EXPLORING DEFECTS AND INDUCED
MAGNETISM IN EPITAXIAL GRAPHENE FILMS

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by

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EXPLORING DEFECTS AND INDUCED
MAGNETISM IN EPITAXIAL GRAPHENE FILMS

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ABSTRACT

Graphene has been demonstrated to have unique properties not only in its virgin state but also by altering its environment through rotations in bilayer graphene, doping, and creating heterostructures with other 2D materials, which all lead to different functional behaviors. Another avenue to altering graphene is by using defects to generate p-orbital magnetism, which is of interest both to fundamental physics and potential application in new classes of spintronic devices. Indeed, atomic hydrogen creating sp^3 defects attached to the graphene surface as well as vacancies in graphene have been shown to induce magnetism, while high energy (MeV) proton irradiation has been shown to produce ferromagnetism at room-temperature in graphite. However, detailed investigations of these systems are absent so that little is known about the density and configuration of defects, the role of interfaces, or how these relate to magnetism.

In this thesis studies of single-layer graphene revealed that atomic deuteration indeed does lead to reversible chemisorption. However, it is found that atomic deuterium treatment of many-layer epitaxially grown graphene on C-face 4H-SiC (EG/SiC) only affects the surface graphene layer and the buried graphene/SiC interface. While this result did not present magnetism from the interface or graphene, x-ray reflectivity and cross-sectional transmission electron microscopy demonstrated a change of the buried graphene/SiC interface which resembles a delamination of graphene from the substrate. In some cases, multiple atomic treatments lead to complete delamination of the graphene film.

Motivated by the results of atomic hydrogenation (deuteration), interlayer incorporation of hydrogen was achieved by accelerating ions to implant them between

graphene sheets using low (100s of eV) energy hydrogen ion implantation. We focus on addressing the role of the damage from implantation in the magnetism which we observe in our samples. The use of polarized neutron reflectivity and x-ray scattering aims to uniquely address the relationship of strain, structural damage or chemisorption, and magnetism in many layer epitaxial graphene. We find that via tailoring the ion distribution (and range) to the sample we can reliably predict the structural and magnetic changes driven by implantation.

1 – Magnetism in Graphene and Graphite

Graphene has generated considerable excitement in the scientific community because of its linearly dispersing electronic bands that lead to novel properties, including extremely high electron mobility [1]. With the very recent discovery of a large band-gap semiconducting form of graphene on SiC substrates [2,3], there are new possibilities for graphene-based electronics.

Our research explores the potential to create magnetic graphene. The integration of magnetism with graphene's high electron mobility could lead to a new class of spintronic materials having long spin lifetimes. In addition to the potential technological applications, the p-orbital magnetism in these materials is, itself, novel and of scientific interest. Our approach to magnetism in graphene exploits its bipartite lattice where, according to Lieb's theorem, an inequivalence in the two lattice sites caused by defects can lead to ferromagnetism [4]. Indeed, high energy proton irradiated graphite has been demonstrated to be ferromagnetic [5]. The use of hydrogen (or deuterium) promises a better pathway for magnetism to arise because it is reversible, it is more controllable for creating nanostructures/nanopatterned regions, and it will not destroy the crystallinity that is intrinsic to graphene's high electron mobility. Density functional theory calculations have shown that atomic hydrogen sticks to the graphene surface [6] and that partially hydrogenated graphene (graphane) should produce a total magnetic moment of $1\mu_B/\text{hexagon}$ [7]. Experimentally, magnetism has been observed in bulk powders [8–12] of hydrogenated graphene as well as in single to few layer samples [13–15].

1.1 - Graphene Grown Epitaxially on SiC

Central to our strategy to study magnetic graphene is the use of epitaxially-grown graphene on the C-face (C-EG) of 4H-SiC (001). C-EG provides a large area sample with an atomically flat interface and is therefore an ideal choice for magnetic and structural investigations using x-ray scattering and neutron reflectivity.

While the majority of work done studying epitaxial graphene/SiC has focused on single and bi-layer graphene on the Si-Face, the C-face-grown graphene has received significantly less attention. Graphene on the C-face of SiC, however, is potentially more interesting as it can have many (2 to 80+) layers of non-interacting graphene sheets with low defect densities in comparison with other methods of graphene growth such as chemical vapor deposition or mechanical exfoliation. These layers of graphene do not behave as graphite because they are randomly rotated with respect to each other, in contrast to the AB stacking seen in bulk graphite and Si-face grown graphene [16]. The buffer layer between graphene and SiC on the C-face has also changed; there is a much weaker interaction than that which is observed in the Si-face grown graphene. This limited interaction leads the graphene layer to behave in a more isolated state without alteration of the sample. In fact, it is difficult to observe the disordered interfacial layers in experiment.

Growth of graphene on SiC is done by sublimation of Si from the substrate by high temperature annealing. This process, however, is uncontrolled in vacuum and the growth of high-quality uniform graphene is impossible at the high growth rates/sublimation rate in UHV. To mediate the growth rate, a controlled environment with a back pressure of silicon is used via a graphite enclosure with a restricted leak to vacuum. This enclosure is in high vacuum but utilizes a pinhole to restrict the flow of Si, creating a backpressure of Si vapor.

This Si vapor pressure has been shown to control the sublimation of Si from SiC, creating high quality, large domain size graphene [17]. Interestingly, the substrate termination also significantly affects the growth rate. Si-face growth leads to very slow growth – allowing for single and bi-layer graphene to be reproducibly grown. The C-face has a much more rapid growth with rotational disorder driving each individual layer to act as a freestanding graphene sheet [18].

The C-face grown epitaxial graphene in comparison to Si grown or exfoliated graphene has a number of unique functional characteristics. For one, large ($>10\mu\text{m}$) domain size films can be grown, leading to samples which exhibit the highest electron mobility of any graphene based system [19]. C-EG exceeding 15 layers has not been studied. Our early work focused on understanding how growth of many layers impacts the interfacial structure and crystallinity of graphene, demonstrating how the growth evolution impacted the buried interface.

1.2 - Magnetism in Disordered Carbon

Carbon materials, in the large majority, exhibit diamagnetic behavior. Beyond conventional carbon materials, there are a few examples of disordered (non-graphitic) carbon materials such as amorphous/activated carbon fibers and carbon nanofoams which exhibit ferromagnetic or superparamagnetic behavior. While the nature of the magnetic ordering is not well understood, speculation as to the origin of spins in these systems have been made by theoretical studies and magnetism has been experimentally demonstrated to arise in these highly disordered carbon materials.

In amorphous carbon/activated carbon fibers there are two theories as to the origin of magnetic spins: the disorder creates a glassy-like magnetism which can be attributed to free/non-bonded π electrons such as dangling bonds [20] or the mixing of sp^2 and sp^3 carbon atoms which are dependent on atomic configurations [20–22]. In both cases the mechanism by which magnetism can arise is similar: disorder creates electrons with unpaired spins. The mixing of sp^2 and sp^3 carbon, which is more relevant to the understanding of potential avenues to magnetism in graphene, has been demonstrated to alter the magnetism of amorphous [23,24] and nanofoam carbon [21].

In comparison with graphite, which will be discussed in the following section, most disordered carbon materials consist of only sp^3 carbon. In amorphous carbon, which starts from this sp^3 skeleton, it is believed that the change in the hybridization of the carbon atoms to partially sp^2 by pyrolysis (a heat treatment at high temperature) leads to net spin which gives rise to magnetism. The result, however, is complicated by the diversity of possible contributions to net spins such as dangling bonds and unpaired orbitals. What is more surprising is the ordering of the spins which not only lead to the onset of superparamagnetic behavior but also, for some samples, ferromagnetism [23,24]. How the ferromagnetic ordering occurs is not well understood. It is speculated by the authors of these studies that the highly defective graphitic sp^2 domains can align, giving rise to ferromagnetism. However, the domain structure and the arrangement of graphitic domains in the powder sample has not been experimentally correlated with magnetic ordering [24].

Carbon nanofoams, a high-surface area low density solid synthesized by laser ablation of glassy carbon [21], also exhibit magnetism. When studied with transmission electron microscopy the foam was shown to have regions of graphite truncated by zig-zag

edges where the graphitic rings fragment. These edge states create unpaired orbitals, contributing spins which order only in a paramagnetic fashion in the sample. Considering the similarities of the carbon nanofoams with pyrolysis treated amorphous carbon, it is surprising these samples do not show ferromagnetic interactions. In the carbon nanofoam, the small (6-7 graphitic rings) sp^2 regions are isolated and it is believed this makes spins difficult to align [20,21]. However, no direct experimental correlation between the magnetism and the graphite structures has been made, making definitive statements regarding how magnetism arises from disorder impossible.

From these studies, the role of the defect structure in the magnetic ordering must be better understood. While the emergence of spins which can contribute to magnetism in carbon is interesting, the emergence of these spins is convoluted by an inherently disordered system. Study of the comparatively well-ordered graphite, however, can help to determine how single defect sites of various types can give rise to spin and potentially magnetic ordering. To better understand how spin can emerge from these defects, theory and experimental evidence for magnetism in graphite is discussed.

1.3 - Magnetism in Graphite and Graphene

Theory behind magnetism in graphene can be subcategorized into two sections, defect (or vacancy) induced and interface-induced magnetism. Defect induced magnetism can be driven by chemisorption of atoms or interstitial/vacancies in the graphene lattice. Interface-induced magnetism arises due to complex interfaces with dangling bond states and defects both from the graphene and the substrate which it is grown on epitaxially.

In the case of hydrogenated graphene (graphane), the magnetism can be attributed to sp^3 defects caused by hydrogen chemisorption or vacancy in the graphene sheet. To understand the ideal theoretical mechanism by which this magnetism can occur, Lieb's theorem is discussed in further detail [25]. The Lieb's theorem states that for a bipartite lattice, which graphene and graphite are as they contain two triangular lattices making up each hexagon, inequivalencies in atoms at the two (A, B) sites lead to a magnetic ground state. The Hubbard model accurately describes graphene's electronic states and can be applied to spins in graphane provided that electron-electron interactions are accounted for (to describe magnetism):

$$H = \sum_{\sigma} \sum_{x,y} t_{x,y} C_{x,\sigma}^{\dagger} C_{y,\sigma} + \sum_x U_x n_{x\uparrow} n_{x\downarrow} \quad (1.1)$$

Where x and y are summed over a finite lattice, t is the hopping matrix, U is the on-site energy, c and $c^{\dagger}$ are fermionic operators, and n is the number operator. The first term describes the hopping of electrons with spin σ from site y to site x . For graphene, t can be treated as constant. The second term is more complicated, with n describing the spin-specific electron density at each site. Coulomb repulsion is quantified in this way, having described interactions of the two populations of spin-up and spin-down electron densities. From this Hubbard model, magnetic information is extracted through Lieb's theorem.

Lieb's theorem assumes two things: U is constant and the lattice being summed over is bipartite, as is the case in graphene(ane). Upon this assumption there are two consequences, a ground state with spin proportional to the difference in occupation of the two lattice sites and the number of zero energy states can be predicted. The spin (S) and number of zero energy states (η) are expressed as:

Fig. 1.1 (a), (b) demonstrates how edge states/graphene fragments can give rise to a magnetic ground state via Lieb's Theorem. In the figure the open black circles represent "A" sites of one of the graphene sublattices while the blue filled circles represent "B" sites of the other sublattice. In (a) there is no net spin while in (b) there is an asymmetry in the number of sublattice sites giving rise to a net spin of 1.

$$S = \frac{1}{2} |N_A - N_B| \quad (1.2)$$

$$\eta = 2a - N \quad (1.3)$$

where N_A and N_B are the number of sites in the two sublattices, N is the total number of sites, and a is the number of sites which are not nearest neighbors (non-adjacent sites).

A graphene fragment, shown in Fig. 1.1 is a simple way to illustrate the calculation of net spin. As shown, Fig. 1.1(a) is nonmagnetic ($N_A=N_B=12$) in the ground state while Fig. 1.1(b) has two zero energy states and a magnetic ($N_A=12 \neq N_B=10$) ground state with $S=1$ [5]. A similar geometrical effect on the magnetism is believed to be what gives rise to magnetism from edge states of graphene [26]. In sufficiently large sheets of graphene, defects also effectively eliminate the symmetry of the sublattice sites. This elimination occurs as a rehybridized carbon atom can no longer contribute to the π -electron system. The p_z vacancy leads to the induction of magnetic spins. In order to theoretically maximize the magnetic moment, defects should populate only one sublattice.

Experimentally defects are randomly created in the case of irradiation or chemical treatment, leading to a more complicated picture than Lieb's theorem. However, there has been observation of ferromagnetism experimentally in graphite [5,27–33]. In the previous section, magnetism from graphite edges had been discussed by graphitization of amorphous carbon [23]. By varying the degree of graphitization, achieved by changing the annealing temperature, a magnetic moment can be induced in these samples. Formation of nanographite, however, creates measurable magnetic moment only within a limited size range of graphitic rings. It was found that the domain size, an indication of the lateral graphite structure, drove the magnitude of the magnetization [33]. The magnitude of the sample magnetization peaked at an average graphite ring size which corresponds to 5-9 graphite rings, suggesting the graphene fragment had net spin from differences in the number of sublattice sites, similar to the Lieb's theorem picture presented in Fig. 1.1. However, the issue is complicated as acid treatment of the samples reduces the magnetic moment. This indicates that more reactive dangling bonds and edge states (which are passivated during the acid treatment) are also contributing spin, making the driving force in the observed magnetism in the nanographite powders difficult to ascertain. This suggests a diversity of possible defects which can contribute spins to magnetism. To better understand the role of defect structure and the profile of magnetism in the samples must be better understood, motivating the use of structural probes like neutron reflectivity and x-ray diffraction.

Magnetism has also been observed in high energy proton irradiated graphite [5,29–32]. Magnetometry and magnetic force microscopy (MFM) measurements both showed that ferromagnetism arises as a function of ion dose. The magnetic signal was shown to

persist with ordering temperature above [5]. However, the cause of the magnetism which was observed is currently a matter of speculation. High energy (MeV) proton irradiation can lead to a diverse range of structural changes to graphite. Defects types such as vacancies, interstitials, dangling bonds, and (potentially) hydrogen chemisorption all can form as point defects or more complicated defect clusters. Each of these events has the potential to create spins which can contribute to magnetism in the sample.

