by an electron collision, leading to the transition into a Fe@MV. Fe@MV to Fe@DV: (j-l) The displacement of the C atom allows the Fe atom to move into an interstitial position. The displaced C in the adatom top site subsequently detaches or migrates.

It was found that, as in previous reports,^{15,37} the Fe atoms exhibit a preference for bonding along the edges of the graphene sheets. The Fe atoms on the graphene edge exhibit substantially more mobility than those trapped in vacancy sites, with the atoms moving up to several nanometres between exposures, which are typically of the order of several seconds. The calculated diffusion coefficient for these edge bonded Fe atoms is $7 \pm 1 \times 10^{21} \text{ m}^2 \text{ s}^{-1}$, with a corresponding activation energy of 0.8 eV (the TEM images are presented in Appendix H). In contrast, as discussed, a Fe adatom incorporated into the graphene bulk was found to only migrate to adjacent atomic positions between exposures, implying a far smaller diffusion coefficient.

The four switching permutations observed (Figure 7.5) and modelled (Figure 7.6) do not include the possible occurrence of incomplete steps, for instance where the displaced C atom in Figure 7.6b moves back into its previously occupied position. Due to the temporal resolution limits of our AC-TEM experiments it is not possible to resolve these intermediate states in the defect transitions. The relatively long exposure time (2 – 3 seconds) can however lead to features in some frames (Figure 7.7a,b) that are consistent with a defect captured between two states, which appears as either a blurred dark contrast feature (Figure 7.7a), or as two separate features (Figure 7.7b). One can discount the possibility that these features originate from the presence of an additional Fe atom along the defect as a subsequent frame (Figure 7.7c) from the same time series as Figure 7.7a and b shows a single darker contrast atom. It is more plausible that these images are the result of oscillations between stable Fe@MV configurations that switch at a frequency that is faster than the exposure time. However, an alternative structure that is consistent with the image shown in Figure 7.7a is that the Fe atom is located in

the out-of-plane bridge position between two C atoms in standard graphene lattice positions. This would then require a mechanism that would allow for the perturbation of the Fe atom out of the plane of the graphene lattice, but remaining localised at the same defect site for a prolonged period, in order to corroborate with the TEM image series. Furthermore, density functional theory (DFT) calculations have demonstrated that when the Fe atom is located out-of-plane then its most energetically favourable position is above the centre of a hexagonal carbon ring, known as the hole site, equidistant from the nearest six C atoms, rather than at a bridge site, as would be required to fit this alternative explanation.^{43,44} Therefore it is possible to discount this alternative bridge site explanation.

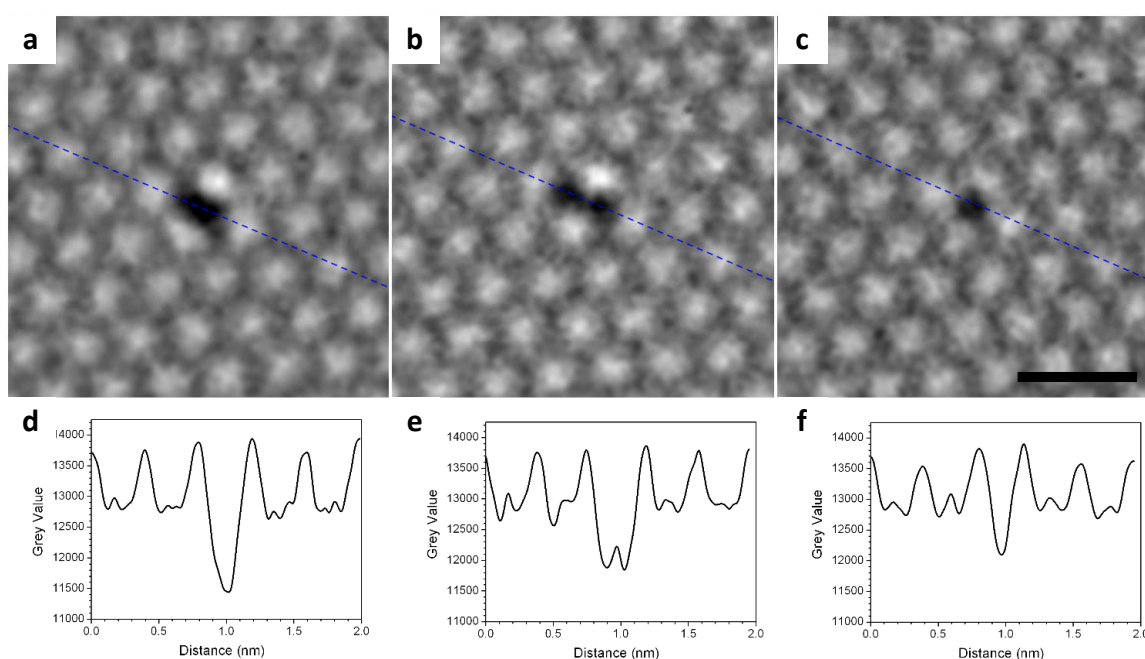


Figure 7.7. A time series of consecutive AC-TEM images of (a) a single, elongated blurred region of dark contrast, (b) a double region of dark contrast, (c) a point of dark contrast, identified as a Fe@DV. (d-f) Intensity line profiles (as grey scale values) taken across the armchair axis, with the defect at the central position (blue dashed line).

During the acquisition of two separate Fe adatom formation and evolution time series it was apparent that Stone-Wales (SW) bond rotations occurred in the bonds proximal to the Fe atom. In Figure 7.8a-c a bond at the top right (Figure 7.8a, gold highlight in Figure 7.8d) adjacent to the Fe in a standard Fe@DV undergoes a SW rotation, leading to the defect state captured in Figure 7.8b (modelled in Figure 7.8e). In addition to the bond rotation it is apparent from the TEM image that another C, marked by an arrow, has entered the graphene lattice adjacent to the Fe. This rotated bond subsequently relaxes back, however the TEM images following this show an elongated region of dark contrast, indicative of a Fe@MV oscillating between two positions, as discussed earlier and shown schematically in Figure 7.8f,g. Subsequently within the time series a Fe@MV is clearly resolved, supporting our oscillating single Fe@MV hypothesis. Figure 7.8h-j shows a similar SW rotation adjacent to a Fe interstitial, ultimately leading to a transition from a Fe@DV to an oscillating Fe@MV state. From these two examples it seems likely that the SW rotation assists in the transformation from Fe@DV to Fe@MV, by increasing the susceptibility of the incorporation of an extra C atom into the structure. This could be simply due to the SW rotation increasing the size of a ring of atoms adjacent to the Fe. The blue arrows in Figure 7.8e and I indicate the larger ring that is formed by the bond rotation, which in the case of Figure 7.8e already contains an additional C adatom (black arrow). Important to note is that subjecting pristine graphene to 80 kV electron irradiation at the imaging current densities used did not result in significant numbers of bond rotations, suggesting that the structure of the Fe-vacancy lends itself to more energetically favourable SW rotations.

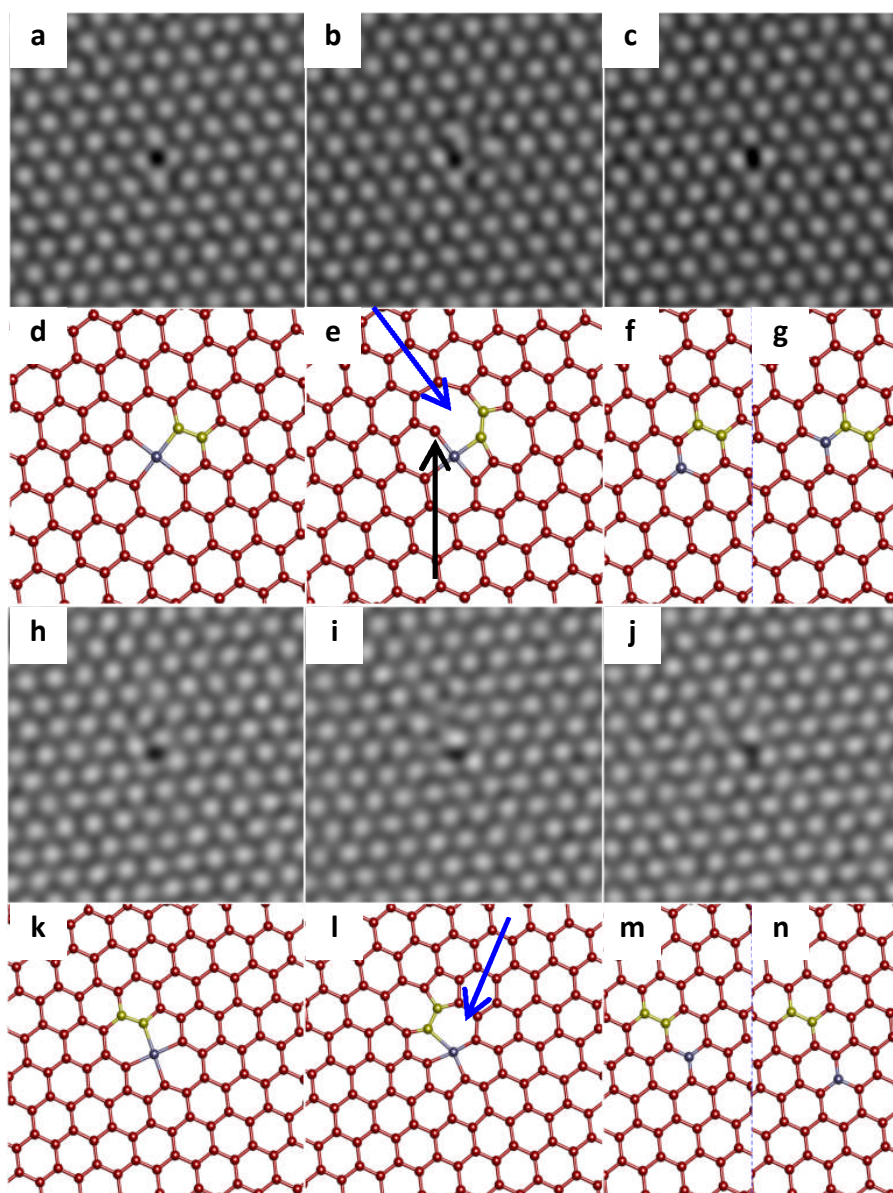


Figure 7.8. (a-c) AC-TEM image series of (a) a Fe@DV, (b) Fe@DV with a nearby bond that undergoes a SW bond rotation, (c) subsequent re-rotation back into a switching Fe@MV state. (d-g) Corresponding atomistic models of (a-c), the black arrow in (e) indicating an additional C adatom and (f,g) showing the two configurations that are recorded during (c). (h-j) A similar AC-TEM images series, with (h) showing a Fe@DV, that is subject to a proximal SW rotation in (i), and which relaxes back to a switching Fe@MV in (j). (k-n) Corresponding atomistic models of (h-j), with (m,n) illustrating the two Fe@MV configurations that switch during the image captures in (j). In the schematics red corresponds to C and blue to Fe, with the gold highlighted atoms indicating the C atoms that undergo SW rotations. Blue arrows indicate the larger C rings that form due to SW rotations which are predisposed to C adatom addition.

7.2.3 Conclusion

By manipulating a focussed electron beam at 80 kV, it is possible to locally control the formation of mono and divacancies in graphene. These have been subsequently been observed to form covalently bonded Fe@MV and Fe@DV metal-defect complexes, with a pronounced effect on the displacement of neighbouring carbon atoms of up to 0.5 Å, supported by DFT calculations. These Fe containing defect structures are stable in comparison to Fe atoms incorporated into the graphene edge. However, they are observed to undergo limited migration to adjacent lattice sites, with four distinct categories of movement observed. Models are proposed that explain the mechanism for these in terms of electron beam mediated migration. It is suggested that the ability to alter the bonding state of Fe in Fe@MV and Fe@DV configurations could be used to select magnetic and non-magnetic states in doped graphene.