Perhaps the most compelling experimental evidence for magnetism arising from carbon itself in proton irradiated graphite is the emergence of x-ray magnetic circular dichroism (XMCD) signal at the carbon K edge [29]. Due to the element specificity of the technique, emergence of XMCD here is definitive evidence of orbital carbon magnetism in proton irradiated highly ordered pyrolytic graphite (HOPG). The orbital nature of the signal also corroborates the role of the π electrons of carbon in the magnetization after the irradiation process. However, this does not address the role of the hydrogen in the magnetism which occurs after the irradiation. Even at high energies hydrogen is believed to remain in the bulk HOPG crystal after implantation [5,31] but, without experimental corroboration and structural understanding of how hydrogen effects magnetism and structure, the role it plays is unknown. Hydrogen in the sample can arrange either by bonding or recombination of protons into molecular hydrogen, each of which can have a wide range of spatial arrangement and can have a role in creating and stabilizing defects in graphite. For this reason the role of hydrogen is likely significant in understanding the magnetism observed in irradiated graphite, but it remains an open question as to where and in what (if any) concentration it remains in the samples [31].

In graphene, the annealing of samples grown on the on the Si (0001) face of SiC in molecular hydrogen creates a structural reconfiguration of the buried interface due to the “lift off” of the graphene layers [34]. Molecular hydrogen does not bond with the graphene sheets but rather intercalates between the interfacial buffer layer and graphene. The intercalation of hydrogen promotes the separation of graphene into a “quasi-freestanding state” where the graphene buffer layer becomes isolated from the substrate. This leads to an enhancement the carrier mobility by decoupling the graphene and substrate as compared to the as-grown film. This structural change is demonstrated by recent x-ray reflectivity investigations [34–37]. The result, showing no expansion of the graphene interlayer spacing, is not expected if hydrogen is incorporated between graphene layers. Hydrogen between graphene sheets should push apart the layers, suggesting that the hydrogen which might be integrated in the film lives only at the interface and in existing defect sites. If this is the case, hydrogen has not been successfully chemisorbed on (Si-face) graphene sheets by molecular hydrogen exposure. By introducing atomic hydrogen, rather than exposing the sample to molecular hydrogen at high temperatures, there is a possibility of H chemisorption rather than affecting the chemically active interface as with molecular hydrogen.

In another study utilizing atomic hydrogenation, with spin polarized scanning tunneling microscopy (STM), the nature of magnetism at single defect sites on graphene was investigated [15]. STM is a local probe and, by measuring the spin polarized state of the film with atomic precision one can correlate atomic defect sites directly with magnetic density. This study, which used an atomic hydrogen source to treat graphene grown on the C-face of SiC, revealed that hydrogen adsorption to a graphene sheet indeed leads to a spin-

split state at the defect site. The authors showed that this induced a magnetic moment which could be manipulated by arranging many H defects using STM and that the resulting magnetism could be predicted reliably by density functional theory. This fundamental corroboration of the principal driving magnetism from point defects in graphene motivates studies which attempt to create and tune magnetism on a larger scale in graphene.

The possibility of interfacial magnetism in graphene grown on the Si-face of 6H SiC hydrogenation via atomic hydrogen source was studied by Giesbers *et. al* [13]. In this work the atomic treatment of samples was done for various lengths of time and at various stages of graphene growth. From this study it was revealed that while hydrogen attachment to graphene cannot be ruled out, the necessary components to creating magnetism in the samples was the presence of Si dangling bonds from the substrate which can interact with the hydrogenated graphene layer to create a localized ferromagnetic state. This is believed to arise from the localized electrons (from Si dangling bonds) to have an exchange coupled interaction from sp^3 carbon which forms when hydrogen bonds to the graphene sheet. Shocking is the magnitude of the moment, $0.9\mu_B$ /carbon hexagon. This most certainly indicates the magnetism is not from graphene itself as the theoretical limit is $1\mu_B$ /carbon hexagon when every A site is affected by chemisorbed hydrogen, but NO B sites are affected by defects, an experimentally impossible result at this scale. While other effects like potential for contamination, as SQUID magnetometry is highly sensitive technique and detecting magnetism from a few atomic layers is difficult, can contribute to the measured moment the role of the interface is proven important. However, this result cannot corroborate the role of hydrogen in the observed magnetism and definitively determines

the interface is an important driver of magnetism in epitaxial graphene on Si-face SiC when exposed to atomic hydrogen.

In other studies, graphene was shown to become magnetic upon interaction with hydrogen atoms via plasma [14,38]. These studies use low energy plasma and treat Si-face graphene grown on 4-H SiC and chemical vapor deposition (CVD) grown graphene transferred to Si/SiO₂ substrate, eliminating the possibility that the magnetism is driven completely by the substrate/graphene interface as in the atomic hydrogen treatment case. In these studies, high (energy) resolution electron energy loss spectroscopy (EELS) suggests that hydrogen can attach to carbon in the film, creating unpaired electrons in the film but other defects from the plasma treatment cannot be ruled out. These unpaired electrons are believed to be responsible for magnetism, as this results in regions which can resemble the Lieb's theorem picture discussed above. Interestingly, the hydrogen plasma treatment does not create a large degree of irreversible damage, by Raman it was shown that annealing at temperatures as low as 400K reveals the beginnings of dehydrogenation of the graphene sheet. Complete dehydrogenation can be achieved at only 650K [38]. While this method suggests the ability to chemisorb hydrogen to a single graphene sheet, multilayer chemisorption and global correlation of defects to magnetism in graphene has yet to be experimentally observed.

1.4 - Exploration of Magnetic Graphene at the University of Missouri

Early work using Raman spectroscopy, characterizing graphene sample quality and various mechanisms for functionalizing graphene with hydrogen (such as atomic hydrogenation and plasma treatment) was vital in developing a robust technique to create magnetic defects in samples. Raman is sensitive to the hybridization of carbon, allowing

to qualitatively see the formation of defects (sp^3 hybridization) upon treatment of graphene (sp^2 hybridization) using various techniques to functionalize the sheets effectively converting sp^2 to sp^3 carbon. The Raman scattering studies done at MU, in addition to discussion of the features of graphene and functionalized graphene seen in Raman spectra, is discussed in Chapter 2. Here, we present a new method of determining thicknesses for many layer graphene grown on SiC.

Central to our strategy was the use of neutron reflectivity, which required relatively smooth surfaces and high surface area samples. Epitaxial graphene grown on the C-face of SiC met these standards, but many-layer samples had not been studied in detail. Using the resources at MU and the Spallation Neutron Source (SNS) at Oak Ridge National Lab (ORNL) we developed an understanding of the structure and roughness of these samples, reconciling roughnesses at different length scales with combined x-ray scattering, neutron reflectivity, and electron microscopy (discussed in Chapter 3).

In Chapter 4, atomic deuteration of many-layer graphene is discussed. From this study it was revealed that while hydrogen did not incorporate between the graphene layers, chemisorption was likely to have occurred at the surface, edges and defect sites. From XRR results we also see a striking change at the buried interface from hydrogen treatment. We show that these results indicate delamination of graphene from SiC without the use of wet chemistry or adhesive transfer methods.

From the atomic hydrogenation study, we learned that without kinetic energy to implant hydrogen, it would not incorporate between graphene layers. To investigate further we accelerated hydrogen atoms using ion implantation. In Chapter 5, we show in-situ structural studies revealing ion implantation leads to defects throughout many-layer

graphene films. By then changing the ion implanted into graphene from hydrogen to helium, we can eliminate the possibility of hydrogen chemisorption to the film. This can aide in our understanding of the structural and magnetic changes we observed in hydrogen implanted films. In Chapter 6, we discuss the structural similarity and differences of helium implanted films.

In Chapter 7, we discuss the implications of implantation on the magnetism and study what drives the magnetism in these treated graphene films. We report for the first time magnetism resulting from low-energy hydrogen ion implanted graphene films. Here we observe how the structure is impacted by hydrogen/deuterium implantation at various implantation conditions. Magnetic measurements of He implanted films and polarized neutron reflectivity (PNR) experiments are underway.

2 – Raman Scattering Studies of Graphene on SiC

Raman spectroscopy is used as a fast and non-invasive technique to obtain information about the electronic and structural integrity of graphene. Raman is an inelastic scattering technique using photons, where the energy scale is on the order of phonons in a crystal. In the case of graphene, Raman can distinguish vibrations in a lattice which are attributed to sp^3 hybridized (“D” peak, traditionally known as the diamond or defect peak) or sp^2 hybridized (“G” peak, traditionally called the graphite or graphene peak) carbon. This distinction in the hybridization from Raman is useful in determining the presence and concentration of defects in treated/functionalized graphenes.

The D peak is associated with an in-plane transverse optical phonon (iTO) interacting with a defect site on graphene, through a second-order intervalley process, and the G peak is associated with doubly degenerate iTO and longitudinal optical (LO) phonon modes. These processes tend to both be present in as-grown graphene, however the D peak should not be present in pristine graphene as it is entirely comprised of sp^2 type carbon. Another main feature of the graphene Raman spectra is the 2D (also referred to as G’) peak, a second order intervalley phonon process which is not associated with defects but rather two iTO phonon processes. Because this process does not require a breaking of symmetry in the sp^2 carbon lattice (as in the D peak), the 2D peak is also present in pristine graphene. The final peak which appears in the graphene spectrum is the D’ peak, associated with an in-plane LO phonon which appears due to an intra-valley phonon process and is again only present in the case of defects being present on graphene [39].

Most of the Raman work on graphene at MU has been done on exfoliated flakes or CVD grown single to few layer graphenes. To understand the effect of deuteration or

Fig. 2.1 shows the Raman spectra of C-EG. The graphene peaks overlap with the SiC 2nd order phonon density of states.

hydrogenation of graphene, CVD grown samples transferred to Si/SiO₂ wafers were studied. Here many important results were reproduced: Raman D-peak intensity increased with deuteration, atomic deuteration with the use of a hot filament is reversible, and deuterium broadens the D-peak in comparison with hydrogen. The focus of this study, discussed in Chapter 4, will be on the effect of exposure of samples to atomic deuterium on the D-peak intensity, which has been used to determine lateral densities of defects on graphite and graphene sheets [40,41].

Studies at MU have also investigated many-layer graphene grown epitaxially on C-face 4-H SiC (C-EG). The presence of a modulated SiC or buffer layer, with SiC second order phonon processes that overlaps graphene Raman peaks, and many layers of graphene make the interpretation of Raman on C-EG difficult. Some of the main implications on the phonon dispersion are blue-shifted G peak, peak broadening at the 2D peak and asymmetry

Fig. 2.2 demonstrates how the presence of graphene attenuates the signal from underlying graphene layers (left) and from the bulk SiC normalized intensity (right).

arising in some peaks [42,43]. Fig. 2.1 demonstrates the overlap of the second order SiC peaks with the graphene D, G and D' peaks. The problem of comparing peaks widths between samples becomes compounded by number of layers and lateral domain sizes. For example, it has been reported that the 2D peak width can be anywhere in the range of 28-80 cm^{-1} , increasing as a function of layer number and domain sizes of graphene [42]. Additionally, work recently done at MU suggests the type and density of defects can cause broadening of the D peak, indicating Raman cannot provide a method for determining the nature (type) of defects on C-EG.

Despite the additional complications of the SiC substrate in understanding the Raman spectra of C-EG, several important details about the sample can be obtained. Using attenuation of Raman intensity, in a way similar to that has been reported in the literature [43], the thickness of samples can easily be obtained. Several samples of graphene on SiC were characterized to determine thickness and surface uniformity. Thickness was determined by normalizing intensity (arb. units) to an absolute intensity (or intensity ratio) using the 1525 cm^{-1} SiC 2nd order Raman peak intensities of a bare SiC

Fig. 2.3 demonstrates the consistency of thickness determined by Raman (blue) as a function of thickness determined by XRR from [45]. A black line is used to show the XRR thickness values, demonstrating consistency between methods.

substrate, effectively normalizing the laser intensity and attenuation of the beam from graphene. Normalizing the SiC intensity ($I_{SiC}(N)$) of samples to the bare-SiC intensity off sample (I_{SiC}^{Sub}) allowed for the determination of number of layers:

$$I_{SiC}(N)/I_{SiC}^{Sub} = (v^{2N}) \quad (2.1)$$

where v^2 is the transmission of one graphene layer squared, 0.955, and N is the number of layers.

This can be done because SiC is attenuated by two passes through graphene leading to an attenuation (from the bulk which normalizes this intensity to 1 for $N=0$) of v^{2N} . This can be visualized using Fig. 2.2, which demonstrates the attenuation of the signal from bulk SiC and from each graphene layer as a function of number of layers, N .

In practice, we show that the graphene thickness can be reliably obtained from Raman intensities and these compare accurately with the thicknesses obtained from x-ray reflectivity [44]. Using an Invia Renishaw Raman spectrometer with a 514nm laser spot size of 2mm and power density $2.5 \times 10^4 \text{ W/cm}^2$ in a confocal backscattered geometry, the SiC 2nd order Raman peak at 1525 cm^{-1} was measured on several samples. Using eq. 2.1, we can obtain the thickness. Fig. 2.3 shows excellent agreement with the XRR results (discussed in Chapter 3) where the Raman thickness is given as N multiplied by the interlayer spacing of graphene $3.37 \text{ \AA}$. These thicknesses were also found to agree with the thicknesses that we measured by the attenuation of the Si signal in x-ray photoelectron spectroscopy (XPS). As compared to XPS, it is noted that the Raman measurements are quicker and easier to perform and are not as limited in depth (the absorption length of the Raman laser is larger than the soft x-rays used for the XPS measurements).

Samples were also characterized using XPS after growth. Layer thicknesses were calculated using the shifted carbon emission spectrum peak intensities and the known attenuation length and atomic sensitivity factors for graphitic carbon and silicon carbide:

$$layers = \left(\frac{l_g}{t_g} \right) \ln \left[1 + \left(\frac{l_g}{\alpha_g} \right) \left(\frac{\alpha_{SiC}}{I_{SiC}} \right) \right] \quad (2.2)$$

where l_g is the attenuation length of graphene, t_g is the graphene layer thickness, I_g and I_{SiC} are the C1s peak intensities of graphitic carbon and silicon carbide, α_g and α_{SiC} are the atomic sensitivity factor of graphitic carbon and silicon carbide respectively. These results combined with XRR confirmed robust thickness determination via Raman scattering.

3 – Structure of Many-layer Graphene on C-face 4H SiC

In order to determine how defects impact the structure and properties of graphene, we study many-layer graphene samples. While C-face graphene on 4H SiC has been studied for few layer samples, there is very little information on thick samples (>15 layers). Given the complicated growth and morphology of the samples, we needed to reconcile how x-ray and neutron results could be combined to determine interfacial structure of these highly rough samples. These results are discussed in Chapter 3, reproduced from our recently published work [44].