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7.3 The Atomic Character of Monovacancies in Graphene

7.3.1 Introduction

Prior to the development of the graphene field, irradiation studies of the graphite surface have constituted the bulk of research into point defects in sp^2 carbon,^{46–48} due to the interest in graphite for nuclear reactors.⁴⁹ This more recently extended to include carbon nanotubes,⁵⁰ and with the advent of graphene this has developed to include several theoretical studies demonstrating the magnetic character of certain graphitic defects.^{51–54} The most fundamental of these defects, the monovacancy, can diffuse and

coalesce to form higher order vacancies,⁵⁵ and as such is a logical starting place from which to study graphene point defects.

The graphene monovacancy, formed by the ejection of a single carbon atom from the lattice, has been the subject of several theoretical studies in graphene, carbon nanotubes and graphite.^{38,53,56–61} These have demonstrated that the monovacancy can exhibit a Jahn-Teller distortion, causing the initially symmetric monovacancy (s-MV) to reconstruct into a closed 5- and 9-membered ring pair. The s-MV configuration has three under-coordinated C atoms that each bond to only two neighbours, whereas the reconstructed monovacancy (r-MV) has been calculated to lower the energy of the vacancy structure, due to a combination of the saturation of two dangling bonds by the reconstruction and the out-of-plane displacement of the third under-coordinated C radical.³⁸ Prior studies of the monovacancy have relied on scanning tunnelling microscopy (STM) studies of graphite, which lack the atomic resolution and clarity to conclusively demonstrate the structure as symmetric or reconstructed.^{38,47,48} With developments in high resolution and, more recently, aberration corrected transmission electron microscopy,^{9,11,12,62,63} it has become possible to characterise vacancy defects in graphene with an unprecedented resolution, allowing for the direct verification of theory by experiment. Since understanding the behaviour of vacancies will be important for exploiting graphene, both in how they influence the local and gross properties and the potential for them to act as dopant sites,^{52,64} a study is presented of the graphene monovacancy as observed by AC-TEM combined with density functional theory (DFT) calculations to effectively interpret the atomic structure.

7.3.2 Results and Discussion

To create monovacancies I utilised our previously reported method of controllable defect creation (see Chapter 6), which uses a high current density electron beam of the AC-TEM at 80 kV to sputter a selected area of graphene for a pre-determined exposure time.⁹ This controlled defect creation technique allowed us to image multiple instances of the monovacancy defect. By operating the AC-TEM at 80 kV it is possible to image the graphene point defects at low beam current density whilst minimising beam knock on damage. The Oxford-JEOL 2200MCO fitted with CEOS 3rd order probe and image correctors was employed to obtain atomic resolution images of graphene vacancies. Some images presented here were taken with the additional use of a monochromated electron beam, yielding significantly finer detail and permitting the resolution of individual atoms.¹³ The chemical vapour deposition (CVD) graphene used was synthesised according to ref. [24], before transfer to a holey Si₃N₄ TEM grid by using a PMMA scaffold. Schematic atomic models were made with Accelrys Discovery Studio Visualizer, and AC-TEM image simulations were conducted through the JEMS software package using the multislice method. AC-TEM images have been subjected to a nearest neighbour smoothing filter to reduce high frequency noise and are taken at dark atom contrast focus. Hybrid exchange DFT calculations with the B3LYP functional^{25–27} were conducted using the CRYSTAL code.^{28,65}

During TEM imaging, after controlled defect creation, both s-MV and r-MV defects were observed. A nearest-neighbour smoothed AC-TEM image of a s-MV is shown in Figure 7.9a, with an accompanying DFT calculated atomic model schematic in panel b. The multislice image simulation of the DFT optimised geometry in Figure 7.9c demonstrates

good agreement with the observed structure, including regions of darker contrast on the three edge C atoms. The origin of this darker contrast is likely to be an edge effect.⁶⁶ Figure 7.9d shows a smoothed AC-TEM image of a r-MV, along with a DFT atomistic model in e and an image simulation in f. Again, Figure 7.9f shows good agreement with the TEM image in Figure 7.9d, including the darker contrast on the single under-coordinated C atom radical. The r-MV TEM image shows a strong contraction along the zigzag axis of the reconstruction (yellow arrows) when compared to the s-MV exposure.

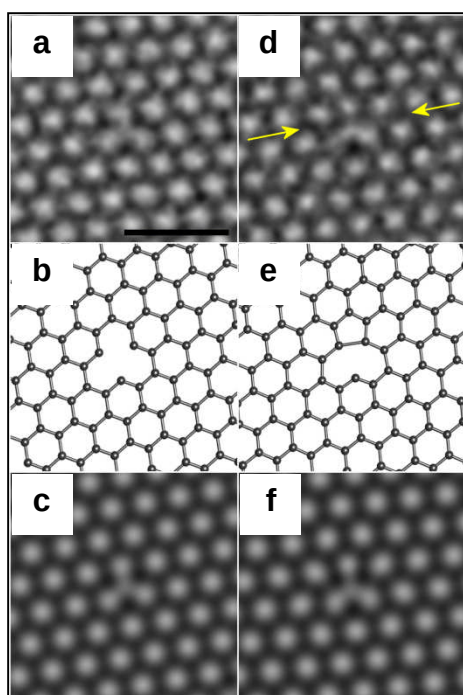


Figure 7.9. (a) Smoothed AC-TEM image of the symmetric monovacancy, s-MV, with three edge C atoms. (b) DFT calculated atomistic model and (c) multi-slice TEM image simulation of (a). (d) Smoothed AC-TEM image of the reconstructed monovacancy, r-MV, with one edge C atom. Yellow arrows indicate the zigzag axis containing the reconstruction. (e) DFT calculated atomistic model and (f) multi-slice TEM image simulation of (e). Scale bar corresponds to 1 nm.

It is possible that the images of s-MV that have been captured are in fact r-MV under oscillation between the three stable r-MV configurations at sufficiently high frequency such that over the duration of an exposure (2-3 s) an average structure reminiscent of a

s-MV is captured. This model is put forward as an explanation for STM findings in ref. [38], thus it is prudent for us to consider if this model applies to our imaged defects. To explore this, Figure 7.10a-c shows multi-slice TEM image simulations of a DFT modelled r-MV in each of the three possible 120° rotations, with the blue arrows marking the reconstructed bond. A simple weighted average of these images, implying no specific rotation preference, yielded the image shown in Figure 7.10d. This demonstrates a good qualitative resemblance to the s-MV observed in Figure 7.9a, and to the multi-slice image simulation of the DFT optimised s-MV geometry shown in Figure 7.10e. By using intensity line profiles it is possible to characterise the distance between the three edge atoms of the averaged image and the s-MV. Intensity profiles taken across the distance between pairs of under-coordinated carbon radicals in Figure 7.10d,e are shown in Figure 7.10f,g, which yield distances of 2.2-2.4 Å for the averaged image, in good agreement with the 2.4 Å found for the s-MV image. This evidence suggests that one cannot differentiate between images of a metastable s-MV or superposed r-MVs in rotation with the temporal resolution available.

Further insights can be gained by examining the time-dependent dynamics of the monovacancies under electron beam irradiation. On numerous occasions stable r-MV configurations were recorded, such as shown in Figure 7.9d, demonstrating that the reconstruction can be stable for time periods of the order of seconds; the time required for a single exposure. Indeed, time series showing r-MVs maintaining their configurations for significantly longer than for a single exposure, in excess of 90 s, indicate that the r-MV does not always undergo rapid oscillations between the three possible stable configurations (see Appendix I). The lifetime put forward in ref. [38] for

the reconstruction is 15 ps at room temperature, which is 11 orders of magnitude lower than the exposure times used for these images. The results indicate that the r-MV does not necessarily undergo rapid oscillations between the three possible configurations, and can lock in to a stable orientation.

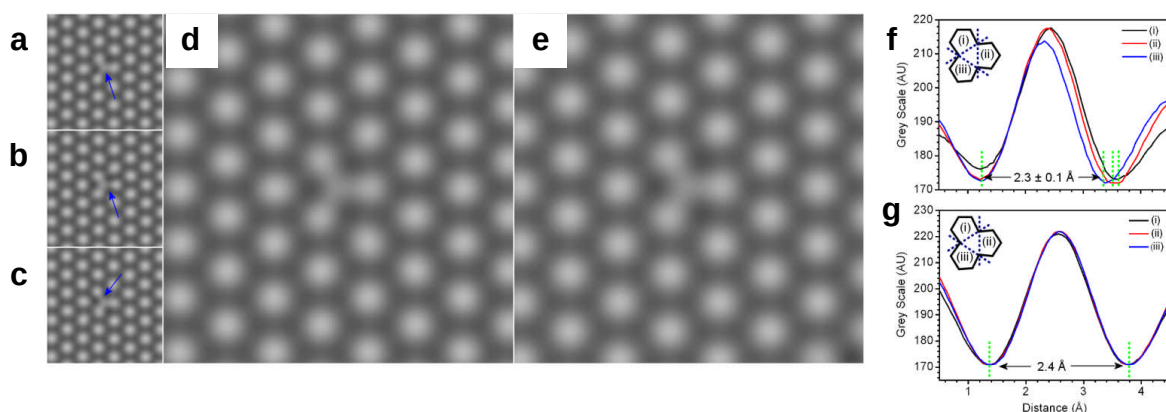


Figure 7.10. (a-c) Multislice image simulations of DFT modelled r-MV, rotated along different 120° axes (bond reconstruction denoted by the blue arrows). (d) An averaged image of (a-c). (e) Multislice image simulation of a DFT modelled s-MV. (f,g) Grey scale intensity profiles taken to measure the distance between the under-coordinated atoms of the averaged image in (d) and the DFT image in (e), respectively. Graph inserts show the profiles taken along the three zigzag axes that cross the gap between under-coordinated atom pairs, labelled (i)-(iii).

To demonstrate that it is possible to differentiate between images of the two types of MV configurations the geometric phase analysis (GPA) technique was applied to AC-TEM images of the defects. The GPA provides a strain field map of the area around the vacancy and is sensitive to variations in atomic structure.^{67,68} Figure 7.11a-f show the GPA analysis of the s-MV defect. Figure 7.11a is the smoothed AC-TEM image of the s-MV used in the analysis, with a magnified insert showing the vacancy with a colour look up table (LUT) applied to enhance visual contrast. Figure 7.11b shows the fast Fourier transform (FFT) of Figure 7.11a, where the circled reflections denote the two Bragg reflections which are used for the GPA. Figure 7.11c-f show the fields of the matrix

elements of the symmetric strain tensor, with a colour LUT scale ranging from $\pm 100\%$ for the strain fields and rotations of ± 1 radian for the rotation component. These show a negligible strain originating from the s-MV defect. Figure 7.11i-l similarly show the GPA calculated strain components for the r-MV shown in Figure 7.11g. The immediate area around the defect exhibits a pronounced strain, which is notably different from the s-MV case. This result is supported from *ab initio* calculations, where the reconstructed bond is known to create a strain in the surrounding graphene lattice.³⁸