3.1 - Introduction

The extensive interest in two-dimensional materials is driven by their p orbitals that extend out of the atomic plane and lead to a broad range of novel properties. Graphene, in particular, exhibits linearly dispersing bands that lead to unusual electronic behavior with exceptionally high electron mobility [45,46] while the in-plane bonding leads to high mechanical strength [47–49]. The atomically thin two-dimensional nature of graphene renders it particularly sensitive to its environment which presents a playground for manipulating its properties for potential applications, such as spintronic devices [50], sensors [49,51,52], and plasmonics [53].

Epitaxial graphene grown on SiC substrates provides excellent atomic-scale control of the graphene layers as well as a natural support upon which to utilize it for applications [17,54]. High quality single-layer graphene has been extensively studied on the Si-face of SiC [55–58]. This conducting graphene layer grows on top of a buffer layer that is insulating, which can potentially enable integration of semiconducting and conducting material for electronic device applications [2,3]. However, atomically thin

single layers of graphene present challenges for the manipulation and fabrication that is necessary for applications. Alternatively, multilayer epitaxial graphene having high electron mobility can be grown on the C-face of SiC where the Dirac cones of individual layer graphene layers are preserved because a rotation between the layers does not destroy this signature electronic property of graphene as would occur in graphitic stacking [18,59]. Therefore, there is considerable potential to utilize epitaxial multilayer graphene supported on SiC substrates.

While extensive structural studies have been performed on single and few-layer graphene on the Si-face of SiC, much less work has been done on multilayer epitaxial graphene on the C-face of SiC, particularly for the very thick layers that are investigated here. Because producing one atomic layer of graphene requires sublimating Si from slightly more than 3 atomic layers of SiC, there is a significant driving force for interface disorder. Prior studies have reported on localized characteristics of this buried interface, such as interfacial asperities with Si vents that allow the escape of Si from below or, at the other extreme, atomically abrupt interfaces having a slight carbon enrichment in the top three atomic layers of SiC [16,60]. However, it is not clear how these vastly different morphologies are reconciled in the overall interfacial structure and it is, therefore, important to understand how these interfacial fluctuations are manifested on different lateral length scales as the number of graphene layers increases.

In this chapter, we use complementary x-ray scattering and neutron reflectivity to investigate the buried interface between multilayer epitaxial graphene and the C-face 4H-SiC substrate. We find that the interface fluctuations are extremely large and depends on the number of graphene layers grown. Nevertheless, on short lateral length-scales,

atomically flat interfaces are observed from SiC terraces. Diffuse scattering that is characteristic of interfaces comprised of atomically abrupt steps is observed in the x-ray reflectivity, providing evidence of the locally flat interfaces. This diffuse scattering, however, significantly complicates the analysis of the reflectivity measurements and the comparison between x-ray and neutron reflectivity measurements. We show how these data can be handled by considering the transversely integrated reflectivity. The analysis has significance beyond the current graphene/SiC system because it can provide a guide for handling other material interfaces where there is significant diffuse scattering near the specular reflection.

Our x-ray scattering study also reveals that the lateral structural correlation length of thick multilayers of graphene is quite long, reaching micron length scales, and it indicates the structural continuity of thick multilayer graphene. Several graphene atomic layers near the substrate are observed to exhibit a slightly expanded interlayer spacing as well as increased RMS fluctuations of this spacing. This suggests that the substrate imposes structural disorder very near the interface but that the disorder quickly diminishes away from it – a fact supported by angle resolved photoemission (ARPES) which shows clearly the linear Dirac cones from these multiplayer graphene samples and indicates a good stacking order near the surface.

3.2 - Experimental Methodology

3.2.1 - *Sample Preparation*

Samples are grown on (000 $\bar{1}$) (C-face) of 4H SiC 9x9 and 4x6 mm wafers from Cree, Inc. The samples are sonicated in acetone and isopropyl alcohol for 30min until all particles are removed. The samples are grown using the confinement controlled

Fig. 3.1 demonstrates a transverse scan of a graphene sample at grazing angles. The inset shows the geometry of the measurement.

sublimation (CCS) method [17,61]. A sample is placed inside the CCS graphite crucible, (0001) face up. After a short out-gassing period ($T < 700$, 15 minutes), the samples are annealed at $T=1200$ C for 15 minutes to stabilize SiC step flow. Samples grown at $T=1450$ C for 2 hours achieve a 10+ layer thickness. Layer formation slows significantly after 13+ layers as the furnace builds up a SiC crust. To grow more than 20 layers of graphene on the C-face, requires the sample to be removed and the furnace to be cured at 1400C for ~20 minutes before reinsertion of the sample for an additional growth cycle; usually 4 or 5 cycles to achieve 30+ graphene layers. The samples studied here contained nominally between 15 and 100 graphene layers.

3.2.2 - X-ray Scattering

The x-ray scattering measurements were performed using a rotating anode x-ray generator with a line beam from a Mo target. A Ge(111) monochromator was used in conjunction with a slit to produce a high-resolution beam containing only $\text{MoK}_{\alpha 1}$ radiation with a wavelength of $\lambda = 0.70926 \text{ \AA}$. In the scattering plane the beam width was 0.12 mm with an angular divergence of 0.003° . The angular divergence out of the scattering plane was several degrees.

Two types of measurements were performed. Near grazing angles data were collected for a fixed 2θ by rotating the sample through the angle ω in order to obtain the full transverse lineshape that contains both the specular and diffuse scattering. The scattering geometry is shown in the inset to Fig. 3.1. The results of these measurements (XRR) are then summarized by plotting either the specular intensity or the integrated intensity versus the wavevector transfer perpendicular to the surface, $q_z = 4\pi\sin(2\theta/2)/\lambda$. Reflectivity is obtained by making a beam footprint correction and normalizing the result below the critical angle to unity. The reflectivity is modeled using the Parratt method through the ReFlpak software [62] where least-squares fitting can be used to determine the scattering length density (SLD), the thickness, and an error-function-shaped interface roughness, for the desired number of layers.

We also measured extended-range x-ray specular reflectivity (EXRR) which encompasses higher angles that include the Bragg reflections from both the stacking of the graphene layers and the SiC substrate. The diffuse background was obtained by using linear scans at a constant angular offset angle from the specular condition and it was subtracted from the on-specular data. A slight miscut angle between 0.01-0.03 was typically observed

(and accommodated in the scans) when comparing the specular condition at grazing angles versus the Bragg reflections. EXRR data are plotted in reciprocal lattice units (rlu) of SiC, l , where $l = q_z c_{\text{SiC}} / 2\pi$ and $c_{\text{SiC}} = 10.0848 \text{ \AA}$ for 4-H SiC. Bragg peaks for bulk SiC are expected at $l = 4n$ ($n = 1, 2, 3, \dots$) and approximately around $l = 3m$ ($m = 1, 2, 3, \dots$) for graphene. A list of samples, their thicknesses (from XRR unless otherwise noted), the measurements done on those samples, and their domain size is given in Table 3.1.

3.2.3 - Neutron Reflectivity

Neutron reflectivity (NR) data was obtained on the reflectometer, BL-4A, at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The SNS a pulsed source optimized for time of flight measurements, allowing for a range of q_z to be measured at a fixed sample angle. Data was collected on a two-dimensional position sensitive detector at room temperature. The data were reduced by integrating a region of interest on the detector along $q_{\parallel} = 0$ and subtracting a neighboring parallel region of interest in order to produce the specular line.

3.2.4 - Transmission Electron Microscopy

Transmission electron microscopy (TEM) was collected by Dr. X. He at the University of Missouri from cross-sections of samples that were prepared using a lift-out method in a focused ion-beam scanning electron microscopy (FEI Scios Analytical). A 100nm thick Pt layer was deposited by a 2kV electron beam to protect the graphene thin film prior to gallium ion beam exposure. Great care was taken to reduce the Ga ion beam damage and implantation to the graphene thin film by progressively reducing the beam energies and currents in the cleaning cross section mode as the sample gets thinner. The

sample cross-sections were then transferred to a 300 kV TEM for imaging. The primary electron beam is incident on the cross-section perpendicular to the surface direction.

3.2.5 - Angle Resolved Photoemission Spectroscopy

ARPES by Dr. Bian's research group at the University of Missouri and was performed using SPECS Phoibos150 analyzer and 21.2 eV photons. The energy and angular resolutions are 20 meV and 0.1° respectively. The base pressure of the ARPES measurement was better than 2×10^{-10} Torr.

3.3 - Results

In order to investigate the structure of graphene on 4H-SiC, extended range (EXRR) and grazing angle (XRR) x-ray specular reflectivity was utilized on multiple (8-10) samples. One sample from these was chosen for neutron reflectivity (NR) investigation.

3.3.1 - Grazing Angle X-ray Reflectivity

Specular reflectivity contains structural information related to the scattering length density (SLD) and how it varies (roughness, σ) across the interfaces of layers in the material being studied. In samples where large surface or interface roughness is present, the extraction of the specular component requires care and the issue is twofold: with increasing q_z , interface roughness causes the specular reflectivity to decrease while the diffuse scattering increases. The experimental sensitivity to the diffuse scattering also depends on the lateral length-scale of the roughness that causes it. In order to distinguish the specular and diffuse components, transverse scans must be performed at each q_z , as illustrated in Fig. 3.1 where several features can be observed. In addition to the specular component (red) at $\omega = 0$ and a nearby diffuse component (blue), Yoneda [63] peaks (blue and green)

Fig. 3.2 shows the reflectivity for three samples (a-c). The dashed curve in (b) is a fit using only a two-layer model. (d-f) show the SLD profiles for each of the corresponding profiles in (a-b). The lines in (d) represent the different roughnesses at the surface and buried interface of SiC/graphene.

arise from an enhancement of the diffuse scattering when either the incident or outgoing beams is near the angle for total reflection. These components are determined by least-squares fitting of the data to a model where the specular peak is taken as a Gaussian lineshape with a resolution-limited fixed width while the other peaks are taken to be Lorentzian lineshapes. The specular reflectivity, shown for three samples in Fig. 3.2(a-c), is generated by using this method to extract the specular component.

The XRR data, shown in Fig. 3.2(a-c), generally exhibit a sharp drop in reflectivity near the critical angle of SiC followed by a weak oscillation due to the graphene film. In

Table 3.1	$t_{Gr}(\text{\AA})$	Measurements	Domain Size ($\text{\AA}$)
C6MO2	66	XRD, XRR	8000
C6MO3	77	XRD, XRR	10300
C6MO4	66	XRD, XRR	10300
C4	200 (Raman)	TEM	
33MO6	94	XRD, XRR	6600
33MO7	73	XRD, XRR	6400
C4CE	76	XRD, XRR, NR	6800
C4DF	82	XRD, XRR	5700
P8	120	XRD, XRR	7400
C2	340	XRD, XRR	2900
C4DE	121	XRD, XRR	8300

Fig. 3.3 is a schematic representation of the 3-layer model used to fit specular reflectivity data. The labeled parameters are discussed in the text.

order to model the specular reflectivity data it was found that three layers were required, one each for the graphene and the semi-infinite substrate as well as a third “transition layer” in between, as shown schematically in Fig. 3.3. A simpler model involving only two layers (graphene and SiC) failed to accurately describe the data for most samples, yielding an oscillation that was too strong and with too much intensity after the critical angle, as demonstrated by the dashed curve in Fig. 3.2(b). This problem was remedied by adding the transition layer, which effectively enabled the introduction of a broader interface between

Fig. 3.4 compares the graphene and surface and buried interface roughness obtained from XRR. The solid lines are linear fits to the data.

the graphene and the SiC. In a minority of samples, a transition layer was unnecessary and a two-layer model was suitable. Adding a fourth layer did not improve the quality of fit.

Fig. 3.2(d-f) shows the resulting SLD profiles as a function of depth, which reveal the large broadening of the graphene/SiC interface. The general shape of the profile is similar for all samples studied, with no sharp transitions defining the film because of the large roughness at the buried interface. Typically, we can identify two distinct slopes, a larger slope associated with the graphene surface and a smaller slope due to the buried interface (“1” and “2”, respectively, in Fig. 3.2(d)), indicating that the roughness of the buried interface is much larger than at the graphene surface.

This trend becomes more dramatic as a function of graphene thickness, as demonstrated in Fig. 3.4, where we have quantified the large broadening of the buried interface by defining a “total substrate roughness”, $\sigma_{sub} = \sigma_T + t_T + \sigma_{SiC}$. It can be seen that as the sample thickness increases, the roughness at the buried interface (σ_{sub}) grows at 2.5 times the rate of the surface roughness of the graphene film (σ_{Gr}). This result is consistent with the stoichiometry of the sublimation process that consumes 3.14 SiC layers (7.9Å) or

every graphene layer produced ($3.37\text{\AA}$), which amounts to ~ 2.4 times the thickness of SiC for every graphene layer.

3.3.2 - *Grazing-Angle Neutron and X-ray Reflectivity: Integrated Reflectivity*

In order to further investigate the composition of the transition layer that was observed by specular x-ray reflectivity, neutron reflectivity was performed because of its sensitivity to the nuclear SLD that provides different contrast to x-rays. In particular, the neutron scattering length for C is larger than for Si whereas the relative size of these scattering lengths is reversed for x-rays. Fig. 3.5(a) shows the NR for a sample having 20 atomic layers of graphene and it can be seen that the reflectivity decays very slowly with q . For comparison, the x-ray specular reflectivity measured on the same sample is shown by the open blue circles in Fig. 3.5(b) where it exhibits a strong precipitous decay with q . The dramatic differences in the q -dependence of the specular XRR and the NR cannot be explained by the composition of the SLDs; rather, the difference can be attributed to the unavoidably lower $q_{\parallel}$ resolution in the neutron reflectivity measurement as compared with the x-ray measurement. Interestingly, as we will show, this effect has implications well beyond instrumental: the significantly different shape of the reflectivity curves reveals important new information about the *lateral* length scale of the roughness at the buried interface.

Because of the lower $q_{\parallel}$ resolution in the NR measurement, we compared the NR and XRR by transversely integrating the x-ray reflectivity along $q_{\parallel}$ over both the specular and diffuse peak (see Fig. 3.1). The result is shown by the open black circles in Fig. 3.5(b) and it is apparent that the q -dependence of the integrated x-ray reflectivity behaves quite differently than the specular reflectivity, where the integrated reflectivity persists to much

Fig. 3.5 shows the grazing angle total reflectivity of both x-ray (b) and neutron (a) measurements of a 20 layer sample. The solid curves are a fit to the model discussed in the chapter. In panel (d) the blue line is the profile fit to the specular reflectivity.

higher q . In fact, *both* the integrated x-ray reflectivity and the neutron reflectivity, which is instrumentally integrated, behave similarly and their persistence to higher q indicate the presence of a much sharper interface than was determined from the specular x-ray reflectivity.

Furthermore, the integration along $q_{\parallel}$ samples shorter lateral length scales. Therefore, this sharper interface occurs on a much shorter lateral length-scale than the large roughness that was determined by the specular reflectivity of Fig. 3.2, which samples a much longer lateral length-scale. The integrated x-ray and neutron reflectivity in Fig. 3.5 were co-refined using a model that required the physical structure and compositional

Fig. 3.6 shows the extended x-ray reflectivity data (black open circles) and corresponding fitted model curves (red line) for three samples.

densities (g/cm^3) of the layers of the sample to be identical for both measurements. Because of the spatially abrupt feature now expected in the structure, we found that an additional transition layer was required in the model (four layers) in order to produce a sharp interface. Five layers did not improve the quality of the fit. The fit and resulting SLD profiles are shown in Fig. 3.5. From the profiles the integration of the diffuse scattering now resolves a narrow interfacial structure (roughness $< 2.5\text{nm}$). This narrow feature was determined to be between the graphene layer and transition layer: the green line in Fig. 3.5(b) shows that requiring the sharp interface to be on top of the film did not accurately describe the data. Several samples were studied using x-ray integrated reflectivity, although only one (C4CE) was studied with both x-rays and neutrons.

Fig. 3.7 is a schematic of the model used to describe EXRR data. The epitaxial graphene layer is separated into two sections: a very thin expanded d-spacing bottom portion and a bulk portion.

3.3.3 - Extended-Range X-ray Reflectivity

X-ray reflectivity was also measured over an extended range (EXRR) of q_z , where the larger values of q_z have two important consequences: the measurements probe interatomic distances in the direction perpendicular to the surface and there is intrinsically a larger lateral integration of $q_{||}$ which, according to our grazing angle reflectivity results, should observe flatter interfaces at these shorter lateral length-scales. EXRR data was collected for two orders of SiC reflections and two to three orders of graphene reflections, depending on the sample. A representative subset of the results is shown for three samples in Fig. 3.6 where q_z is given in 4H-SiC reciprocal lattice units (rlu), 1.

The EXRR data was analyzed using a structural model that is illustrated schematically in Fig. 3.7. In order to fit the data, it was necessary to allow for two vertically stacked graphene layers on top of the carbon-terminated C-face 4H-SiC. A thin graphene

bottom layer, “B”, with N_B atomic sheets with a slightly expanded inter-planar spacing d_B^{Gr} is located near the SiC substrate while the majority of the graphene resides in the “T” layer having N_T atomic sheets with inter-planar spacing d_T^{Gr} .

The reflectivity in the kinematic approximation is obtained by adding the contributions of each layer:

$$R_{Spec}(l) = \frac{4c_{SiC}^2 r_e^2}{l^2} \left| \rho_{SiC}^A \frac{F_{SiC}(l)}{1 - e^{-i2\pi l}} + \rho_G^A A_G^B(l) + \rho_G^A A_G^T(l) \right|^2 e^{-4\gamma_{SiC} \sin^2(\frac{\pi l}{2})} \quad (3.1)$$

where r_e is the classical electron radius, ρ_G^A and ρ_{SiC}^A are the atomic areal densities for graphene and SiC, respectively. γ_{SiC} relates to half-unit-cell surface steps of the 4H-SiC [60] and our analysis finds very small values between, 0.05 and 0.15, consistent with the very smooth interface that we discuss below. The first term in eq. 3.1 arises from the semi-infinite SiC substrate, where F_{SiC} is the 4H-SiC structure factor. $A_G^B(l)$ and $A_G^T(l)$ are the amplitudes from the two graphene layers shown in Fig. 3.7. A detailed discussion of these amplitudes and the model for EXRR is given in the final section of this chapter.

Fig. 3.8 shows fits to the angular width of the graphene Bragg peaks vs. wavevector. The solid curves determine domain size by the equation discussed in the text.

It was necessary to include a small amount of disorder through a root-mean-square (RMS) fluctuation of the inter-planar distance between the atomic sheets of graphene, Δd_{Gr}^B and Δd_{Gr}^T , for the bottom and top graphene layers, respectively. The number of atomic graphene sheets, N_B and N_T for the bottom and top graphene layers, respectively, also exhibit fluctuations and these were modeled as a binomial distribution with corresponding roughness values of σ_B and σ_T . In the case of the top layer, additional height distributions were required to describe σ_T , as discussed at the end of this chapter. The thermal Debye-Waller factor at room-temperature for graphite is expected to be 0.05-0.095 $\text{\AA}$ [64] which is comparable to Δd_{Gr}^T for our samples, but Δd_{Gr}^B was found to be larger, indicating more disorder near the graphene/SiC interface.

The graphene lateral domain size, L , of the film can be determined from transverse scans (rocking scans, as shown in the inset of Fig. 3.1) performed at the graphene Bragg positions. Unlike at grazing angles, the specular width is not resolution-limited and the

Fig. 3.9 shows high resolution TEM images of 60L samples. In (a) the graphene/SiC interface is shown. In (b) a SiC step is shown where the graphene film follows the substrate step. In (c) a defect Si “volcano” site is seen.

broadening is due to the finite crystalline domain size (laterally) of the graphene. It can be shown that transverse angular width $\Delta\omega$ will vary as a function of q_z according to $\Delta\omega = [(2\pi/q_z L)^2 + \eta^2]^{1/2}$ where a mosaic-like rotational disorder η is included [65]. The results are illustrated in Fig. 3.8 for three samples and this method was used to determine the graphene domain sizes for all samples. The graphene domain sizes vary between 0.5-1.0 μm .

3.3.4 - Cross-Sectional Transmission Electron Microscopy

Electron microscopy provided additional insight into the local buried interface structure. Representative high-resolution TEM (HR-TEM) images for a sample (C4, not studied by x-rays) having 60 layers of graphene are shown in Fig. 3.9. In Fig. 3.9(a) it can be seen that the graphene layers exhibit a wavy structure, particularly in comparison to the atomically uniform planes of the SiC. The RMS variation of these graphene planes is much larger than the Δd_{Gr}^T determined from any of the EXRR measurements, indicating some disruption of the graphene atomic planes during the sectioning of the sample for the TEM measurements. Beam damage has also been reported in prior TEM measurements by Colby et. al on similar samples [66]. The EXRR measurements give a global quantitative

indication of the RMS fluctuations without perturbing the sample and it is noted that the lateral crystalline domain size of the graphene found by x-ray diffraction is much larger than the field of view of the TEM image. One can see a thin graphene layer adjacent to the SiC substrate with a thickness that is consistent with the NB values observed in the EXRR measurements. It is also observed in Fig. 3.9(a) that the SiC/graphene interface is abrupt on the atomic scale. Nevertheless, as observed in Fig. 3.9(b), large steps on the order of 10nm in height can be observed at the interface, disrupting an otherwise atomically flat interface between graphene and the SiC substrate. Here it can be seen that the graphene film follows the contour of these large step edges of the substrate. In addition, local defects as in Fig. 3.9(c), which have been previously identified as vents for the escape of Si during the sublimation process, can also be found [67]. These results support the interpretation of the specular XRR and the EXRR measurements: the former averages lateral length-scales on the order of 50 μm and finds very broad interfaces that are several tens of nm in height whereas the latter averages $<5\mu\text{m}$ laterally and observes much sharper interfaces. However, the limited field of view of microscopy makes it difficult to understand the frequency of occurrence of these features and their overall contribution to the interface roughness.

3.4 - Discussion

These results show that the buried interface between graphene and C-face SiC exhibits a complex behavior that is manifested on two lateral length scales along the interface. At shorter length scales there is an atomically abrupt transition between the SiC and the graphene layer whereas the interface displays extensive roughness over much longer lateral length scales. Below, we discuss the interpretation of these results. In particular, an important aspect of this investigation is that it also demonstrates how such

information can be obtained by x-ray and neutron reflectivity measurements. Most studies that utilize reflectivity do not carefully consider the implications of diffuse scattering. Here, however, we find that the diffuse scattering informs both the interpretation of interfacial structure as well as how to analyze the reflectivity data so that this investigation can be useful for a broad range of materials systems that have complex interfaces.

The x-ray specular reflectivity (XRR) measurements performed at grazing angles reveal a very rough buried interface between graphene and the SiC, as observed in Fig. 3.2. The width of this interface grows proportionally to the thickness of the graphene that is produced (see Fig. 3.4), indicating that the origin of the roughness is from the growth process itself. Indeed, it takes [16] more than three atomic layers of SiC to produce one atomic layer of graphene so that the interface roughness is driven by the sublimation of Si. This effect is significant, and the buried interface width can be *larger* than the total thickness of the graphene that is produced. By comparison, the surface roughness of the graphene (Fig. 3.4) is nearly three times smaller, suggesting that the roughness at the buried interface is driven by the lateral variations in the local growth rate. The lateral length-scale over which this interface roughness is observed can be estimated from the relatively high reciprocal-space resolution of these measurements: at $q = 0.1 \text{ \AA}^{-1}$ the measurements of the specular reflection average about $50 \mu\text{m}$ laterally. Over this distance many asperities can be encountered at the buried interface, such as large steps and Si vents, as seen by HR-TEM in Fig. 3.9 (b) and (c), so that these sublimation-induced features are expected to be responsible for the large roughness observed at the buried interface.

In stark contrast, x-ray reflectivity measured over an extended angular range that includes Bragg reflections (EXRR) reveals an atomically abrupt interface between the

Fig. 3.10 shows the width of the diffuse scattering peak compared to the perpendicular wavevector transfer for a 55 layer sample. The solid curve reveals an average terrace width of 650nm from best fits to the data.

graphene and the SiC (see Figs. 3.6 and 3.7). The reason for this result relates to *both* the specific nature of the disorder at the buried interface and to the lower reciprocal-space resolution in EXRR measurements as compared to specular XRR.

To better understand this point and the structure of the buried interface, it is useful to look more closely at the XRR measurements. Central to this issue is a diffuse scattering peak that appears near the specular reflection in Fig. 3.1, which generally arises from laterally-correlated interfacial disorder [63]. A plot of the width of this diffuse scattering peak, $\Delta q_{\parallel}$, versus q_z for a sample with 55 layers of graphene is shown in Fig. 3.10. It reveals a curve having a shape that is well-known to arise from a random distribution of flat terraces. A fit to a model [68] yields the average length of a flat terrace to be 650nm. Therefore, we would expect large flat regions to exist despite the XRR results in Figs. 3.2 and 3.4 that indicate a very broad buried interface. This apparent contradiction is resolved

Fig. 3.11 shows the abrupt interface in the density profile, detailing the Si and C density extracted from the x-ray and neutron reflectivity co-refinement.

by integrating both the specular and diffuse component when compiling the XRR data, which was done in Fig. 3.5(b). As can be seen, the integrated XRR leads to a sharp buried interface in the scattering-length-density profile in Fig. 3.5(d) as compared to the profile of the broad buried interface that was obtained using only the specular component. By including the integrated diffuse component, the reflectivity then measures the SLD over a lateral length-scale that is *shorter* than the length of a flat terrace, thereby giving a sharp interface.

This new understanding of the diffuse scattering allows us to interpret the neutron reflectivity results in Fig. 3.5(a) and (c). Because the lateral resolution in the neutron reflectivity measurement was much poorer than for the x-ray measurement, the diffuse scattering from the terraces, which appears very near the specular reflection, is unavoidably integrated in the neutron measurement. Therefore, the SLD profile (Fig. 3.5(c)) obtained from the neutron measurement exhibits a sharp buried interface just as in the integrated XRR measurement.

Having confidence in the similarity of the integrated XRR and the NR data allowed us to perform a co-refinement of both data sets, which yielded the SLD profiles shown in Figs. 3.5(c) and (d). We are also able to directly obtain the composition of C and Si from this analysis. It is noted that from a single SLD profile we do not know the relative contributions of C and Si to the SLD because we do not know the densities of each element, ρ_C or ρ_{Si} , respectively. However, having *both* the x-ray and the neutron data with the co-refinement allows us to solve for these densities using the known scattering lengths for these elements, b_C^X and b_{Si}^X for x-rays and b_C^N and b_{Si}^N for neutrons. The SLD is comprised of both elements according to:

$$SLD_{Neutron} = b_C^N \rho_C C + b_{Si}^N \rho_{Si} \quad (3.2)$$

$$SLD_{X-ray} = b_C^X \rho_C C + b_{Si}^X \rho_{Si} \quad (3.3)$$

The result of using both SLD measurements to obtain the densities of the atomic species is shown in Fig. 3.11, where it can be seen that there is a remarkably sharp interface between the graphene and the SiC substrate (which is essentially represented by the Si density). The slight variation of the Si density in the substrate is an artifact of not integrating additional diffuse scattering from the short length-scale asperities at the interface that we know are present from the very large roughness in the specular XRR and which also appear in the TEM (e.g. Fig. 3.9(b) and (c)). This diffuse scattering will be very broad in angle; for example, it is that diffuse scattering which gives rise to the Yoneda scattering in Fig. 3.1 and it is, therefore, impractical to capture all of the intensity. In our analysis, that diffuse scattering contribution has been subtracted out from our integrated XRR.

Understanding the origin of the diffuse scattering also allows us to explain why EXRR measurements reveal an atomically abrupt buried interface rather than the highly

rough interface found from grazing-angle reflectivity. Because the EXRR measurements are performed at higher q_z , they intrinsically have a lower lateral resolution in reciprocal space where the diffuse component is more easily integrated during the measurement; therefore, EXRR measurements represent the atomic scale structure relative to the long and flat terraces rather than the structures that lead to a large roughness. For example, previous synchrotron EXRR measurements on substantially thinner graphene films report atomically abrupt interfaces with a slight carbon enrichment of the first three SiC layers at the interface [60]. These sharp interfaces are measured despite the fact that the x-rays irradiate a macroscopic sample having large interface roughness. Other measurements, such as HR-TEM can select regions that show near perfect interfaces, however, electron microscopy does not have the field of view to put the various features found in Fig. 3.9 into context. We have shown here that understanding the step structure allows us to use different measurements (XRR, NR, EXRR) to tie the vastly different aspects of this complex buried interface together.

Interestingly, the step structure appears not to change with extensive sublimation. A synchrotron x-ray scattering study on much thinner epitaxial graphene films on C-face SiC (7 times thinner) has observed diffuse scattering nearly identical in shape and magnitude to that shown in Fig. 3.10 [19]. This similarity indicates that the step structure is intrinsic to the SiC and it does not significantly change upon sublimation; rather, it is the size and/or number of surface asperities that increases with longer sublimation times in order to produce the highly rough interface while the atomically flat regions are left intact, although, there will be fewer of them as the graphene film thickness increases.