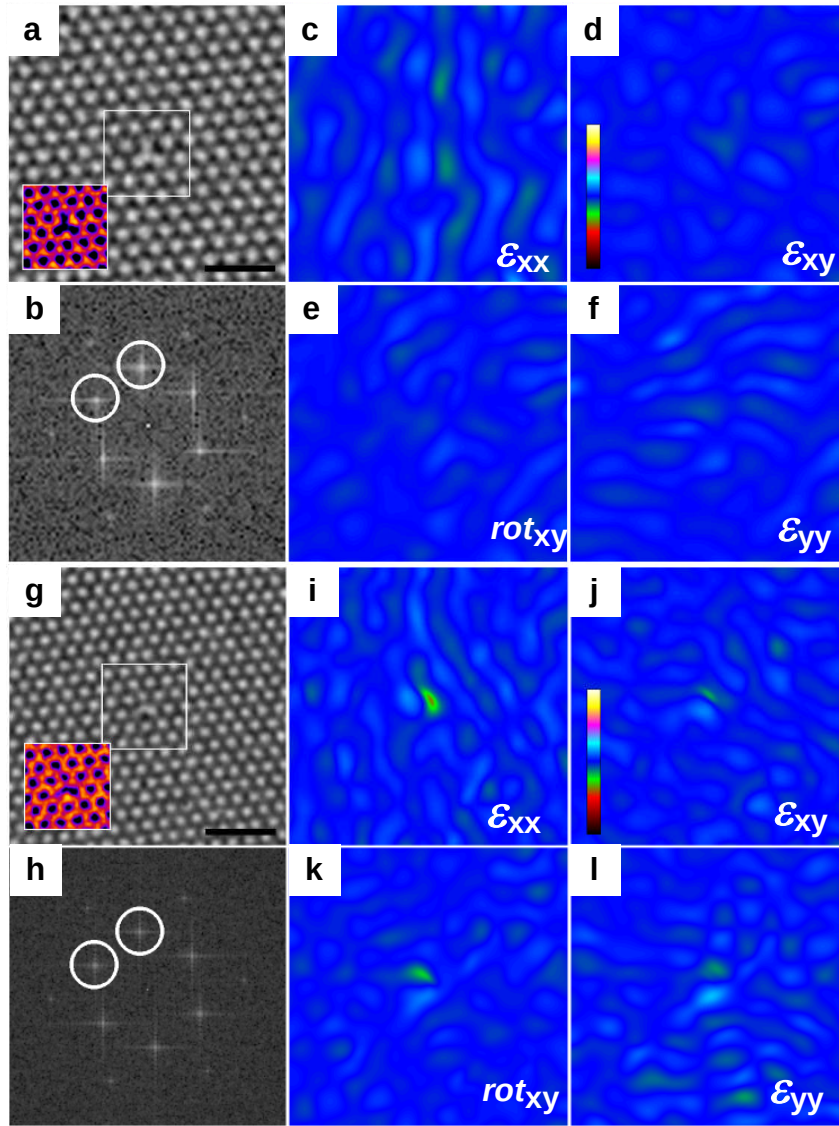


Figure 7.11. Geometric phase analysis (GPA) of the two monovacancy bonding configurations. (a) Smoothed AC-TEM image of the s-MV used for calculating the GPA maps, with the insert showing a smoothed colour LUT of the vacancy. (b) FFT of the TEM image, with the two {100} reflections used to calculate phase maps circled. (c-f) Calculated fields of the symmetric strain matrix around the s-MV, with the elements (ϵ_{xx} , ϵ_{xy} , rot_{xy} , and ϵ_{yy}) labeled. (g) Smoothed AC-TEM image of the r-MV used for calculating the GPA maps, with the insert showing a smoothed colour LUT of the vacancy. (h) FFT of the TEM image, with the two {100} reflections used to calculate phase maps circled. (i-l) The calculated strain matrix elements around the s-MV. Scale bars denote 1 nm. CLUT palette covers the range $\pm 100\%$ (± 1 radians for rot_{xy}), with blue corresponding to zero.

Figure 7.12a shows a smoothed AC-TEM image of an r-MV, with the insert showing a magnified view. The improved resolution in this image compared to the other AC-TEM

images shown here, which enables the visualization of individual carbon atoms, is due to the use of a monochromated electron beam. In Figure 7.12b grey scale intensity profiles are shown, labelled (i-iii), taken between the three edge atoms of the MV, with (i) corresponding to the reconstructed bond. These show that the reconstruction has a length of 1.9 Å, in good agreement with the calculations, which show 1.90 Å. The distances between the edge atoms that are not bonded were measured to be 2.8 ± 0.1 Å. In Figure 7.12c a smoothed, non-monochromated AC-TEM image of a s-MV is shown, accompanied by a magnified view in the insert. The intensity line profiles of the distances between the edge C atoms are shown in Figure 7.12d, with distances of between 2.3 Å to 2.6 Å, with our theoretical predictions indicating a distance of 2.44 Å, which is a minor deviation from the pristine lattice case of 2.46 Å. In figure 4e an average of three consecutive AC-TEM images of a r-MV is shown, which was executed to improve atomic contrast and was possible due to minimal variation in the beam astigmatism between exposures. This image shows the three atoms opposite the bond reconstruction, which includes the under-coordinated carbon, with sufficient clarity to use intensity line profiles to extract the bond lengths of the carbon radical. These line profiles, taken across the appropriate armchair axes to include both the under-coordinated C bond and C-C bonds from the bulk lattice, are shown in figure 4f. From these we find a bond compression to 1.37 Å and 1.21 Å for the bonds lying along armchair axes labelled (i) and (ii), respectively. These deviate from the bulk C-C bond lengths, found from the same plots, of 1.52 ± 0.02 Å and 1.58 ± 0.02 Å, yielding a respective bond compression of 77% and 90% for the two cases. However, it is important to note that the nature of AC-TEM imaging physically precludes the measurement of any bond length contribution in the z-axis; thus any out-of-plane

displacement of the under-coordinated C would lead to an illusory bond compression in the TEM image, due to it corresponding to the projection of the bond into the 2D x-y plane.

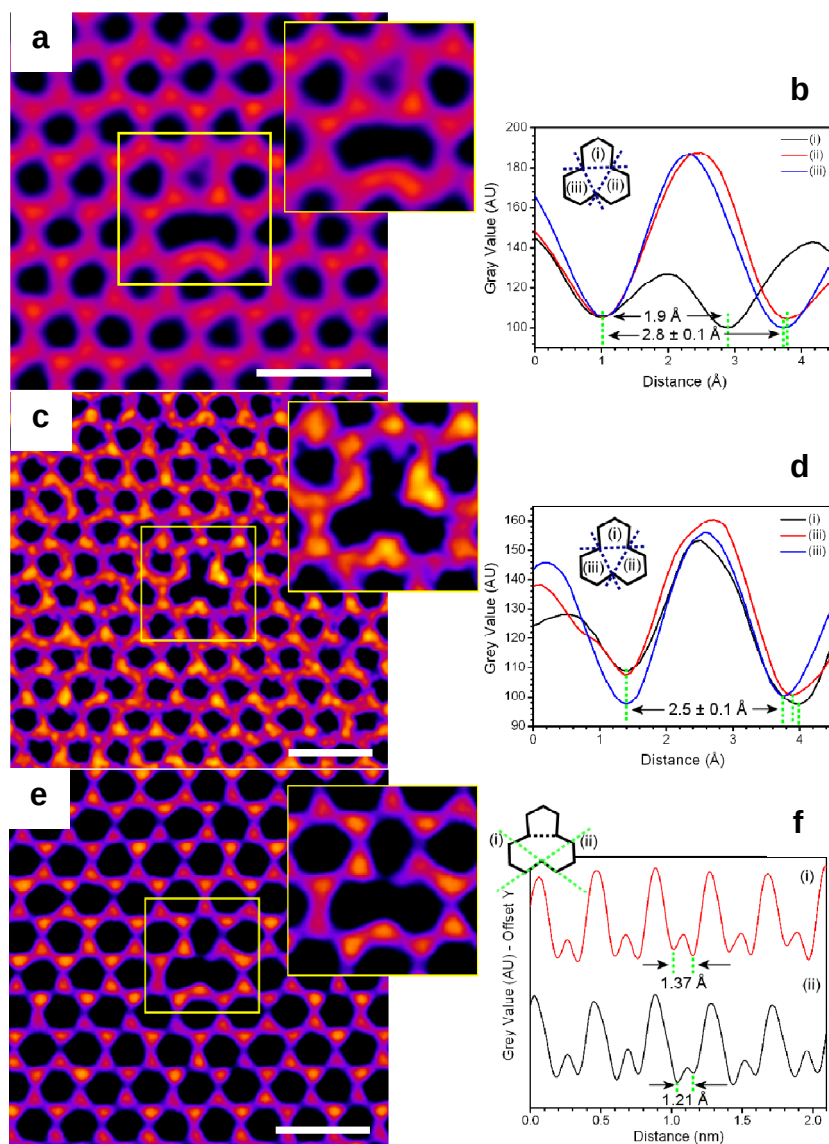


Figure 7.12. (a) Smoothed AC-TEM image of a r-MV, with the highlighted region around the defect magnified in the insert. (b) Intensity line profiles taken between the edge atoms of the MV, as illustrated in the insert, labelled (i)-(iii). (c) Smoothed AC-TEM image of a s-MV, and a magnified view of the defect. (d) Intensity line profiles taken for the inter-atomic distances between the three edge atoms. (e) Average of three consecutive r-MV AC-TEM images, and a magnified view of the r-MV inset. (f) Line profiles taken along two of the armchair axes, (i) and (ii), as shown in the insert schematic. These axes each cross one of the compressed C-C bonds with the under-coordinated C atom of the r-MV. Scale bar denotes 0.5 nm.

From theoretical studies, the migration of monovacancies in graphitic materials is thought to occur by a switching mechanism.^{55,56,60} In this mechanism, one of the vacancy edge atoms switches to the opposite side of the vacancy, shifting the vacancy to an adjacent lattice position. This is observed in the experimental images (Figure 7.13a-c). In Figure 7.13a a smoothed AC-TEM image of a r-MV is shown, with an accompanying atomistic model shown in Figure 7.13d. The blue arrow in the schematic illustrates the motion of the unsaturated C atom, which breaks the reconstructed bond on the opposite side of the MV, leading to the configuration observed in Figure 7.13c and modelled in Figure 7.13g. In between these two frames an intermediate frame was captured, shown in Figure 7.13b. It is hypothesised that this image is a result of the exposure capturing the transition in progress, leading to a superposition of the configurations shown in Figure 7.13e and f. However, in addition to this expected migration, a vacancy migrating by one zigzag lattice plane is observed. Figure 7.13h,i show smoothed AC-TEM images, captured with a monochromated beam, of a r-MV undergoing such a lattice transition. The dashed white circles and arrow indicates the migration path of the vacancy hole, with equivalent dashed blue annotations on the atomistic model in Figure 7.13j. The atom highlighted in dark blue in the atomistic models of Figure 7.13j,k appears to remain fixed, whilst the vacancy structure rotates about it. In order to be certain that the vacancy has in fact shifted lattice positions, rather than the bond reconstruction merely reforming between one of the two remaining pairs of under-coordinated C radicals in the same vacancy, it was crucial to align the two images with respect to other common features. In Figure 7.13l,m the wide field view of the area around the defects are shown, with Figure 7.13l and m corresponding to blown up views of Figure 7.13h and i, respectively. The r-MV is

highlighted by the yellow dashed circle, and the images are aligned with respect to one another by using the larger defect cluster, highlighted by the blue dashed circle, and by referring to the amorphous carbon residue along the lower part of the image. Using these features to align the images, in order to compensate for sample drift, it is clear that the transition observed corresponds to a lattice transition, rather than just a rotation of the reconstruction about the vacancy. This migration type was observed to occur 13 times in the data set, significantly more frequently than for the simple switching mechanism in figure 5a-c. All of these lattice shifts were imaged to occur immediately in the subsequent exposure, with no intermediate superposition state recorded.