Fig. 3.12 shows ARPES taken from a 20 layer graphene sample. The measurement geometry is shown in the inset. The spectrum is taken through the K point in the graphene Brillouin zone signaled by the solid red line of the inset.

Our study also reveals important aspects of the thick epitaxial multilayer graphene that were not apparent in previous studies of thinner graphene layers. From EXRR fits it was revealed that the first 1-2nm of graphene layers near the interface with SiC have a slightly expanded interlayer spacing compared to the majority of the layers away from that interface, $d_B^{Gr} > d_T^{Gr}$. Interestingly the value of d_B^{Gr} , which exhibits variations among samples, extends to a range which is comparable to turbostratic graphite ($d = 3.440\text{\AA}$) and thus suggests stacking disorder close the interface where the most recently formed graphene exists. It seems that this disorder anneals away during the growth of more graphene from below as the majority of the graphene exhibits consistent values of d_T^{Gr} among samples of different thicknesses. This results is also consistent with previous studies

done on thinner graphene films on C-face 4-H SiC where the graphene interlayer spacing was found to be slightly larger than for graphite (3.354Å) because of epitaxial multilayer graphene's stacking rotations (which are different than graphite) [60]. Our model for the EXRR data allows for RMS variations of the interlayer spacing where we find that Δd_B^{Gr} is typically significantly larger than Δd_T^{Gr} , which was found to take on the thermal value. Therefore, this result also suggests more disorder in the several layers of graphene near the substrate. That the high structural quality of the top graphene layers is preserved can be seen in an ARPES measurement shown in Fig. 3.12, where the Dirac cone can be observed, indicating the non-graphitic stacking of graphene on C-face SiC [18].

3.5 - Summary

In summary, we have found that there are two length-scale regimes that characterize the buried interface of epitaxial multilayer graphene grown on C-face 4H-SiC. On long length scales, a very large roughness develops at the buried interface growth front in proportion to the graphene thickness, which is due to the sublimation of Si. However, the interface is atomically abrupt on shorter length scales due to the intrinsic flatness of SiC terraces which are preserved during the growth of multilayer graphene. We showed that the existence of these two length scales is manifested in the nature of the diffuse scattering that is present in reflectivity measurements and by carefully considering these effects we showed that we could employ complimentary x-ray and neutron reflectivity to obtain the composition profile of C and Si at the buried interface. In general, diffuse scattering is usually not carefully considered in reflectivity measurements and our results show that the conclusions drawn from such data can depend critically on how the diffuse scattering is

handled. The lessons learned in this study will be valuable for informing other studies of complex interfaces that are present in many material systems of interest.

3.6 - EXRR Modeling

Here we describe the details of the amplitudes appearing in eq. 3.1, which result from the different layers shown in the schematic diagram of Fig. 3.7. The first term represents the amplitude arising from the semi-infinite C-face 4H SiC substrate whereas $A_G^B(l)$ and $A_G^T(l)$ are the amplitudes arising from the bottom and top graphene layers, respectively.

The amplitude of a graphene film is constructed from the basic form of the amplitude for a disordered thin film, as described elsewhere [69]:

$$A = \psi \frac{\xi - 1}{\psi - 1} \quad (3.4)$$

where ψ is an average phase factor $\langle e^{iqd} \rangle_d$ from a distribution of interlayer spacings of graphene, d . Here, we will assume a Gaussian distribution of these spacings,

$$\psi = e^{-2(\pi l \Delta d)^2 / c_{SiC}^2} e^{i2\pi l d / c_{SiC}} \quad (3.5)$$

where Δd is the width of the distribution of d -spacings. The fluctuation in the graphene film thickness is described by a binomial distribution of M discrete layers so that,

$$\xi = \left(\frac{N}{M} \psi + \left(1 - \frac{N}{M} \right) \right)^M \quad (3.6)$$

where N is the average number of layers in the film and the variance of the layer height-distribution is given as $S^2 = N(1 - N/M)$. In the present case, we find that the graphene films are in the Poisson limit where M tends to infinity and $S^2 = N$.

The amplitudes for the bottom and top graphene layers are then constructed from eq. 3.4 using $d = d_T^{Gr}$ or d_B^{Gr} and Δd_T^{Gr} or Δd_B^{Gr} for the bottom and top graphene layers, respectively, for ψ and ξ . For the bottom graphene layer,

$$A_G^B(l) = e^{i2\pi l d_{1st}^{Gr}/c_{sic}} f_C(l) \left(\psi_B \frac{\xi_B - 1}{\psi_B - 1} \right) \quad (3.7)$$

where $f_C(l)$ is the atomic form factor of carbon. d_{1st}^{Gr} accommodates the phase shift due to the distance of the first graphene layer from the substrate. Because our EXRR measurements had limited data in between the Bragg positions, our measurements were relatively insensitive to d_{1st}^{Gr} . This value was found to vary between 1.6-3Å, giving a contraction in the first layer that is consistent with other studies [60].

The top layer was constructed similarly except that a larger film thickness fluctuation was required, and we used a weighted average of three distributions of graphene layers,

$$A_G^T(l) = e^{i2\pi l d_{1st}^{Gr}/c_{sic}} f_C(l) \xi_B \psi_T \left(\sum_{n=1}^3 g_n \frac{\xi_n - 1}{\psi_T - 1} \right) \quad (3.8)$$

where g_n describes the weighting of the distributions subject to $\sum_{n=1}^3 g_n = 1$. ξ_n depends on one of three possible layer heights, N_n , with $n=1, 2, 3$. The average total thickness of the graphene film is $\bar{N} = N_B + \sum_{n=1}^3 g_n N_T^n$. Because of the Poisson limit, $\bar{N}$ is also the total variance so that the graphene roughness is given as $\sigma_{EXRR} = \sqrt{\bar{N}}d$.

All parameters in the model were allowed to refine using nonlinear least squares fitting. The resulting fits for three samples are represented by the red lines in the plots in Fig. 3.6. In the analysis, Δd played an important role, both in diminishing intensity oscillations at the graphene Bragg reflections as well as in accounting for the intensity ratios between different orders of reflections. Careful consideration of each of the

Fig. 3.13 shows best fit (red curves) for data from sample 33MO6 (symbols) compared to constrained fits (blue curves). These show the first, second, and third graphene Bragg reflection from left to right. The constraints are discussed in the text.

parameters of the model were required and these are explored in Figs. 3.13 and 3.14, where the need for these parameters were studied by applying constraints to the model and comparing to the best fit for sample 33MO6.

To explore the necessity of having a bottom graphene layer that is different than the top, a fit without a difference in these layers is shown in Fig. 3.13(a). Here ratio of intensities among different orders of reflection cannot follow the measured values while there are oscillations (fringes) that are too large in amplitude. In Fig. 3.13(b) it can be seen that allowing the Δd of the two layers to be different (while still requiring their d values to be the same) makes a significant improvement in the quality of fit. However, further

Fig. 3.14 shows best fit (red curves) for data from sample 33MO6 (symbols) compared to constrained fits (blue curves). These show the first, second, and third graphene Bragg reflection from left to right. The constraints are discussed in the text.

significant improvement (red curve in Fig. 3.13(b)) is obtained by allowing the presence of a thin and slightly expanded graphene layer that accommodates the intensity shoulder towards lower q .

We also determined that the expanded thin graphene layer appears at the bottom rather than on the top of the thicker graphene layer. Fig. 3.13(c) shows that if the thin expanded layer is on the top, there is an overestimation of intensity in the tails of the Bragg reflections. This problem does not occur when the thin layer is on the bottom because $\Delta d_B^{Gr} > \Delta d_T^{Gr}$ Gr allows for a greater attenuation of the top layer intensity arising from the factor ξ_B in eq. 3.8.

We determined that the thin and thick graphene layers cannot be laterally located next to each other, with both starting at the substrate rather than being vertically stacked as in Fig. 3.7. This case is shown in Fig. 3.14(a) where, similar to what occurs in Fig. 3.13(c), there is too much intensity in the tails of the Bragg reflections because of the lack of attenuation coming from ξ_B (with $\Delta d_B^{Gr} > \Delta d_T^{Gr}$) that would now be absent from eq. 3.8.

Correctly describing the height distributions of the graphene layers was vital for capturing the shape of the graphene Bragg reflections. Fig. 3.14(b) shows a fit with a perfectly uniform ($N = M$) bottom layer while maintaining the height distribution of the top layer obtained from a best fit. While this seems to work for the low order reflections, the third order intensity is significantly in error and the effect of having a smooth interface between the bottom and top layers is more subtle. It turns out that in order to compensate for a smooth interface in the bottom layer, the modified fit (blue curve) required larger Δd_B^{Gr} (it also affects peak shape) in the bottom layer which then causes too much attenuation at the higher order Bragg reflections. A good fit (red curve) was obtained in the Poisson limit ($M \gg N$) so that the bottom layer roughness is given by $\sigma_B = \sqrt{N^B}d$.

The height distribution of the top graphene layer plays a dominant role in the shape of the Bragg reflections. In Fig. 3.14(c) the importance of multiple height distributions in fitting the data is demonstrated, where it can be seen that a single Poisson distribution cannot adequately describe the data. In particular, strong oscillations occur in the model that are not present in the data. Using three distributions, as given in eq. 3.8, removes these oscillations.

4 – Atomic Deuteration of C-face Graphene on 4H SiC

Given the promising results [13] from graphene treated with atomic hydrogen, which showed ferromagnetism at room temperature, we aimed to reproduce the magnetic graphene sample from the literature to study with polarized neutron reflectivity. This would allow us to resolve where the magnetism was arising from, definitively answering the question with regards to the role of the buried interface in the induced moment. In this study we show that while we do not observe magnetism, a marked change in the buried interface occurs upon atomic deuterium exposure on C-face grown many-layer graphene. These results, reproduced from our recent publication [70], are presented in Chapter 4.

4.1 - Introduction

Graphene has generated considerable excitement in the scientific community because of its linearly dispersing electronic bands that lead to novel properties, including extremely high electron mobility [1]. Graphene can be grown epitaxially by sublimation of Si on either the Si-face or C-face of 4-H SiC [16,45,71]. Graphene grown on the C-face of 4-H SiC has multiple rotational stacking orders which allows for the growth of many non-interacting graphene sheets [18] in contrast to the AB stacking observed on Si-face films [56]. With the very recent discovery of a large band-gap semiconducting form of graphene on SiC substrates [2,3], there are new possibilities for graphene-based electronics.

The influence of the interface between epitaxial graphene (EG) and SiC has been shown to play a key role in the electronic properties of graphene, namely on the Si-face where intercalation of hydrogen is shown to create a “quasi-freestanding” graphene layer

with improved mobility [34,58,72,73]. In this case, the H₂ is thought to break bonds of Si-C between the substrate and the carbon “buffer”, which otherwise passivates Si dangling bonds from the substrate [34]. Additionally, chemical functionalization and defects in graphene change its behavior, with the potential to create magnetism [13,22,74], become insulating, modify the wetting properties [75], and change the optical characteristics of the film [11]. Functionalization and the ability to utilize highly ordered graphene on substrates for device integration are vital to the future success of graphene-based electronics.

While there has been interest to understand the structure and interface of C-face EG/SiC [60], little work has been done to modify or functionalize it. In order to exploit the possibility of decoupling the high-quality C-face EG/SiC from the substrate we investigate the use of atomic deuterium as an avenue both to functionalize graphene and passivate the buried interface.

4.2 - Experimental Methodology

4.2.1 - Sample Growth and Treatment

Epitaxial graphene was grown on C-face 4H-SiC by SiC decomposition using the confinement controlled sublimation (CCS) method described by de Heer *et al* [17]. For studies showing reversibility of atomic deuterium treatment of samples, chemical vapor deposition (CVD) growth of single layer graphene on copper was used [76]. These samples were transferred to SiO₂/Si substrates for Raman measurements.

Atomic deuterium treatment was performed using 1 mTorr of D₂ exposed to a tungsten filament that was heated to 1500°C in order to crack the molecular deuterium. Treatment was done at room temperature for exposure times of 15 minutes. In order to

minimize damage, the sample prepared for XTEM was treated for 10 minutes rather than 15 minutes. Annealing of samples after treatment was done in a vacuum furnace at 1000°C, where we expect hydrogen to leave the graphene sheet. This temperature is below the mobility of Si and C, where temperatures exceeding 1350°C are required to begin graphene growth and temperatures exceeding 1200°C are required to reconstruct the C-face surface of 4-H SiC [16].

4.2.2 - Raman Scattering

Raman spectra were obtained using an Invia Renishaw spectrometer measured at room temperature with 514nm laser in a confocal backscattered geometry. The laser power density for these measurements was $2.5 \times 10^4 \text{ W/cm}^2$ with an exposure time of 100 seconds. For the measurements on epitaxial graphene on SiC, all intensities were normalized to a bare SiC standard substrate in order to compare intensities of different samples taken at different times. These will be referred to as the “normalized intensity”.

4.2.3 - X-ray Scattering Measurements

X-ray measurements were performed on a rotating anode with Mo $K_{\alpha 1}$ radiation utilizing a Ge monochromator to produce a line beam having angular divergence of 0.003 degrees. Both grazing angle x-ray reflectivity (XRR) and diffraction (XRD) measurements were performed in the specular geometry (wavevector transfer normal to the sample surface). The specular component from XRD is obtained by subtracting a background (off-specular) scan over the same range in q_z where $q_z = (4\pi/\lambda) \sin(2\theta/2)$. XRR was taken by integrating the transverse lineshape at each q_z , where the specular component was extracted by simultaneous fit of diffuse and Yoneda [44,63].

4.2.4 - Cross Sectional Transmission Electron Microscopy

Cross-sections of samples were taken by Dr. X. He at the MU Microscopy Core using lift-out in focused ion-beam scanning electron microscope (FEI Scios Analytical). Great care has been taken to reduce the Ga ion beam damage and implantation to the graphene thin film by progressively reducing the beam energies and currents in the cleaning cross section mode as the sample gets thinner. The sample cross-sections were then transferred to a 300 kV transmission electron microscope for imaging. The primary electron beam is incident on the cross-section perpendicular to the surface direction. Conventional bright field high resolution TEM images (HRTEM) are taken at 300 kV with the sample oriented along [10-10] zone axis of 4H-SiC. Both samples we investigated are thin and around 25 nm according to the log-ratio method using the zero-loss peak and low energy loss peak in the EELS spectrum. The HRTEM images were taken close to the Scherer focus condition, which is about -72 nm. This study was done on a single 60L sample.