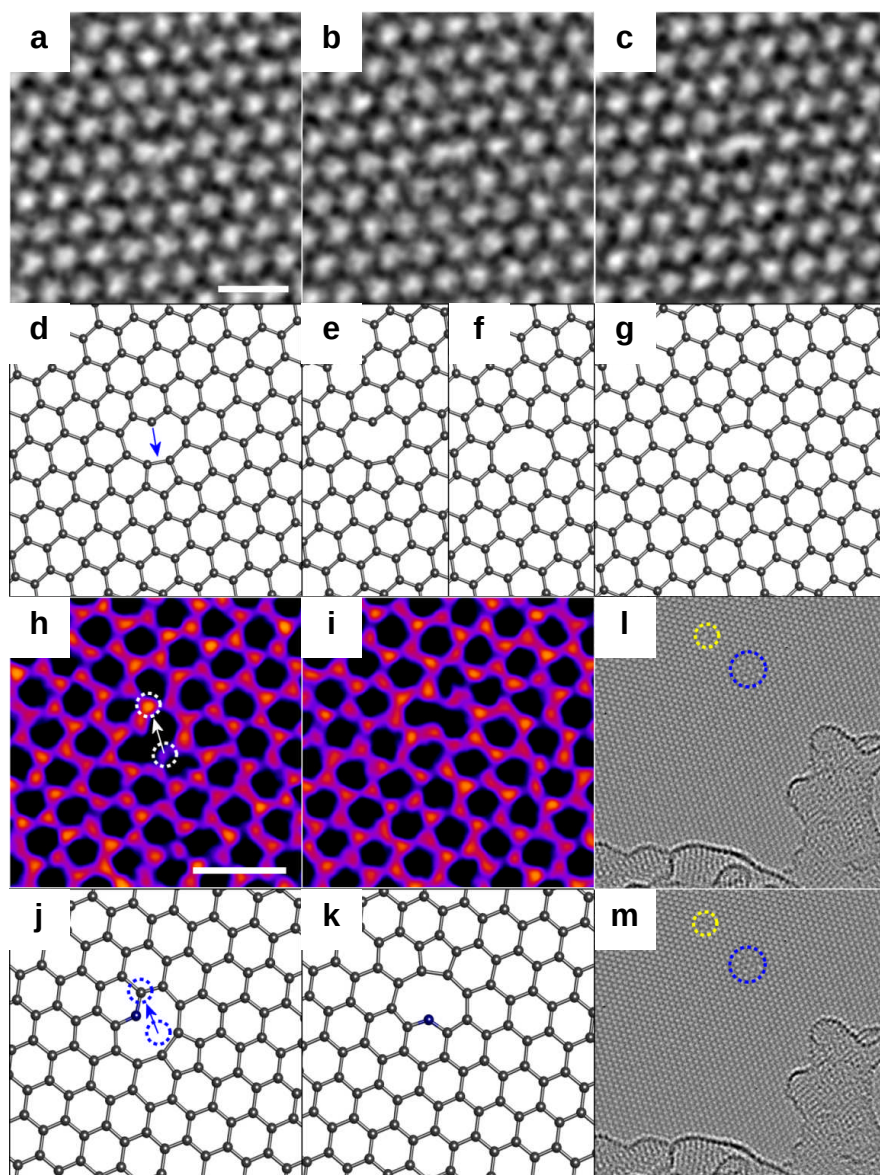


Figure 7.13. (a) Smoothed AC-TEM image of a r-MV, which switches lattice positions *via* an intermediate position, shown in (b), ending in a new r-MV (c). (d-g) Atomistic models of the images shown in (a-c), respectively, with (e) and (f) showing models representing the superposition necessary for the image in (b). (h,i) Color LUT of smoothed AC-TEM images of a r-MV undergoing a lattice shift. The dashed white circles show the migration of the vacancy. (j,k) Atomistic models of the AC-TEM images shown in (h,i), respectively. The dark blue highlighted atom is fixed during the transition, and the dashed blue circles indicate the migration of the vacancy. (l,m) Large field AC-TEM images, corresponding to (h,i) respectively, with the r-MV defect highlighted by the yellow circle. The blue circle highlights a more complex defect used as an alignment marker to compensate for drift between the two images. Scale bars are 0.5 nm.

The failure to observe the r-MV swapping the reconstructed bond around the vacancy site, as proposed to explain the observation of s-MV in STM images by ref. [38], and discussed earlier, is somewhat surprising, as the same reference also suggests a low energy barrier for the bond alternation of 0.13 eV. For such an energy barrier one would expect bonding switches to occur readily under the electron beam. It is possible that the lack of observed reconstruction swapping is due to the under-coordinated C atom (highlighted in dark blue in Figure 7.13j,k) being functionalized by a low mass contaminant, such as hydrogen, precluding the formation of a third sp^2 bond and preventing any oscillation of the reconstruction. In this model the under-coordinated C atom in the r-MV is effectively saturated, offering an explanation as to why the reconstructed bond is not observed to alternate between the three edge C atoms of the MV. This hypothesis can be extended by including the results shown in Figure 7.10, which demonstrated that it was not possible to differentiate by AC TEM between an oscillating r-MV and a s-MV: It is therefore possible that the imaged s-MVs are oscillating r-MVs, and the imaged r-MVs have been stabilised from oscillation by the functionalisation of the under-coordinated C radical. If this is indeed the case it may be possible to observe a deviation in the length of the nearby C-C bonds, which presents a promising avenue for further research, however the AC-TEM here cannot be used to categorically confirm bond compression due to the imaging of the projection of an out-of-plane displacement on to a 2D plane leading to a perspective induced shortening. Evidence to support the functionalisation hypothesis may be obtained in the future by employing techniques such as atomic resolution electron energy loss spectroscopy (EELS).

7.3.3 Conclusion

Here the monovacancy in graphene has been characterised extensively by AC-TEM imaging, and finding two distinct configurations for the monovacancy; the symmetric (s-MV) and the reconstructed monovacancy (r-MV). Geometric phase analysis and bond length measurement have demonstrated that these are two distinct types of defect, with the reconstructed configuration leading to pronounced strain and displacement in the lattice immediately around it. Also explored are the mechanisms by which the observed s-MV could be a superposition of an oscillating r-MV, and find that it is not possible to distinguish between them. However, the observation of stable r-MV over extended exposures either suggests the stable existence of two defect types, the s-MV and the r-MV, or that functionalisation of an under-coordinated C radical may act to lock the oscillating r-MV into a stable configuration that can be subsequently imaged. These studies shed light on our understanding of defect structures and their behaviour in the graphene lattice, which is fundamental to the development of doping and nano-engineering techniques.

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7.4 Reference

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Chapter 8

Final Discussion, Conclusions and Future Outlook

8.1 Thesis Summary

This doctorate thesis has been divided into three broad sections: The methods and procedures for synthesis of large area few-layer graphene by copper catalysed chemical vapour deposition; studying the behaviour of nanoscale features in few-layer graphene films by AC-TEM, namely folds and grain boundary intersections; and finally creating and analysing atomic level defects in monolayer graphene by AC-TEM.

8.2 Discussion and Conclusions

Graphene holds much promise in a variety of applications; however a major limitation in its implementation has been the prevalence and inhibiting effects of defects. Chemical vapour deposition of graphene presents an avenue for the scalable deployment of graphene, but these defect structures are significantly more numerous than the mechanically exfoliated benchmarks. Realising the growth of large area CVD graphene, that exhibits a quality that approaches that of mechanically exfoliated graphene, is a major goal in the implementation of graphene in commercial devices.

The atomic resolving power of AC-TEM offers the opportunity to rigorously analyse the behaviour and structure of these defects. Boundaries between adjacent few-layer graphene grains offer potential sites of scattering; however the way these grains intersect has important ramifications in their electrical performance. It is now understood that these grain boundaries do not act as strong scattering sites, provided that the atomic stitching is complete. The observed overlap configurations that are discussed in this thesis may also act to mitigate the scattering caused by incompletely stitched graphene layers. Ultimately improvements to the CVD synthesis parameters will be required in order to tune the graphene grain stitching and overlap to minimise deleterious effects to carrier mobility. Furthermore, improvements to the transfer of grown graphene from the catalyst to the target substrate will need to minimise the formation of out-of plane folds and creases, as it was found that these produce a marked strain in the graphene. In the few-layer case studied here, the strain is found to be sufficient to distort the graphene from its bulk AB-Bernal stacking configuration in the area around the crease.

In order to develop a fine understanding of atomic level defects an improved defect creation technique was required over that used previously. These methods required subjecting the graphene to a highly energetic beam of electrons or ions in order to invoke sputtering events in the crystal structure. The disadvantages of this are twofold; firstly the defects are created in a scatter-gun fashion throughout the sample, with no appreciable spatial control; and the creation process requires either a separate instrument from the TEM, in the case of ion sputtering, or a lengthy re-calibration step of the TEM in the case of employing energetic electrons above the sputtering threshold

of carbon. Our method resolves these problems by varying the current density, rather than the electron accelerating potential, which also permits controlling the defect creating zone to within the probe area. This technique provides an opportunity to rigorously analyse the full spectrum of defects that pervade graphene, such as dopants and vacancies.

It was found that selectively creating vacancies in a graphene sheet in the AC-TEM could lead to the formation of single atom doped sites, due to vacancy quenching by surface adatoms. The study here demonstrates that iron contamination, likely from the copper etchant solution, can occupy these vacancies in two different stable configurations. The switching of the iron dopants between the two different configurations in all four permutations, i.e., Fe@MV to Fe@MV, Fe@MV to Fe@DV, Fe@DV to Fe@MV and Fe@DV to Fe@DV, is observed. Further work on the behaviour of isolated monovacancies demonstrated that there are two apparent configurations, where previous work had assumed that vacancy would always undergo a reconstruction to minimise its energy. It is hypothesised that the MV always possesses a reconstruction between two of the under-coordinated carbons, and that when an s-MV is imaged it is in fact a superposition of the three possible rotations of a r-MV. Imaged instances of stable r-MV may in fact be stabilised due to the functionalisation of the remaining under-coordinated carbon.

8.3 Future Outlook

Employing the controlled defect creation technique in further experiments that seek to understand the influence of atomic defects on the graphene's properties is the logical evolution of this work. By utilising *in-situ* electrical measurements it would be possible

to directly quantify the effect of nano-engineered defects on the graphene's properties. Such experiments could provide a valuable insight into the relative importance of certain defect structures on graphene's overall resistivity, as well as the effect of particular edge configurations on the band structure. The experiment can also be "flipped", in that one could study the evolution of defects under high current flow. This would be of particular interest for employing graphene as a copper replacement/supplement in interconnect technology, as any equivalent of the electromigration phenomenon in copper would need to be mitigated.

Appendix A

HR-TEM Background

In a TEM the electrons are accelerated from an electron source, a field emission gun (FEG) for modern instruments, through a potential V_0 . Employing the de Broglie relation ($\lambda = h/p$) one can relate this accelerating potential to the electron's wavelength, λ , for an electron of charge e , mass m and momentum p .

$$eV_0 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$
$$\therefore \lambda = \frac{h}{\sqrt{2meV_0}} \quad \text{Equation A.1}$$

Equation A.1 is the non-relativistic form, which gives a 5% error at 100 kV. Higher accelerating potentials must account for relativistic effects.¹

The specimen also exerts a small, positive potential ϕ_0 on the transmitted electron beam, yielding an effective refractive index n : the ratio of the vacuum wavelength λ to the interacting beam of wavelength λ' .

$$n = \frac{\lambda}{\lambda'} \approx 1 + \frac{\phi_0}{2V_0} \quad \text{Equation A.2}$$

This specimen potential, from a sample t thick, generates a phase shift θ of the perturbed beam with respect to the direct beam.

$$\theta = \frac{2\pi(n-1)t}{\lambda} = \frac{\pi\phi_0 t}{\lambda V_0} = \sigma\phi_0 t \quad \text{Equation A.3}$$

σ is an elastic interaction constant. For sufficiently thin specimens the term $\phi_0 t$ can be written as a projected potential ϕ_t in the direction parallel to the beam axis. Such a specimen also renders any beam attenuation effects negligible, thus no adsorption term is necessary.

The phase shift can be used to model an exit wave function for the thin specimen.

$$\psi_e(x, y) = \exp(-i\sigma\phi_t(x, y)) \quad \text{Equation A.4}$$

Equation A.4 can be simplified further by assuming a particularly weak specimen potential, which is known as the weak phase object approximation. This typically only holds for the very thinnest and lightest of specimen materials, and even then only at certain accelerating voltages. The limit $\phi_t \ll 1$ can then be applied, allowing a Taylor expansion of Equation A.4, which yields Equation A.5 to the first order.²

$$\psi_e(x, y) = 1 - i\sigma\phi_t(x, y) \quad \text{Equation A.5}$$

The microscope transforms the exit wave from the specimen into an image imperfectly, so to model the image we need to convolve ψ_e with a point spread function h . The point spread function characterises the degree to which a point of information from the object is spread into a disk in the image, and can be written as Euler's formula; $h(x, y) = \cos(x, y) + i \sin(x, y)$. Convoluting with the exit wave yields:

$$\begin{aligned} \psi(x, y) &= \psi_e(x, y) \otimes h(x, y) \\ \psi(x, y) &= 1 + \sigma\phi_t(x, y) \otimes \sin(x, y) - i\sigma\phi_t(x, y) \otimes \cos(x, y) \end{aligned} \quad \text{Equation A.6}$$

Converting this to intensity is achieved by multiplying $\psi(x, y)$ by its complex conjugate.

$$I = \psi\psi^*$$

$$I \cong 1 + 2\sigma\phi_t(x, y) \otimes \sin(x, y) \quad \text{Equation A.7}$$

We can define a contrast transfer function H , which is the point spread function h in reciprocal space. It is governed by an aperture function (A), an envelope function to characterise the wave attenuation (E), and the lens aberrations (B). The lens aberration function expresses all the contributory aberrations of the microscope, however for a well aligned instrument this can be well approximated to just the objective lens spherical aberration, C_s , and the focus, Δf .

$$H(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})B(\mathbf{u})$$

$$B(\mathbf{u}) = \exp(i\chi(\mathbf{u})) = \cos(i\chi(\mathbf{u})) + i \sin(i\chi(\mathbf{u}))$$

$$\chi(\mathbf{u}) = \pi\Delta f\lambda u^2 + \frac{\pi}{2}C_s\lambda^3 u^4 \quad \text{Equation A.8}$$

From Equation A.7 for the intensity calculation, it is apparent only the imaginary $i \sin(i\chi(\mathbf{u}))$ part of the lens aberration ends up contributing to the final intensity, as the cosine term cancels out. Using this, it is possible to write the contrast transfer function, for the case of coherent illumination of a weak phase object, as:

$$H(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})2\sin(\chi(\mathbf{u})) \quad \text{Equation A.9}$$

The $\chi(\mathbf{u})$ term is the component of interest, as it represents the phase difference between transmitted beams. There is a maximum in the image contrast when $\chi(\mathbf{u}) = \pm\pi/2$ n for n as any odd integer, and is a minimum when $\chi(\mathbf{u}) = \pm m\pi$, for any integer m . From Equation A.8, it can be seen that $\chi(\mathbf{u})$ depends on the objective defocus, the accelerating potential and the spherical aberrations of the objective. We

shall look at the importance of both the objective defocus (Figure A.1) and spherical aberration on the contrast transfer function (in the main text, Figure 2.15).

To minimise the variation in atom contrast in an image the transfer function needs to be consistent across a large frequency range. Plotting $H(\mathbf{u}) = 2 \sin(\chi(\mathbf{u}))$ for different focus values, as in Figure A.1, shows that for initial increases in defocus the point of first crossover, u_1 , also increases. Increasing the defocus further generates a second maximum in between 0 and u_1 , which can be seen clearly in the $\Delta f = -90$ nm case, with further defocus effectively drastically reducing u_1 as the second peak becomes positive, flipping the contrast. This is shown in the curve for $\Delta f = -100$ nm.

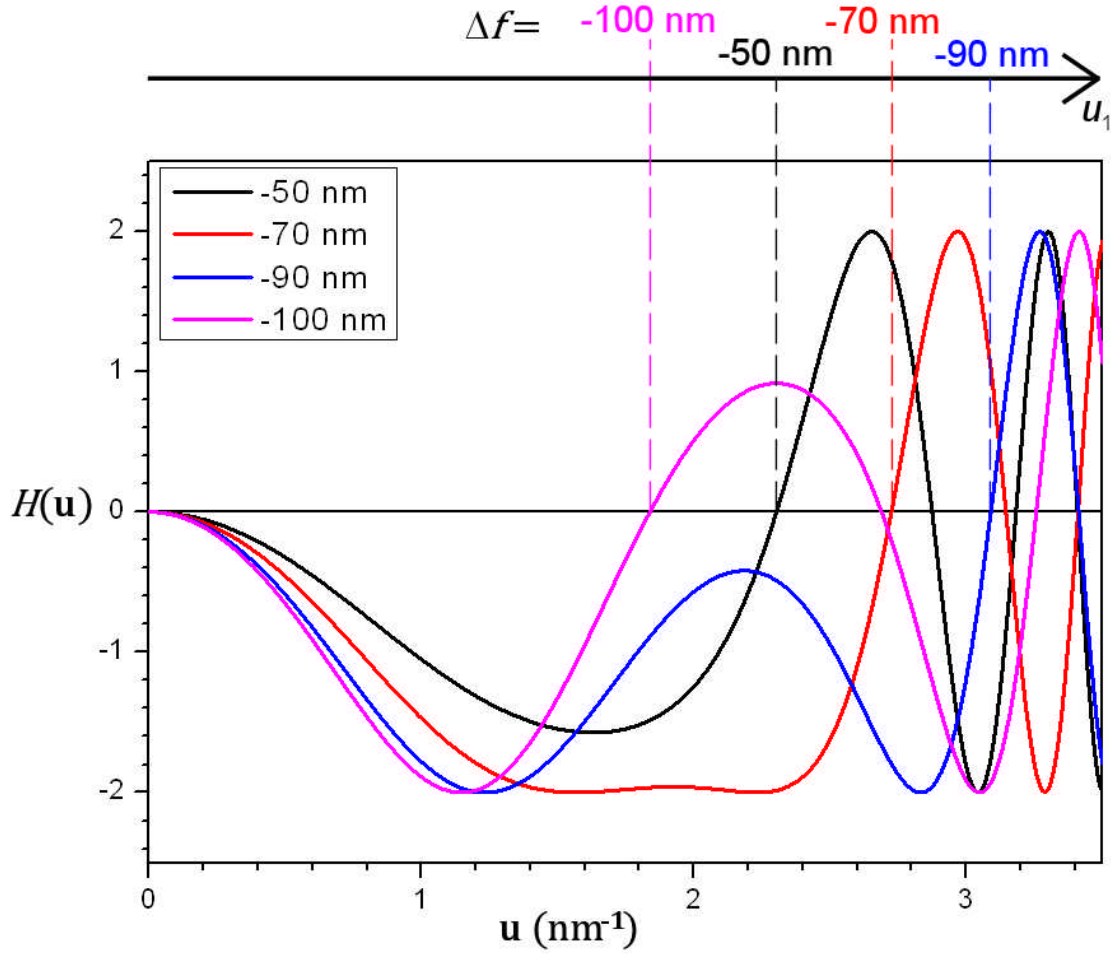


Figure A.1. The effect of defocus on the contrast transfer function, for a microscope at 80 kV and $C_s = 1$ mm. Increasing the defocus initially leads to a concomitant broadening of the region of constant contrast, i.e., an increase in the point of first crossover u_1 . However, with further increases to the defocus the contrast flip happens at lower frequencies, as shown with the defocus of -100 nm case here.

From this it is apparent that there is an optimum compromise, where the defocus is sufficiently large to maximise u_1 , yet small enough to prevent the second maximum from having a significant effect on the phase. This best compromise, taking into account the spherical aberration as well, is known as the Scherzer defocus, Δf_{Sch} .

$$\Delta f_{\text{Sch}} = -(C_s \lambda)^{1/2} \quad \text{Equation A.10}$$

Therefore the Scherzer defocus for the microscope conditions used in the shown plots would be at about -80 nm.

The point of first crossover, u_1 , is known as the point resolution limit of the microscope. This is less than the hard information limit to the microscope, however to extract more useable information beyond this requires more sophisticated techniques. The information limit is determined by the envelope function, E , which imposes a decay in the amplitude of the contrast transfer function. The amplitude of the contrast function eventually reaches zero; this is the information limit, and is determined by the spatial coherence, reduced by using a FEG source, and the chromatic aberration of the source, which can be improved by employing a monochromator.

Appendix B

Aberration Correction in the TEM

There are two major sources of aberrations in the TEM; spherical and chromatic. Spherical aberration is where rays from an incident beam at larger radial distances from the optic axis (or larger angles of incidence) are focussed more strongly. Chromatic aberration occurs due to the wavelength dependence of the electron optics, where electrons of different energies are dispersed by the lens, rather than focussed to a single point.

The point resolution limit of a TEM at the Scherzer defocus is dependent only on the wavelength and the spherical aberration ($[C_s \lambda^3]^{\frac{1}{4}}$). With the switch in modern TEMs to more coherent FEG electron sources there was a large disparity between the now greatly increased information limit and the resolution limit, emphasising the necessity for some means to correct for spherical aberration. It had been suggested, by Scherzer in 1947,³ that integrating a multipole lens that generated a negative value for C_s would be able to compensate for the positive aberration caused by the objective, thus resulting in a corrected image. The technology took some time longer to develop, however now such correctors are available. For instance, in the OJ 2200MCO microscope mostly used in this thesis, two hexapole lenses and two transfer lenses doublets are employed to handle the correction. The hexapole lens effects the beam in two ways; first it deviates

the beam proportionally to the radial distance from the optic axis (approximately an r^2 dependence), which is a negative C_s , and the symmetry of the lens also leads to a threefold astigmatism, warping the beam from a circular cross section to a three-fold symmetry. The first is desirable; it is the entire point of the lens, but the second is not. To compensate for the threefold astigmatism a second multipole lens is positioned after the first, with a transfer lens doublet in between to flip the beam, allowing for the astigmatisms to be mutually cancelled by one another but adding the negative C_s values.^{4,5}

Configuration of the C_s corrector is accomplished by first recording a Zemlin tableau of diffractograms, that is a series of diffractograms at a range of beam tilts, of amorphous material (see Figure B.1). The amorphous material yield Thon rings for their diffraction pattern, which corresponds to the oscillations of the contrast transfer function. When the microscope is near to focus, a series of concentric elliptical rings is recorded. The level of eccentricity of these corresponds to the focus and the two-fold astigmatism of the beam. Larger deviations in the defocus or astigmatism will result in further, non-elliptical patterns. Since these patterns, and their corresponding defocus and astigmatism conditions, are known, it is possible to use them to solve for the spherical aberration by imaging diffractograms at a range of beam tilt angles. Thus a Zemlin tableau of diffractograms at a range of beam tilts taken whilst at underfocus can be used to obtain an estimation of the C_s , which can then be compensated for by the correctors.

A common issue that typically arises when setting the correctors is the difficulty in obtaining an accurate Zemlin tableau. Ideally the amorphous material, typically carbon, should be sufficiently thin, uniform, flat and large to ensure that there is both a constant

defocus across it and that the limited extent of its area does not cause any artefacts in the reciprocal space image. For instance, in the experiments conducted in this thesis on graphene it was necessary to obtain tableaux from amorphous carbon residue located on the graphene. This proved problematic for two reasons: First, an excess of amorphous carbon will obviously preclude the obtaining of high quality atomic images of graphene. As a result extensive cleaning is used to remove the majority of it, which in turn makes it difficult to find sufficiently contaminated regions in which to obtain a reliable tableau. Secondly, the action of the electron beam on amorphous carbon on graphene is to cause it to coalesce into denser strands, rather than remain a uniform and spread out film. Regularly checking the current status of the amorphous film that is being used to calibrate the correctors is therefore crucial, to ensure that the film has not coalesced.

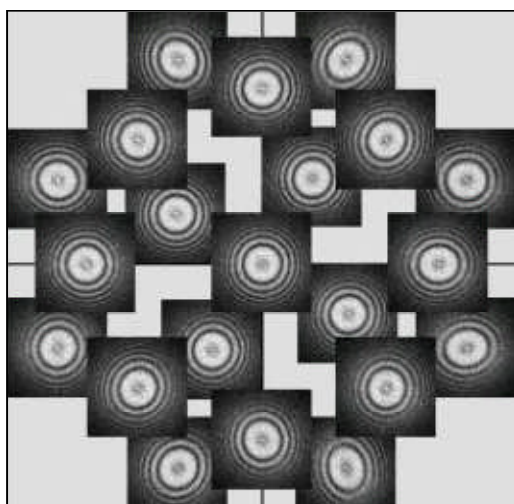


Figure B.1. A Zemlin tableau taken at 36 mrad outer tilt on the OJ2200 MCO. Diffractograms along the perimeter are taken at maximum beam tilts, with smaller tilts corresponding to those more central.