4.3 - Results and Discussion

4.3.1 - Raman Scattering

Raman scattering gives access to information regarding the carbon hybridization [77], defect density [41], and thickness of graphene samples [43]. The “G” ($\sim 1580\text{cm}^{-1}$) or graphite peak of the Raman spectra of carbon materials has been correlated with sp^2 type carbon that should be the only species in pristine graphene. The “D” ($\sim 1350\text{cm}^{-1}$) or diamond peak can be correlated with sp^3 hybridized defects in graphene [39].

Fig. 4.1 shows the reversibility of atomic deuterium treatment of single-layer CVD grown graphene via Raman scattering. The attachment and detachment of atomic D is indicated by the appearance and absence, respectively, of the D ($\sim 1350\text{cm}^{-1}$) peak relative to the G ($\sim 1580\text{cm}^{-1}$) peak. Black circles (bottom) are the untreated sample, red (middle) is the deuterated sample, and blue was annealed (top) after treatment.

In order to determine if atomic deuteration would affect our graphene/SiC samples, Raman measurements were first performed on CVD grown single-layer graphene. As shown in Fig. 4.1, the appearance of the D peak in Raman revealed that chemisorption of deuterium does occur upon atomic treatment and that the process is observed to be reversible, since the D peak disappears by annealing at high temperature.

Epitaxial graphene on SiC, in contrast to single layer graphene transferred to SiO_2/Si substrates, has additional peaks in the Raman spectra due to the SiC [78]. Raman spectra of a 78L graphene sample is shown in Fig. 4.2, where the D and G peaks are labeled in order to help distinguish them from the SiC related peaks. The subtracted Raman spectra (black dots) is obtained by subtracting a SiC spectra, normalized to the intensity of the SiC spectra from the graphene sample, from the raw graphene/SiC Raman data (blue dots).

Fig. 4.2 shows the raw (blue) and substrate-subtracted (black) Raman spectra of 78L graphene grown on C-face SiC. The G and D peaks of graphene are labeled and the subtracted data are shifted vertically for clarity. In the raw data, the graphene peaks appear in the presence of other features arising from the SiC substrate.

We analyzed the D peak intensity, which is indicative of the sp^3 bonding, in order to look at the effect of deuteration. In Fig. 4.3(a) the change in D peak intensity, ΔD , was obtained by subtracting the normalized D peak intensity measured before treatment from the normalized intensity measured after treatment. As can be seen, ΔD increases with the number of atomic layers of graphene, indicating that the number of incorporated deuterium atoms increases with the number of graphene layers. However, the increase with deuteration is rather small, as demonstrated in Fig. 4.3(b), where $\Delta D:G$ is the ratio of the D to G peak normalized intensities measured for the deuterated sample with the same quantity measured before deuteration subtracted. Since the G peak scales with the thickness of the graphene layers, the rapid decrease with thickness in Fig. 4.3(b) suggests that the attachment of deuterium is not occurring uniformly through the multilayer

Fig. 4.3 (a) shows the change in D peak intensity upon deuteration, ΔD . The increasing ΔD intensity with layer number indicates an increase in deuterium attachment with increasing graphene thickness. (b) shows the $\Delta D : G$ ratio, which is highest for thin samples and it suggests that atomic deuterium is not incorporating between the graphene layers.

graphene and it is likely to be attaching closer to the surface and/or buried interface. The latter is suggested because, as will be demonstrated in the next section on x-ray diffraction, deuteration strongly modifies the buried interface. The result of Fig. 4.3(b) clearly

indicates that the amount of deuterium incorporating in between the layers is not significant.

4.3.2 - X-ray Diffraction

In order to investigate the possibility of interlayer incorporation, XRD was used to investigate the graphene interlayer spacing (d-spacing) for the 78L and 35L samples. Fig. 4.4 shows data from the 78L sample, which demonstrates that there is no shift in the first order Bragg position, indicating that there is no expansion or contraction of the graphene d-spacing with exposure to atomic deuterium. Additionally, there are no changes in the

Fig. 4.4 demonstrates that there is no observable change in the first order graphene Bragg reflection that arises from the interlayer spacing of the graphene. The data is offset vertically for clarity and plotted in 4H-SiC reciprocal lattice units. Solid lines represent a best fit to a model described by Mazza *et al* [43].

shape of the Bragg peaks, as can be seen by comparing an identical solid curve (model obtained from ref. [32]) that is compared to each of the three data sets in Fig. 4.4. Therefore, atomic deuterium has no apparent effect on the x-ray diffraction.

4.3.3 - X-ray Reflectivity

XRR, which is sensitive to the vertical density profile of the sample but not its crystallinity, was also performed in order to investigate the graphene/SiC interface, as shown in Fig. 4.5. The data in Fig. 4.5 (a-c) were fit with a reflectivity model [79] using standard software [62] that describes the sample composition, layer thickness, and layer roughness for three layers. The layers of the sample are the graphene, the “transition layer” describing the SiC/graphene transition, and the SiC substrate. A schematic of the layer structure used to describe the model is shown in the insets of Fig. 4.5(d-f), where “T” corresponds to the transition layer. The scattering-length density (SLD) profiles obtained

from this analysis, Fig. 4.5(d-f), for three samples that were atomically treated with deuterium revealed that the interface between graphene and SiC changed dramatically. As can be seen there is a marked SLD decrease, as indicated by the arrows in Fig. 4.5(d-f). In all cases the graphene film does not change thickness with treatment, as was shown by x-ray diffraction in Fig. 4.4.

We interpret the change at the interface to be a signal of the initiation of graphene delamination from the SiC substrate. Given that the total graphene layer thickness does not change, as determined in Fig. 4.4, we note that the large density decrease at the interface in Fig. 4.5(d-f) cannot be explained by composition mixtures of graphene and SiC so that the result must be due to the opening of a nanoscale gap (within which we cannot confirm or exclude the presence of deuterium). Indeed, when samples were exposed to 2-3 cycles of atomic deuteration followed by annealing, the graphene film completely fell off the substrate. We note that this decoupling does not arise from thermal cycling because thick multilayer graphene films on SiC are stable even though they undergo several high temperature (>1400 C) thermal cycles during the growth process. This suggests that long exposure times to atomic H could be potentially useful for freestanding or (dry) transferrable graphene grown on C-face SiC. While it is known that H [34,58,72] and metals [80] can intercalate between few-layer graphene and the Si face of SiC, our present study using atomic deuterium demonstrates the first signs of complete decoupling of epitaxial graphene from the host substrate on C-face EG/SiC. These results show that XRR is a very sensitive indicator of the initiation of delamination of graphene from the SiC substrate.

Fig. 4.5 (a-c) show data for virgin (red triangles) and treated (black circles) samples as well as fits (red solid line for virgin and black solid line for treated) for each case. Panels (d-f) show the corresponding profiles for each of the samples both before (red solid line) and after (black dashed line) treatment. These profiles are offset such that the graphene layer starts at $z=0$. Three samples having different number of atomic layers of graphene were investigated: 78 layers in (a) and (d); 35 layers in (b) and (e); and 4 layers in (c) and (f). The arrows indicate the lower density at the graphene/SiC interface. A schematic of the sample layer structure for each of the samples is shown below each of the profiles with only the 78L sample having a 4 layer model to describe W on the surface.

The peak observed in Fig. 4.5(d) for $z < 0$ in the treated sample is due to a small amount of tungsten that was deposited onto the sample surface from the filament used to crack the D_2 gas. Tungsten was only measurable in this sample as it saw a long exposure time to the filament prior to atomic treatment. An additional layer was added to the reflectivity model, as shown in the inset, from which we estimate $\sim 20\%$ surface coverage

Fig. 4.6 shows XTEM of a 60 layer graphene sample (a) before and (b) after atomic deuteration. In panel (a) the white bar shows the sharp interface between graphene and SiC. In panel (b) the beginnings of sample delamination are shown between the white bars.

of tungsten islands (based on density) with a thickness of ~ 5 nm. The strong x-ray absorption of tungsten causes a slope of the reflectivity below the critical angle, which allowed an accurate determination of this layer without inhibiting the ability to characterize the graphene layer and the buried interface.

4.3.4 - Cross-sectional Transmission Electron Microscopy

In order to further investigate the delamination observed in XRR, XTEM was performed on a sample having 60 atomic layers of graphene. This sample was imaged both

before and after exposure to atomic deuterium. Before exposure, Fig. 4.6(a) shows that the interface between graphene and SiC is sharp and clearly visible on this length scale. However, the addition of deuterium causes a dramatic change at this interface. Fig. 4.6(b) shows the marked change that occurs after exposure to deuterium, evident from the region of lighter contrast and highlighted by the vertical white bars, where a significantly broader interface develops. Although the TEM is unable to identify the nature of this change, it indicates that the exposure to atomic deuterium causes a significant change at the interface. It also corroborates the x-ray reflectivity results, that are measured over a much larger (tens of μm) field of view than the TEM and are, therefore, able to detect the initial stages of delamination of the epitaxial multi-layer graphene from the SiC substrate.

4.4 - Summary and Conclusions

We have shown that atomic deuteration of graphene occurs at the surface, the buried interface, and at defect sites of epitaxial many-layer graphene on C-face SiC. While XRD revealed there was no interlayer incorporation of deuterium, XRR showed that the exposure to atomic deuterium did lead to a significant density reduction at the graphene/SiC buried interface, indicative of delamination of the graphene from the SiC substrate. Multilayer epitaxial graphene films are found to completely delaminate from the substrate after 2-3 cycles of atomic treatment, indicating a potential pathway to dry transfer of high-quality EG/SiC to other substrates for device integration.

5 – Structure of Low-energy Hydrogen/Deuterium Ion Implanted Graphene

Driven by results from atomic treatment of many-layer graphene, which exhibited no chemisorption of hydrogen between layers, we searched for a mechanism by which interlayer chemisorption of hydrogen could occur. This aim led to accelerating hydrogen ions, via conventional sputter gun, into the graphene/SiC samples. The implantation of hydrogen/deuterium exposes each graphene sheet to a distribution of hydrogen/deuterium atoms and it has been found from theory [6] and our prior work [70] that H/D atoms in proximity to a graphene sheet will lead to chemisorb onto the sheet [6]. Our work on structural characterization of low-energy H/D implanted graphene films is presented in Chapter 5.

5.1 - Introduction

Ion implantation in materials has been studied extensively, allowing for controllable substitutional doping of materials, surface cleaning, and nanopatterning of devices [81]. Using the experience of the semiconductor industry, carbon materials can similarly be modified to perturb the chemical, electronic and potential magnetic properties of samples.

Studies of ion implanted graphite have been done at high (exceeding 25kV) energies with hydrogen, helium, carbon, and argon ions [30,82–88]. Regarding hydrogen implantation, graphite was investigated because it is used in nuclear fusion devices due to its mechanical and thermal properties. These early studies were driven by the aim of understanding how hydrogen implantation in this application leads to graphite damage and

hydrogen uptake [88–90]. From these experiments an interlayer expansion and a decrease in the crystalline size of graphite from TEM studies was observed [89,90]. Hydrogen recombination and tunneling are believed to, in part, drive the change in graphite crystal size although experimental corroboration of hydrogen's presence in implanted graphite has yet to be completed [87].

The structural change upon implantation was also found to depend on the energy of the ion, which affects the ion range into graphite [88]. It was shown by high resolution TEM studies that along the surface normal the graphite interlayer spacing was largest at the surface and decreased as a function of depth into the sample. This gradient in the d-spacing from ion implantation suggested that ion damage was an important component, rather than only hydrogen chemisorption, in structural damage of graphite by hydrogen. In fact, the creating of strain in this way was recently found to be a potential avenue to magnetism in graphene [91]. These first-principals calculations show that (theoretically) small perturbations in strain drive magnetic changes in samples, suggesting the tuning of magnetism in graphene via strain could be achieved although experiment has yet to observe this phenomenon.

In graphene, functionalization of individual sheets is of interest as this can lead to modification of chemical, mechanical, electronic, and magnetic properties of the film. For example, graphene oxide sheets have been studied extensively due to their potential for reduction to make graphene powders as well as the utility in chemical reactions, replacing the chemically active oxygen site with other functional atoms such as fluorine and hydrogen [8,92]. Hydrogenated graphene also has been shown theoretically to lead to the electronic and magnetic modification of graphene. Via Lieb's theorem it is believed that

Table 5.1	Thickness (N)	Ion Energy(eV)	Ion Fluence (10^{16} ions/cm ²)	Ion (H/D)	<i>In-situ</i>	Distribution of Ions
C2	78	2000	34.2	H	Yes	Interface
C4	60	500	34.1	H	Yes	Graphene
33MO7	20	500	12.8	D	Yes	Interface
33MO6	20	500	3.8	D	Yes	Interface
C6MO5	50	360	46.8	H	No	Graphene

the properly hydrogenated graphene sheet can become magnetic at room temperature [22].

Hydrogenation can also lead to the controllable opening of a bandgap in the otherwise gapless graphene [93], making the use of graphene possible in semiconductor applications.

Further motivated by the possible controllable functionalization of graphene, we implant graphene samples with H ions. We aim to understand the structural modification of graphene grown epitaxially on C-face 4-H SiC at various implantation energies via: (1) x-ray diffraction to determine changes in the graphene lattice structure, (2) electron microscopy to determine local changes of the buried interface and film, and (3) neutron/x-ray reflectivity to determine the interfacial structure and composition of implanted samples. In these studies, we address the effect of the location of the ion distribution relative to the graphene/SiC interface on the structure of the film, investigating the formation of carbon interstitials and hydrogen chemisorption to graphene sheets. Via combined NR and XRR we for the first time address the question of whether hydrogen implanted into graphene films remains – indicating the possibility of chemical functionalization of graphene sheets via ion implantation.

5.2 - Experimental

5.2.1 - Sample Preparation

The samples studied here contained nominally between 20 and 78 graphene layers. In the study a total of five samples were studied. Details on the sample thickness

determination and treatment process are given in Table 5.1. Sample preparation is discussed in Chapter 3.

5.2.2 - Ion Distribution Calculations

Ion distribution in samples was calculated using SRIM software [94] which approximates the path of implanted ions for an amorphous sample which matches the sample density and composition. SRIM directly outputs the final ion (and target atom) distributions (RANGE.txt file) assuming an amorphous target of given density. For the calculations shown here (done for 10^6 ions) SiC was assumed to have a density of 3.211g/cm^3 and graphene a density of 2.2g/cm^3 . These ion (atom) distributions are given in units of density/fluence. In order to determine the density, the ion fluence (experimentally determined) is multiplied by the SRIM distribution. Final atom distributions show the location of the carbon atoms in the film which are moved from their original site after the simulation (10^6 ions) is complete.