The effect of chromatic aberration (C_c) is to increase the defocus spread of the image, which reduces the contrast of high detail features. To minimise C_c it is necessary to

reduce the energy spread of the electron source, or find a means to disperse and selectively remove electron energies. In the OJ 2200 MCO, a double Wien filter and an energy selection slit are located after the Schottky source, which can be used to reduce the spread of beam energy. The first Wien filter spatially disperses the energy of the incoming beam, which is then incident on a thin slit aperture. The slit is used to select the energy range of electrons that are allowed to pass, with finer slits restricting the passage of less dispersed electrons and resulting in a finer final beam energy spread. After passage through the slit the beam encounters a second Wien filter that recombines the beam. Practically, a balance is struck between the desire for a narrow beam energy spread, and using a correspondingly fine slit, and the need for sufficient beam brightness to image the sample at sensible exposure times. For the monochromated work here typically a 5 μm slit was used, resulting in a beam energy spread of approximately 0.2 eV at 80 kV.

Profile of the Focussed Electron Beam for Controlled Defect Creation

Defects were created at 2.5×10^6 magnification by focussing the beam to crossover on a region of graphene observed to be free of most contamination (a small quantity of amorphous carbon in the viewing area is desirable, as it is required for correcting the astigmatism of the beam). The beam profile is shown in Figure C.1. The total beam current recorded on the Faraday cup was measured as 1 nA, corresponding to $6.241 \times 10^9 e^- s^{-1}$. From the Lorentz fit we can extract a FWHM value of 8.67 nm, corresponding to an area of 59.4 nm^2 . The beam current density (BCD) is given by dividing the total beam current by the area, $= 6.241 \times 10^9 / 59.4 e^- s^{-1} \text{ nm}^{-2}$. This gives an approximate $\text{BCD} = 1 \times 10^8 e^- s^{-1} \text{ nm}^{-2}$. This is an average value since the beam profile is Lorentzian.

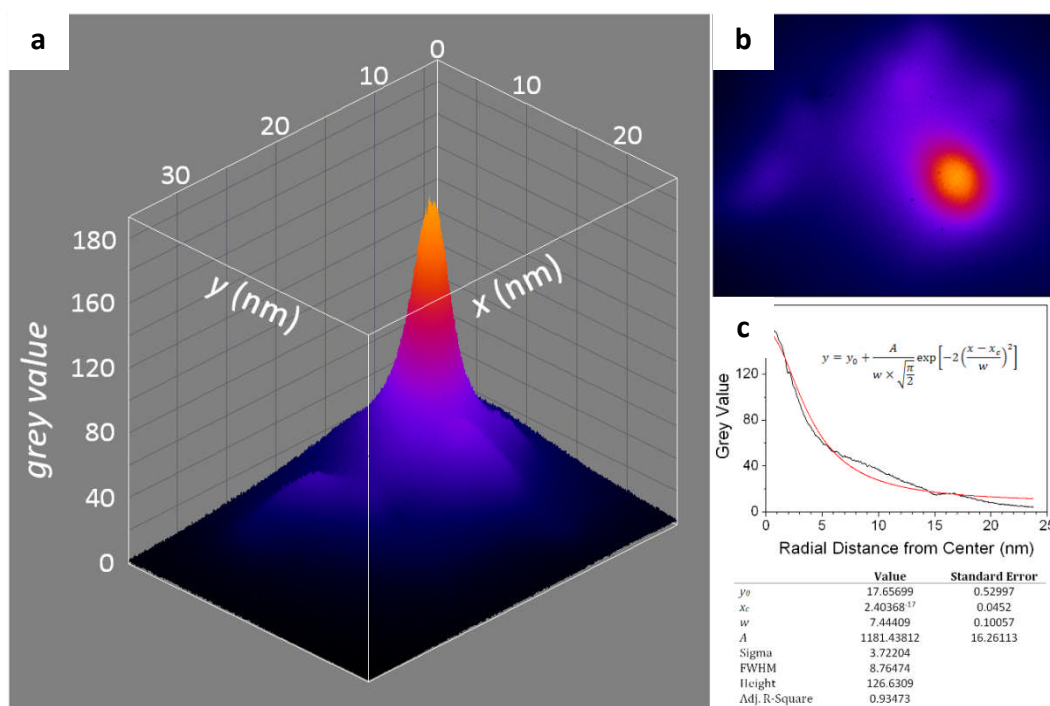


Figure C.1. (a) A 3D plot of beam intensity (grey value) with position, (b) the beam intensity recorded on the CCD detector; (b) contains > 90% of the total beam intensity. (c) A cross section plot with a fitted Lorentzian curve used to determine a characteristic radius for the beam.

Appendix D

The Evolution of the Divacancy Defect

In Chapter 6 the quantification of defects (*via* a Normalised Defect Value term) simplifies the divacancy case to 6, rather than having a separate NDV for each of the three different types of divacancy defect (Appendix F discusses the different divacancy types in more detail). This is because it was found that the divacancy readily shifted between configurations even whilst under only a low dose of electron beam irradiation. Figure D.1 illustrates the rapid evolution of the divacancy between the three stable configurations by showing an AC-TEM time series of the same divacancy. It can be seen from the time scale that it would not be possible to reliably determine whether a particular divacancy type was formed from the high dose defect creation exposure or had shifted whilst under a low dose imaging exposure. Thus it was decided to employ an average value for quantifying the divacancy defect complexity.

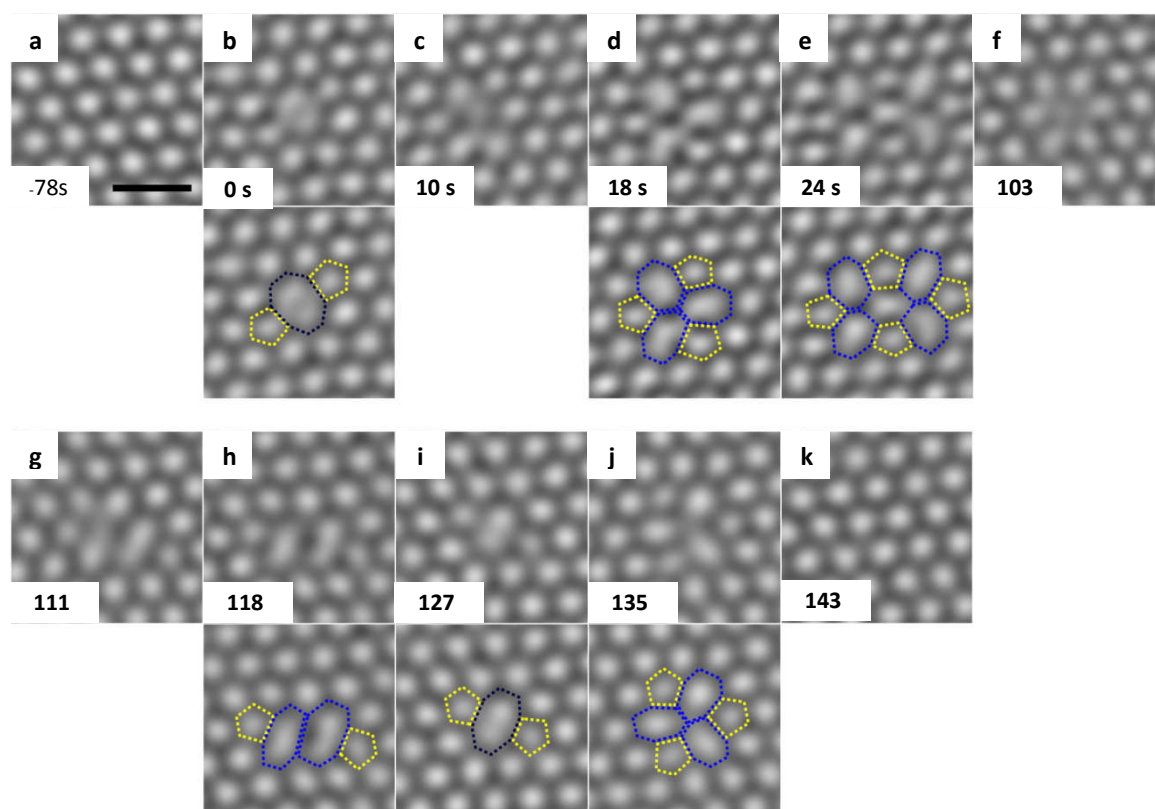


Figure D.1. AC-TEM time series showing the evolution of the same divacancy defect under continuous irradiation by the electron beam (imaging BCD). The insert numbers denote the time, in seconds, relative to the first defect image. (a) Pristine graphene lattice before irradiation. (b) Divacancy formed by 30 s exposure to the focussed electron beam. (c) Blurring of the image; indicative of a bond rotation and reconfiguration in progress. (d) A divacancy having undergone a SW bond rotation. (e) The same divacancy shifted through another SW bond rotation. (f,g) Further bond reconfigurations in progress. (h) The divacancy reconfigured into a dislocation dipole/twin monovacancies. (i) Reformed back into a divacancy, rotated to along a different armchair axis to that shown in (b). (j) The divacancy having undergone a SW bond rotation, as in (d) but directed along a different lattice plane. (k) The divacancy quenched back to a pristine graphene lattice. Panels with highlighted bonds are shown beneath (b),(d),(e),(h-j); the non-transient states. The colour scheme is the same as that used in the main text. Scale bars denote 0.5 nm.

Appendix E

Exposing a Single Carbon Atom to Angstrom Focussed Electron Beam at 80 kV

In order to assess whether a monovacancy could be produced by only exposing a single carbon atom to an Angstrom sized electron probe, we used a JEOL JEM-ARM 200F transmission electron microscope, equipped with both probe and image spherical aberration correctors operating at 80 kV in scanning TEM mode. We imaged monolayer graphene at high magnification, shown in Figure E.1a. The location of a single carbon atom was identified from the image and then the STEM probe was positioned such as to expose only a single atom for 5 minutes. A probe current of 32 pA was used. The red x in Figure E.1a identifies the position where the Angstrom probe was placed for 5 minutes. After exposure the area was imaged again, shown in Figure E.1b. Figure E.1c,d show a and b after applying a Fourier band pass filter. We then repeated this 3 times and in all cases no defects were observed in the area exposed. A 32 pA probe current with an Angstrom diameter probe gives a beam current density of $2.54 \times 10^{10} e^- \text{ nm}^{-2} \text{ s}^{-1}$ which is two orders of magnitude more than achieved using the focused TEM probe. This indicates that it is not just the beam current density that a single atom receives that is

important, but also the area of the sample that is exposed to a high beam current density.

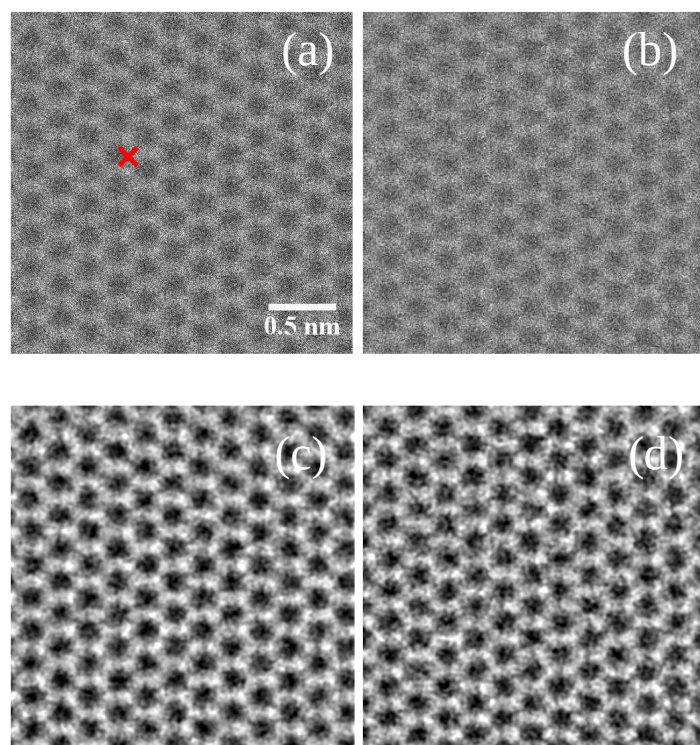


Figure E.1. STEM images of monolayer graphene (a) before and (b) after the STEM probe was positioned on a single atom, labelled with $\times$ in (a). (c) and (d) Images in (a) and (b) after a Fourier band pass filter.

Appendix F

Schematic Atomic Models of Defect Structures in Graphene

Figure F.1 - Figure F.6 are to help explain how some of the defect structures were formed and the terminology of the normalised defect value (NDV) used.

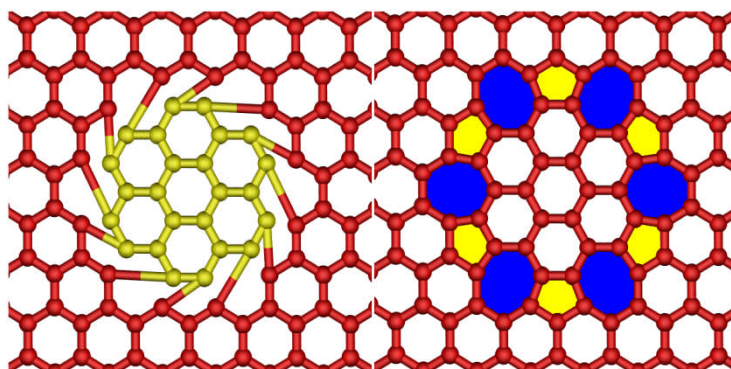


Figure F.1. Schematic models showing how the 5-7 closed loop structure is configured.

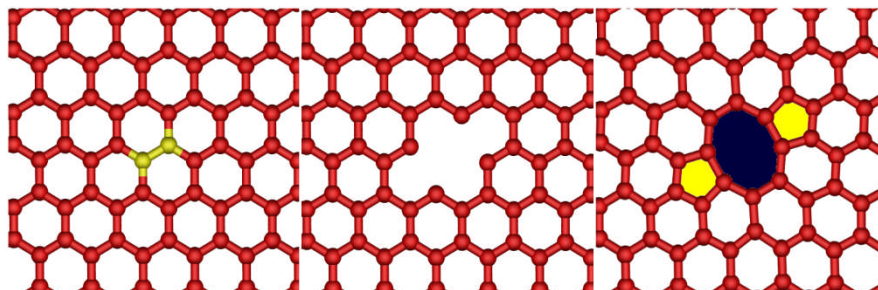


Figure F.2. Schematic models showing how a divacancy is formed.

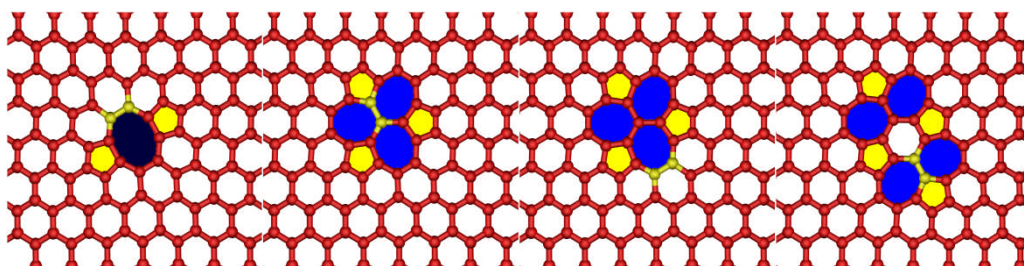


Figure F.3. Schematic models showing a divacancy transforming via successive Stone-Wales rotations (bond rotated indicated in gold).

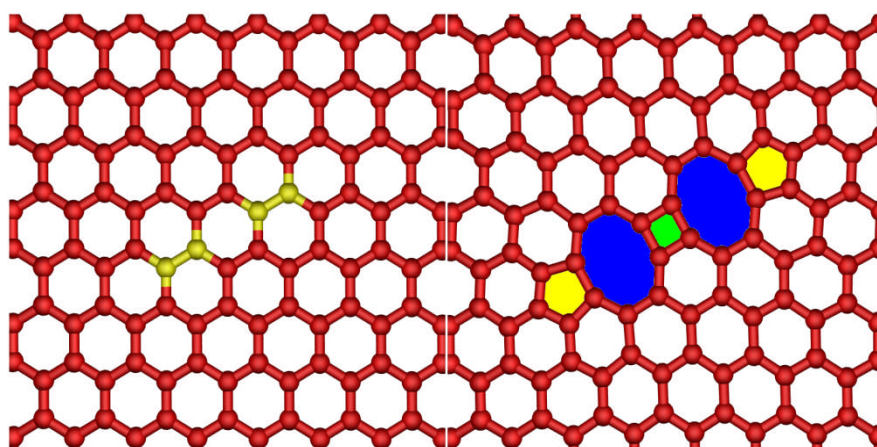


Figure F.4. Schematic models showing how the removal of two carbon dimers along the arm-chair lattice direction of graphene leads to a defect structure.

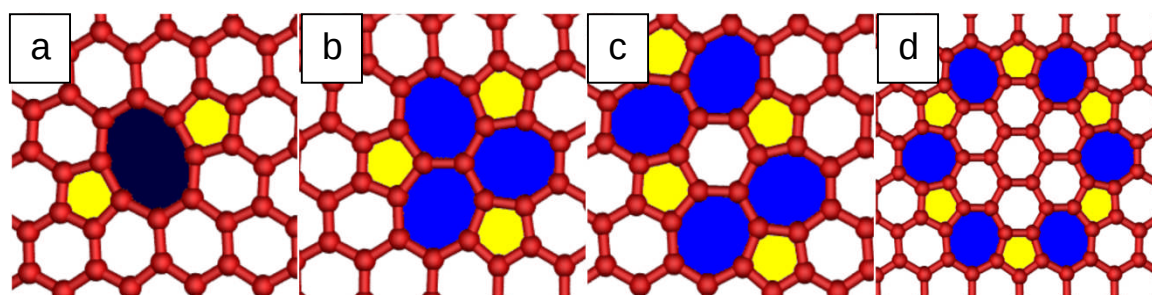


Figure F.5. Schematic models of defect structures to illustrate normalized defect values of (a) 3, (b) 6, (c) 9 and (d) 19. Due to divacancy defects shifting between a, b and c on short time scales and under imaging BCD, a mean defect value of 6 was used for any single and isolated divacancy defect.

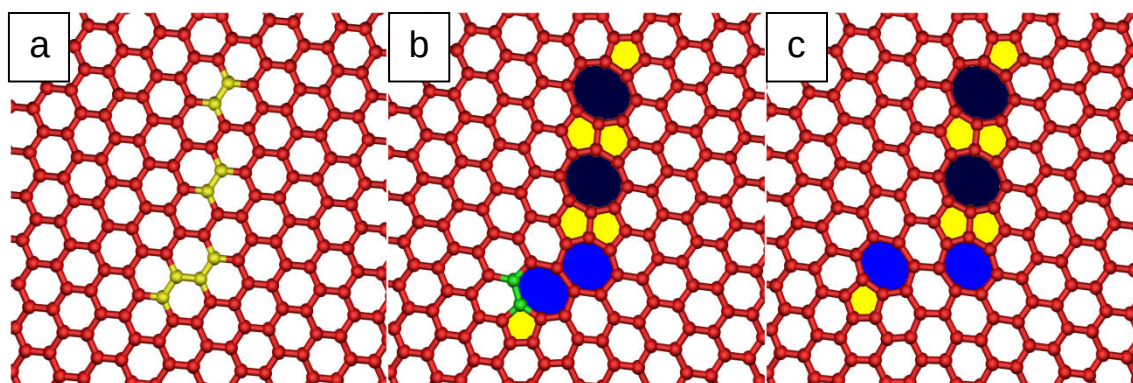


Figure F.6. Schematic models showing how the defect structure in figure 3(c) was formed. (a) shows the atoms sputtered. (b) shows the green bond rotated to form (c).

Appendix G

Calculations of Sputtering Cross-Section and Beam Induced Heating

The sputtering cross section as a function of beam energy was calculated according to ref. [6], taking into account out-of-plane atomic vibrations due to zero-point fluctuations in the Debye model approximation. Graphene flexural phonon modes exhibit a quadratic dispersion relationship and thus the Debye model will not exactly predict the correct mean-square-velocities. None-the-less it is still possible to gain valuable insights into the sputtering cross-section using the equations in ref. [6]. Figure G.1 shows the cross-section as a function of beam energy for three different temperatures. In the Debye model, a temperature approaching the Debye temperature of 1287 K is needed to thermally excite enough out-of-plane vibrations to generate the sputtering cross-section of 1.2×10^{-2} barn that we observe.

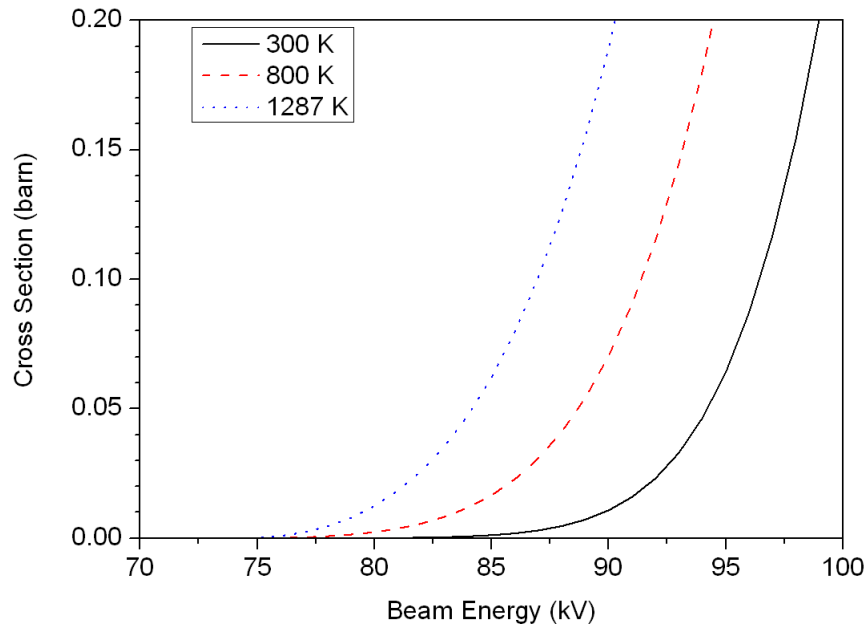


Figure G.1. The carbon atom displacement cross section versus electron beam energy at temperatures of 300, 800 and 1287 K (the Debye temperature). At 80 kV cross sections of $\sigma_D(300 \text{ K}) = 7 \times 10^{-5} \text{ b}$, $\sigma_D(800 \text{ K}) = 2.4 \times 10^{-3} \text{ b}$ and $\sigma_D(1287 \text{ K}) = 1.2 \times 10^{-2} \text{ b}$ are expected, with the experimental cross section found to be $\sigma_D = 1.4 \times 10^{-2} \text{ b}$.

Figure G.2 shows how changing the threshold energy for sputtering affects the cross-section at a temperature of 300 K and incident electrons with 80 keV energy. A threshold energy of 19.7 eV leads to our observed cross-section of $1.2 \times 10^{-2} \text{ barn}$.