From this result it was determined how deeply into the film ions are expected to stop. Calculations were done to determine the distribution in all samples prior to implantation. In Fig. 5.1 SRIM calculations for two samples, 33MO7 (20L, Fig. 5.1(a)) and C4 (60L, Fig. 5.1(b)), with ion energy of 500V and an incident ion angle of 45° are shown. The thickness of these samples were determined by Raman and x-ray reflectivity [44]. These thickness measurements determine the entire thickness of the film – not only the highly crystalline portion which is measured by x-ray diffraction measurements. Hydrogen/deuterium dose was calculated from these results by integrating the total area of the portion of the ion distribution which remains in the graphene. This

Fig. 5.1 demonstrates the calculated ion range and distribution which was calculated using SRIM. (a) is calculated for 33MO7 and (b) is calculated for C4. Sample thickness was determined as discussed in the text. The vertical bar shows where the Gr/SiC interface defined for the calculation (based on experimental thickness). These plots are direct results of SRIM simulations, an output in the RANGE.txt file.

integration gives a fraction of total ion fluence which remains in graphene and can be used to extract ions per carbon atom.

5.2.3 - X-ray Diffraction

X-ray diffraction data was collected *in situ* during ion implantation using a rotating anode x-ray generator with a point beam from a Cu target for samples C2, C4, 33MO7 and 33MO6. A multilayer focusing elliptical mirror monochromator was used to focus the beam to a size of 1x1mm. In-situ EXRR data was collected as a function of ion dose for the first order graphene Bragg reflection. Data was collected immediately following ion implantation for each of the reported fluences. Sample alignment did not change during the duration of the experiment allowing for reliable comparison of sample (001) reflection intensity and position. Data showing the changes in the first order graphene Bragg peak for two samples is shown in Fig. 5.2. Ion flux was measured for each implantation condition:

Fig. 5.2 shows the evolution of the graphene Bragg peak for 33MO7 with the ion distribution near the graphene/SiC interface (a) and C4 with the ion distribution entirely in the film (b). The peak shifts to lower q_z signifies an increase in the graphene interlayer spacing. Solid lines are fits using the models described in the text.

$3 \pm 1.5 \mu\text{A}/\text{cm}^2$ for 2kV acceleration voltage, $1.1 \pm 0.6 \mu\text{A}/\text{cm}^2$ for 500V. Sample C6MO5 was measured ex-situ using a four-circle high-resolution x-ray diffractometer (X'Pert Pro, Panalytical with $\text{Cu}\alpha_1$ radiation) and had an ion flux of $0.3 \pm 0.05 \mu\text{A}/\text{cm}^2$ for 360V acceleration voltage. Data was collected with the scattering vector along the surface normal, $q_z = 4\pi/\lambda \sin(2\theta/2)$.

5.2.4 - Neutron/X-ray Reflectivity

Neutron reflectivity (NR) data was obtained on the reflectometer, BL-4A, at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory using the method described in Chapter 3. In combination with x-ray reflectivity (XRR) measurements, these measurements supply a robust method of determining hydrogen content in implanted graphene samples. Reflectivity data for a bare SiC sample implanted with H ions was collected ex-situ using a four-circle high-resolution x-ray diffractometer (X'Pert Pro, Panalytical with $\text{Cu}\alpha_1$ radiation).

5.2.4 – X-ray Photoelectron Spectroscopy (XPS)

XPS was run on a SIGMA PULSE system which utilizes MECS monochromator (quartz crystal mirror for the Bragg reflection) and focusing of Al-K α radiation on a Rowland circle with 500mm diameter. This allows for high-resolution measurements which can be run in-situ during sample annealing. The sample environment is in UHV, with a sample stage which allows for annealing to nominally 800-900K. A single sample, 33MO6, was studied after D ion implantation. The sample was studied before annealing, during (in-situ) annealing, and after the annealing process was finished. For comparison, an untreated sample was also run under the same conditions.

5.3 - Results

5.3.1 - In-situ X-ray Diffraction

The results of H/D implantation for the various samples relies heavily on the relative location of the ion distribution. For one, the character of the change in the Bragg peak shown in Fig. 5.2 is dramatically different between the two samples shown. In Fig. 5.2(a) a long tail going to low q appears whereas in Fig. 5.2(b) the primary change is a broadening of the Bragg reflection. Additionally the expansion ($\Delta d/d$) of the film, which is taken from the center of mass of the graphene first order Bragg reflection, is one parameter which is heavily reliant on the ion profile in the sample. If the ion distribution is centered about the graphene/SiC interface, the expansion profile (as seen in Fig. 5.3(a)) with ion fluence is much steeper than when the ions all remain in graphene. Additionally, when the ion fluence is integrated and converted into an average ion density in the film, the two regimes more clearly separate as shown in Fig. 5.3(b). This difference was the first indication that the integrated damage, rather than the number of ions might be responsible

for the two regimes. To better understand this point, modeling of EXRR data was performed.

From SRIM calculations it was determined that ions distributions in implanted samples could be described as either affecting only the graphene film or having a range which put the distribution at the buried interface between graphene and SiC, affecting both the film and substrate. These two classifications of the ion distribution lead to unique structural changes with increasing ion fluence as observed from in situ XRD studies. The data can be analyzed with models dependent only on this component of the moment transfer. Using the model previously determined for many layer graphene (Chapter 3) as a starting point, each of the conditions for ion energy were investigated. The full equation is expressed as:

$$R_{Spec}(l) = \frac{4c_{SiC}^2 r_e^2}{l^2} \left| \rho_{SiC} \frac{F_{SiC}(l)}{1 - e^{-i2\pi l}} + \rho_G A_G(l) \right|^2 \quad (5.1)$$

Where F_{SiC} is the structure factor of SiC, r_e is the classical electron radius, c_{SiC} is the SiC c lattice parameter (10.0848Å), ρ_{SiC} is the atomic density of SiC, and ρ_G is the atomic density of graphene. A_G is the amplitude of the scattering from the graphene film. This term is dependent on the features of the film such as thickness and interlayer spacing.

Due to the vastly different expansion profiles and structural changes depending on ion implantation conditions, EXRR required different models depending on the ion distribution in relation to the sample profile. In the samples studied there are two classifications – ion dose deeper than the buried interface between graphene/SiC (demonstrated in Fig. 5.1(a), data shown in Fig. 5.2(a)) and ion dose primarily in graphene

Fig. 5.3 shows the expansion ($\Delta d/d$ obtained from the center of mass of the graphene first order Bragg peak) vs. ion fluence (a) and ion density in graphene (b) for the samples studied. As shown, there are two expansion regimes which depend on the ion range. Ion doses at the interface cause a much larger expansion in comparison to the dose entirely in the film.

(demonstrated in Fig. 5.1(b), data shown in Fig 5.2(b)). The two classifications affect only the amplitude term related to graphene, A_G .

For samples with the ion distribution being centered near the SiC/Gr interface, as in sample 33MO7 plotted in Fig. 5.1(a), the model used for untreated graphene was not possible. In order to fit the data, a linear strain gradient (LSG) of the graphene d-spacing was needed. This behavior was observed in three samples, two treated with deuterium ions at 500V acceleration voltage (33MO6, 33MO7) and another treated with hydrogen ions at 2kV acceleration voltage (C2). The models for the implanted samples do not consider an interfacial layer of graphene with expanded d-spacing, which is present in virgin samples as it will be damaged and impossible to resolve over a small range in q_z . The amplitude (A_G) for the graphene film with the LSG (α) is expressed:

$$A_G(l) = \sum_{j=1}^M P_j \sum_{n=1}^j e^{iq_z d_{Gr} n} e^{-i\alpha q_z [(j-1/2)n - 1/2n^2]} \quad (5.2)$$

where $P_j = \binom{M}{j} p^j (1-p)^{M-j}$ and $\sum_{j=1}^M p_j = 1$ is the binomial coefficient for layer j in M , d_{Gr} is the graphene d-spacing of the top layer, and M (which is large causing the distribution to be in the Poisson limit) is the maximum number of graphene layers in the binomial distribution, and $p=N/M$ (where N is the average number of layers in the distribution) [69]. The LSG term α accounts for the strain gradient in the film, which appears in the data as a long tail going to low q .

The LSG model describes the non-uniform d-spacing in graphene after ion implantation. Each layer (n) has a unique d-spacing which increases (or decreases) with increasing layer number, allowing for layers at the top (or bottom) of the film to have the largest d-spacing. Because we have a limited range of data in q_z , we cannot distinguish if the layers near the surface or near the interface have the largest d-spacing according to the strain gradient. To demonstrate the need for the LSG model, a fit of sample 33MO7 constraining $\alpha=0$ (labeled No LSG) is shown in Fig. 5.4. As shown, the long tail going to low q_z and the peak shape is not accurately described by the model used for untreated many-layer graphene. With increasing fluence the d-spacing of graphene and its LSG term α increase, without reaching saturation at the doses measured. This behavior is exhibited for samples 33MO6, 33MO7, and C2 in Fig. 5.5(a,b).

For samples having the ion distribution primarily in graphene the model used to describe virgin many-layer graphene on 4-H SiC [44] was adequate. This equation allows for two portions of the graphene film, an expanded portion (A_G^+ with d-spacing d_+) and bulk

Fig. 5.4 demonstrates the LSG model accurately describes the data for sample 33MO7 as compared to the model found to describe virgin graphene (no LSG or $\alpha=0$).

portion (A_G^B with d-spacing d_b). The expanded portion of the film accounts for 15-30% of the film for both samples. The amplitude terms for both portions of the film are described by a binomial distribution of graphene island heights [69].

$$A_G = A_G^+ + A_G^B \quad (5.3)$$

$$A_G^B(l) = e^{i2\pi l d_{1st}^{Gr}/c_{sic}} f_c(l) \xi_+ e^{i2\pi l d_b/c_{sic}} \left(\sum_{n=1}^3 g_n \frac{\xi_n - 1}{e^{i2\pi l d_b/c_{sic}} - 1} \right) \quad (5.4)$$

$$A_G^+(l) = e^{i2\pi l d_{1st}^{Gr}/c_{sic}} f_c(l) \left(e^{i2\pi l d_+/c_{sic}} \frac{\xi_+ - 1}{e^{i2\pi l d_+/c_{sic}} - 1} \right) \quad (5.5)$$

$$\xi = \left(\frac{N}{M} e^{i2\pi l d_x/c_{sic}} + \left(1 - \frac{N}{M} \right) \right)^M \quad (5.6)$$

Fig. 5.5 (a) shows the relationship between ion fluence and graphene d-spacing for samples 33MO7, 33MO6, and C2. (b) shows the relationship of ion fluence with the LSG term α .

Here $f_c(l)$ is the atomic form factor of carbon. d_{1st}^{Gr} accommodates the phase shift due to the distance of the first graphene layer from the substrate. Because our EXRR measurements had limited data in between the Bragg positions, our measurements were relatively insensitive to d_{1st}^{Gr} . This value was found to vary between 1.6-3Å, giving a contraction in the first layer that is consistent with other studies [60]. Because of our lack

Fig. 5.6 demonstrates the change in graphene thickness (ΔN) is required to accurately describe the broadening of the graphene Bragg peak. Sample C4 is the sample shown.

of sensitivity to this parameter, it was fixed based on the best fit to the virgin (untreated) sample XRD pattern. Again, N is the average number of layers and M is the maximum number of layers. In eq. 5.4 g_n describes the weighting of the distributions subject to $\sum_{n=1}^3 g_n = 1$. ξ_n depends on one of three possible layer heights, N_n , with $n=1, 2, 3$. The average total thickness of the graphene film is $\bar{N} = N_+ + \sum_{n=1}^3 g_n N_B^n$. In eq. 5.6 d_x refers to either d_+ for the expanded portion of the film or d_b for the bulk portion of the film.

The primary implication of ion implantation on films with the dose entirely in graphene was the decreased intensity and increased peak width with increasing ion fluence. This behavior was observed in two samples, one treated with an acceleration voltage of 500V (C4, data plotted in Fig. 5.2(b)) and another with an acceleration voltage of 360V (C6M05). In order to accommodate for the changes in the graphene Bragg peak with implantation, the model allowed for the decrease of crystalline size in the graphene layers.

This decrease of crystalline size in graphene manifests itself in the model as a decrease in the average number of layers $\bar{N}$. A decrease in N ($\Delta N = \bar{N}_{Virgin} - \bar{N}_{Implanted}$) from the sample affects the peak broadening and is required to fit the data, as shown in Fig. 5.6. Here the peak broadening is not captured when the graphene layer number is constrained (grey line) or when the LSG model is used (blue line). ΔN (plotted as $\Delta N/N_{Virgin}$) is shown to increase with ion fluence for both samples C4 and C6MO5 in Fig. 5.7(a), with the decrease in crystalline graphene contributing to the 001 Bragg reflection slowing at high fluence.

The expanded portion of the graphene described by A_G^+ (with d-spacing d_+ in Fig. 5.7(b)) in eq. 5.1 cannot, due to only being able to measure the graphene 001, be determined to be at the top or the bottom of the main portion (A_G^B) of the graphene film. While we cannot determine the location from the data we believe, given the larger expansion seen in samples having the ion range deeper in the sample, we believe this distribution to describe the top portion of the graphene film for samples with the all ions implanted in graphene. While the location of the expanded portion of graphene relative to the substrate cannot be definitively determined, the presence of the expanded layer is clear from the asymmetry in the peak shape of the graphene 001 Bragg peak. The tail going to low q_z indicates the presence of a portion of the film with higher d-spacing than the bulk. The d-spacing of both this expanded layer and the bulk portion of the film increase with fluence but the bulk d-spacing saturates at high fluence while the surface portion continues to expand. This behavior is shown in Fig. 5.7(b) for both sample C4 and C6MO5.

Fig. 5.7 demonstrates the change in the model parameters for both sample C4 and C6MO5 with increasing ion fluence. (a) shows the change in the graphene d-spacing for both the bulk (black circles) and expanded (blue circles) portion of the film. (b) shows the increasing ΔN or loss of crystalline graphene with ion fluence described in the text.

5.3.2 - Neutron and X-ray Reflectivity

Neutron reflectivity, which is sensitive to hydrogen content of samples, was used with x-ray reflectivity to determine both the layer structure and the hydrogen retention of

implanted samples. By combining neutron and x-ray reflectivity, sample parameters can be determined with greater confidence. Because neutrons scatter from nuclear density while x-rays scatter from electrons, the scattering power of each element provides different contrast between the two techniques. Using this difference to our advantage, one can extract the sample composition and ion concentration. A co-refinement of XRR and NR results from the same sample was used to determine the hydrogen content of the film and substrate after implantation by determining the SLD of the graphene layer which will not be impacted dramatically by hydrogen in XRR but will be dramatically affected with NR.