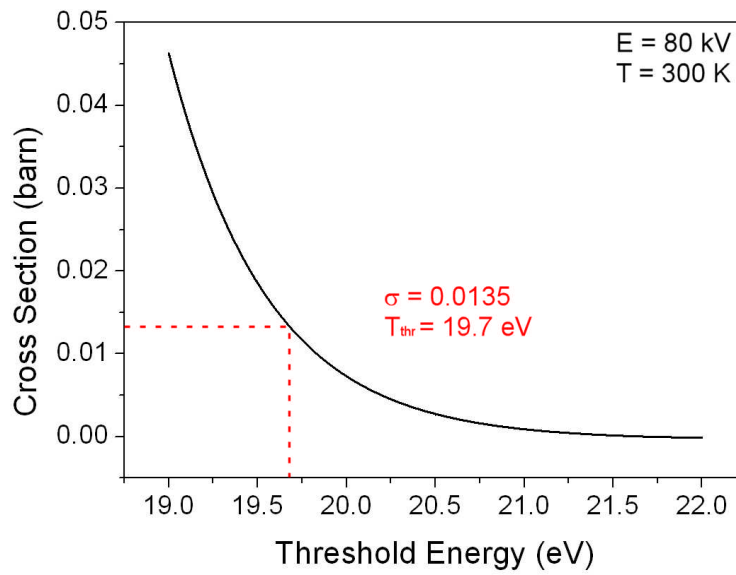


Figure G.2. Sputtering cross-section as a function of threshold energy for sputtering at 300 K and for 80 keV incident electrons.

Figure G.3 shows how the sputtering-cross section depends upon the mean-square-velocity, $\overline{v^2}$ for 80 keV incident electrons based on the Debye model. A $\overline{v^2}$ of $2.7 \times 10^6 \text{ m}^2 \text{ s}^{-2}$ is needed to produce the observed sputtering cross-section of 1.2×10^{-2} barn, which is approximately double that calculated at room temperature.

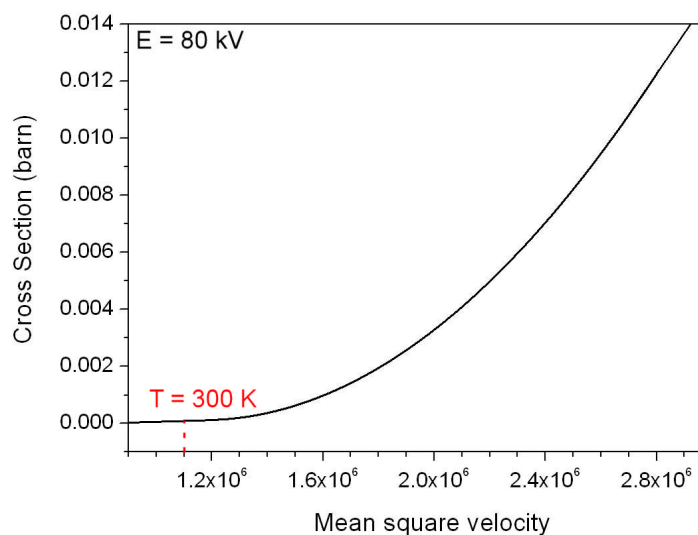


Figure G.3. Sputtering cross-section as a function of mean-square-velocity ($\text{s}^2 \text{ m}^{-2}$).

Figure G.4 shows the predicted temperature increase in our sample based on the model in ref. [6]. In our experiments the graphene is mounted on a SiN TEM grid rather than the more commonly used copper TEM grid. SiN has low thermal conductivity, and therefore the graphene is not in contact with a heat sink. This may impact on the results since the dissipation of heat may be restricted.

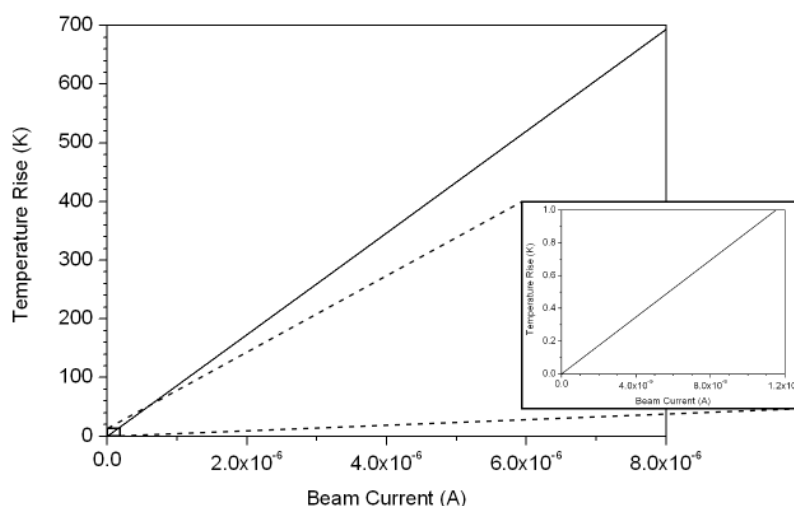


Figure G.4. The effect of beam current on sample temperature, with the sample modelled as a monolayer of graphite and values of thickness $3.2 \text{ \AA}$, thermal conductivity $4 \times 10^3 \text{ Wm}^{-1}\text{K}^{-1}$, beam diameter 8 nm , inelastic mean free path $0.4 \times 10^{-10} \text{ m}$ and distance to heat sink of $1 \text{ }\mu\text{m}$ used.

Appendix H

Calculation of the Fe Diffusion Coefficient at the Graphene Edge

A time series of AC-TEM images (Figure H.1) of Fe atoms bonded to the edge of graphene were used to calculate a diffusion coefficient, following the method of ref. [7]. The frames were first aligned with respect to one another, to counter for sample drift, and then the distance the Fe atom moves between frames is measured. By employing Einstein's definition of the diffusion coefficient, in 1-D we can calculate the diffusion coefficient D , by using our measured Fe drifts, x , and the average time between exposures, t (approximately 9 seconds).

$$D = \frac{\bar{x}^2}{2t} \quad \text{Equation H.1}$$

This yields $D = (7 \pm 1) \times 10^{21} \text{ m}^2 \text{ s}^{-1}$, which can be used to calculate an activation energy $E_A = 0.8 \text{ eV}$.

$$D = ga^2\nu_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad \text{Equation H.2}$$

With the geometric factor g approximated to 1, a the lattice constant for graphene and ν_0 the jump frequency, which is approximated to 10^{13} .

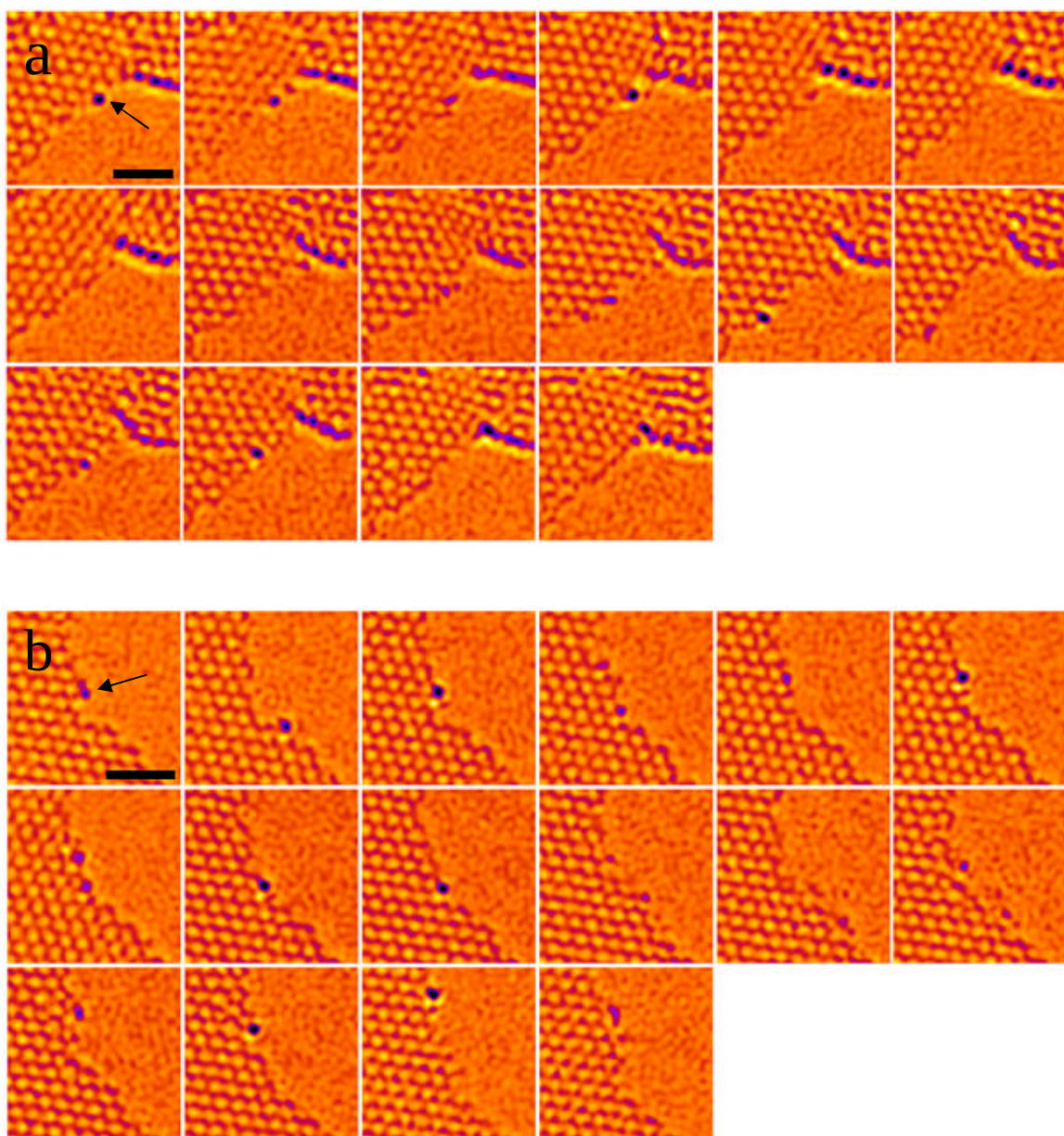


Figure H.1. (a) and (b). Two AC-TEM time series illustrating the migration of a Fe atom (arrow) bonded at the graphene edge. Scale bar denotes 1 nm.

Appendix I

Reconstructed Monovacancy Time Series

Figure I.1 shows a reconstructed monovacancy (r-MV) that is stable for 150 s, supporting our conclusion that the symmetric MV (s-MV) cannot be a superposition of oscillating r-MVs.

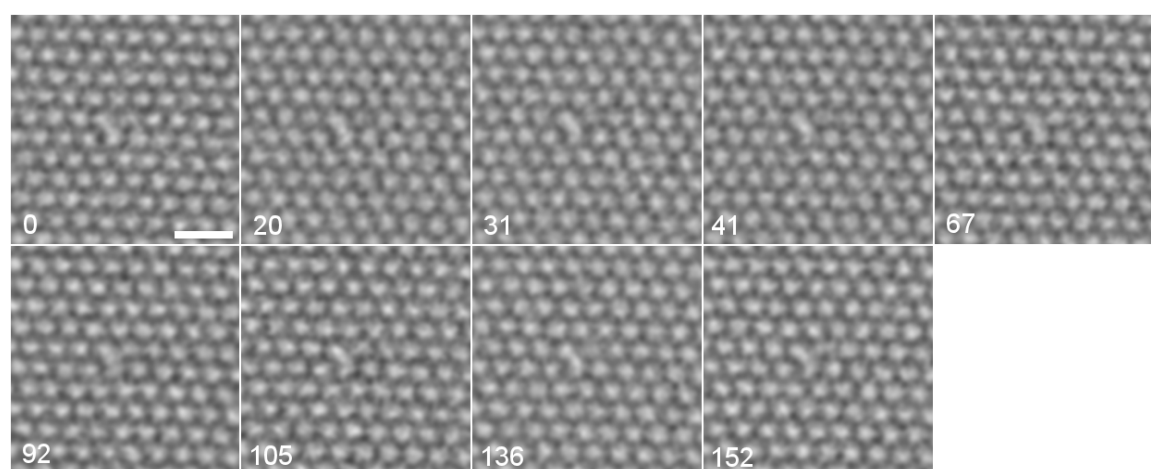


Figure I.1. An aligned AC-TEM image series of a reconstructed monovacancy, showing no change in the bonding configuration for up to 152 seconds. Bottom left number denotes the time elapsed since the capture of the first image. Scale bar is 0.5 nm.

Reference

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