The sample studied with reflectivity, C2, was modeled with a 4-layer model. The graphene layer, a transition layer between graphene/SiC accommodating the rough interface, and the SiC substrate are included in this model. C2 has a thin tungsten layer on the surface, which impacts the profile shape in reflectivity. This layer was taken into account in the XRR/NR co-refined model by adding a 4th layer to the top of the sample. This is a small amount of tungsten (W), 5nm with 20% surface coverage, on the surface of the sample and is described by the layer labeled W in the color schematic of the layer structure at the bottom of Fig. 5.8(c) and Fig. 5.8(d).

NR and XRR data from C2, before (only for x-ray) and after hydrogen ion implantation at the SiC/Graphene interface is shown in Fig. 5.8(a, b). Because hydrogen is a weak scatterer of x-rays, the effect of implantation does not greatly impact the x-ray SLD of graphene but does lead to a roughening of the sample indicated by the sharper drop in reflectivity seen in Fig. 5.8(a) and the broadening of the graphene/SiC interface in the corresponding profile in Fig. 5.8(c). While this broadening is not as significant as what was seen from atomic deuterium treated samples in Chapter 4, it is necessary to fit the data.

NR, in contrast to XRR, is highly sensitive to the (negative) SLD of hydrogen. The effect of hydrogenation is indicated by the drop in graphene SLD, which can be seen when comparing the calculated profile for the pristine sample and the profile for the implanted sample seen in Fig. 5.8(d). Here, from the fitted curve in Fig. 5.8(b), the lower SLD after ion implantation is apparent.

From the SLD profile the calculated hydrogen content was $0.3(\pm 0.05)\text{H:C}$ compared to the $0.38(\pm 0.04)$ which is determined to be in the sample from SRIM calculations considering total ion dose. This is the first corroboration of hydrogen remaining in graphene or graphite after proton irradiation. Because H content can have a significant impact on the mediation of damage created by implantation, quantifying the amount of hydrogen in the film is an important step in understanding of the defect structure of implanted graphene films.

Hydrogen content is calculated by comparing the SLD from neutron scattering to that of x-ray scattering. These SLD are determined from the fits to the reflectivity data and used to calculate the number density of hydrogen (ρ_H):

$$SLD_{Neutron} = b_C^N \rho_C + b_H^N \rho_H \quad (5.7)$$

$$SLD_{X-ray} = b_C^X \rho_C + b_H^X \rho_H \quad (5.8)$$

Fig. 5.8 shows XRR (a) and NR (b) data and fits for sample C2 for ion implanted and untreated graphene films. Panel (c) shows the resulting XRR profile for the fitted curves of the untreated and implanted film. Panel (d) shows the calculated NR for the virgin sample as well as the profile from the fit of the NR data from the implanted film. The sample used for NR had a small amount of tungsten (W), labeled in the sample profiles, on the surface which leads to the peak in the sample profile SLD seen in XRR (c) but not in NR (d) due to the low nuclear SLD of tungsten (W).

Here b_C^N and b_C^X are the scattering length of carbon for neutrons and x-rays respectively and ρ_C is the number density of carbon atoms. b_H^N and b_H^X are the scattering length of hydrogen for neutrons and x-rays, where the scattering length of hydrogen for x-rays is negligible.

Analysis allowing for hydrogen uptake was also done for the SiC near the interface but there was not a significant difference in the SLD of SiC at this interface from the bulk value. While this might suggest hydrogen is not retained in SiC, it cannot be ruled out as

the transition layer between graphene and SiC varies sample to sample. Therefore, without an initial NR measurement, exact change in SLD cannot be determined. Given the high retention of hydrogen in the graphene film, it is surprising that the SLD of the transition layer (shown in the sample profiles of Fig. 5.8) does not seem to be significantly impacted by implantation but without further investigation with NR we cannot reliably determine hydrogen content at this interface.

From XRR studies of SiC implanted with hydrogen at 360V acceleration voltage we found that Si is highly reactive with H, creating a depleted layer for the affected region of SiC. This is shown by the decrease in SLD and increasing layer thickness (signaled by the arrow) in Fig. 5.9(a). It has been suggested that the sputtering of Si from SiC, forming carbon rich clusters, is responsible for this density loss and in fact this has been used to lower the growth temperature of graphene/graphite on SiC [95,96]. As shown in Fig. 5.9(b) the thickness of the depleted SiC layer increases with increasing fluence. However, with the introduction of a graphene capping layer analogous to the metal capping layers used for ion implantation of oxides, the sputtering of material by implantation is highly suppressed [97]. For this reason, the formation of pores and reduction of SiC density is apparently not present in implanted graphene/SiC films. Indeed from Fig. 5.8(c) we see a much smaller decrease in the SLD of the transition layer than we do at the surface of the bare SiC substrate. The suppression of the reduction of SiC density does not, however, indicate the reason by which H implanted into the graphene samples does not seem to remain in the substrate. In order to better understand this, future NR studies of the substrate should be done to test for hydrogen retention after ion implantation.

Fig. 5.9 shows profiles from fits to XRR (a) data from a SiC substrate implanted with increasing fluence. The arrow is to guide the eye to the trend with increasing fluence. From the profile a thickness is extracted and plotted vs. fluence in panel (b), showing a sharp onset followed by a gradual increase in thickness with increasing ion fluence.

5.3.3 - Cross-sectional TEM

TEM taken before, Fig. 5.10(a), and after, Fig. 5.10(b), ion implantation was also done for C4 (having the dose entirely in graphene) to further investigate the damage to the graphene crystallinity. While the FIB process does damage to the graphene layers while cross sectioning the samples, we still can see differences before and after implantation. Here the graphene planes, evident prior to implantation, become highly damaged and indistinguishable after ion implantation. Fig 5.10 also shows the FFT of images before (c) and after (d) ion implantation. The scattering from the SiC and Graphene (Gr) related diffraction is labeled, in both images the SiC spacing is found to be the expected $2.52\text{\AA}$ [16]. Further evident of the damage to graphene by FIB sample preparation is the increased interlayer spacing of the unimplanted film, found to be $3.5 \pm 0.1 \text{\AA}$ compared to the $3.37 \text{\AA}$ found from XRD.

Fig. 5.10 shows TEM of a 60L graphene sample (C4) both before (a) and after (b) ion implantation with ion dose primarily in graphene. It is clear the crystalline planes of the virgin sample are highly damaged compared to the implanted sample. A FFT of images taken before (c) and after (d) ion implantation show the decreased crystallinity and orientation of the graphene planes.

5.3.4 – XPS Measurements of H/D Implanted Samples

XPS measurements were done both on a pristine sample and on a sample (33MO6) after implantation to see evidence for hydrogen bonding to graphene. An in-situ annealing in UHV study of D implanted sample 33MO6 was done. This study annealed the sample for 1000s in steps of 100C, starting at 50C. The temperatures are 150C, 250C, 350C, 450C and 550C which were reached at 1000s, 2000s, 3000s, 4000s, 5000s respectively. From this study three observations were made: (1) the O1s peak intensity was much higher than pristine samples but this intensity diminished with annealing at low temperatures suggesting this was due to additional adsorption of CO₂ and other molecules on the surface of graphene when exposed to ambient molecules after implantation in UHV conditions.

The change in intensity of the O1s peak is shown as a function of annealing time in Fig. 5.11. (2) the Si2p peak dramatically changes shape compared to pristine samples (which have two clear peaks as in the post-anneal spectra in Fig. 5.12) suggesting a change in the chemical environment of Si at the interface of graphene/SiC, as shown in Fig. 5.12. Here there appears to be multiple components to the Si 2p peak prior to annealing, suggesting a complex interface which is chemically different than the virgin sample [98]. This result suggests that, like what was demonstrated in Chapter 4 with atomic treatment of graphene on C-face SiC, the graphene/SiC interface is highly sensitive to hydrogenation. (3) the C1s peaks show evidence of a mix of sp^2 and sp^3 carbon and the ratios of these populations changes with annealing (increasing the sp^2/sp^3 area ratio).

The sp^3 carbon peak occurs at higher binding energy than the sp^2 peak, making distinguishing the two possible by peak fitting during in-situ data collection. The effect of annealing is shown in Fig. 5.13, with the inset showing the C1s peak before and after annealing along with fitted components. Here the ratio of sp^2/sp^3 carbon increases as a function of annealing time, suggesting the carbon in the film (and potentially at the interface or in SiC) is being converted back to sp^2 carbon. This conversion does not appear to be temperature dependent, as the rate of conversion does not change upon ramping the temperature from 50-550C. While the amount of carbon changing hybridization cannot be determined, this result supports the conclusion that graphene forms hydrocarbon bonds upon ion implantation and these bonds are reversible. However, as the structural changes observed by XRD persist, these hydrogen-carbon bonds are not solely responsible for the structural changes observed with hydrogen ion implantation.

Fig. 5.11 shows the loss of intensity of the O1s peak in the carbon XPS spectra, this is indicative of the loss of organics at the surface of the sample. This loss of intensity was onset at low (100-200C) temperatures.

Fig. 5.12 shows the change in the Si2p spectra before (red) and after (black) annealing. For reference, the Si2p spectra is after annealing matches that of virgin graphene. This change occurred at very low annealing temperatures – beginning at around 100C. The peak at lower binding energy is associated with the chemical environment of Si in SiC and the peak at higher binding energy is associated with Si dangling bonds or chemical bonds with oxygen/carbon at the SiC surface (or graphene/SiC interface).

Fig. 5.13 shows the change in the sp^2/sp^3 carbon signal (C1s) peak area ratio as a function of annealing time. The sample continued to convert to sp^2 carbon while annealing up to 550C. The inset demonstrates the change in the C1s spectra, with the solid lines representing fits of the two components of the C1s peak.

5.4 - Discussion

The main structural implications of ion implantation on the structure of MLG films depends on the ion distribution in the film. Implantation at acceleration voltages which create an ion distribution that remains in the graphene leads to damage which does not create a large interlayer expansion in comparison to samples treated with the dose at the graphene/SiC interface. While the final H:C ratio was much higher in these samples, the excess hydrogen content did not lead to significant interlayer expansion. Rather, the

damage which is created primarily results in decreased crystalline size/highly disordered graphene which is accounted for the XRD modeling by ΔN .

Previous work on implantation in graphite suggest this highly damaged region may be due to clustering and recombination of ions as they stop in the sample [84,86,99]. These works find that clustering of hydrocarbons created by implantation and recombination of atomic hydrogen to molecular hydrogen cause irreversible damage to graphene. When near the surface of the film, damage from recombination and ion clustering can create both exfoliation (random orientations of graphene) and decreased crystalline size [84]. The recombination of ions to form H_2 (beyond the saturation of uptake) can cause exfoliation of graphene sheets much like the chemical exfoliation processes used to make graphene powders from graphite [100–102]. In high concentrations, graphene/graphite cannot uptake additional hydrogen leaving the ions open to this recombination. However, in our films the nature of the damage is unclear. By creating random orientations, we expect powder diffraction rings which are not observed from x-ray diffraction but is observed from beam damaged TEM samples (Fig. 5.10(d)). Additionally, why do films have such a small interlayer expansion and why does ΔN occur only in films which have the dose entirely in graphene? To address this, we investigate the total integrated intensity of the diffraction and investigate the role of hydrogen density in creating damage.

The decrease in crystalline size which we describe as ΔN must be related to the total integrated specular (along q_z) intensity of the scattering of the sample. If the sample does not lose crystalline graphene, the total integrated intensity should stay constant. In order to corroborate our interpretation of ΔN we integrate the intensity found for the model of the data for samples C4 (ion distribution in graphene) and 33MO7 (ion distribution

centered at the graphene/SiC interface). These results are shown in Fig. 5.14. Here we see that for the sample found to have ΔN , C4, the loss of integrated intensity is much more pronounced than in 33MO7. This could be due to small orientational disorder but supports the claim that the film remains ordered rather than powder like (as is suggested by Fig. 5.10(d)). Because the ion density in these films is much greater (for the same ion dose) than in the case where the ion distribution is centered at the interface, we attribute this difference between the films in part to ion clustering and recombination near the graphene surface causing partial exfoliation and ripples to form in the graphene sheets.

The disorder due to implantation can also be seen locally from cross sectional transmission electron microscopy. In Fig. 5.14 the damage from ion implantation with the dose primarily in graphene is demonstrated by comparison of imaging of sample C4 both before (a) and after (b) implantation. Here the crystalline planes of graphene are damaged significantly by both the ion implantation and FIB sample preparation process (damage which is also present in pristine samples [44]), making observation of the decreased crystalline size impossible to resolve. However, x-ray diffraction in Fig. 5.2(b) demonstrates there are still crystalline portions of the film. TEM of graphite implanted with hydrogen ions of similar energy also show highly disordered regions of graphite near regions beyond the saturation (calculated to be 0.4-0.5H:C [84]) limit of H:C ratio [88–90]. Randomly oriented crystallites (powder-like) which decrease in size with increasing fluence in graphite were shown to appear upon ion implantation [88]. While we do not observe powder-like crystallites, the decrease in crystalline size and change in crystalline orientation is consistent with our interpretation of in-situ XRD of ion implanted many-layer graphene (with the ion distribution primarily in the film).

Fig. 5.14 shows the change in integrated intensity for a sample with the dose in graphene (C4) vs. a sample with the dose centered at the graphene/SiC interface (33MO7). The loss of integrated intensity signifies the loss of crystalline graphene, consistent with our interpretation of ΔN from XRD models.

In order to investigate damage in the film further we perform FFT of the TEM images. From comparison of FFT images taken before and after ion implantation, the damage to graphene is clear. While the result does not give us quantitative information due in part to beam damage during cross section preparation, the qualitative change upon ion implantation is clear. In Fig. 5.10(c) the broad graphene peaks prior to ion implantation are oriented along the SiC direction. However, after implantation in Fig. 5.10(d) there is no clear orientation of graphene and the scattering from the film becomes broadened and powder-like, forming a ring. We know from XRD, particularly from the analysis of the integrated intensity in Fig. 5.14 which would drop to near zero in the case of a complete powder, the film does not form multiple domains to give diffraction rings. Nevertheless, the film remains crystalline (from XRD) in significant quantities (as shown in 5.14) and we therefore suspect TEM sample preparation created significant damage as we see in pristine samples (Chapter 3). While the TEM could not observe the remaining crystalline

graphene demonstrated to remain from XRD, it clearly shows the decreased order of the film.

From fitting of XRD data it was revealed that ions with the distribution centered near the graphene/SiC interface create a strain gradient in the film which increases with fluence. The LSG model captures this expansion profile in many-layer graphene but does not address whether the buried interface or the surface experiences the largest interlayer spacing. Hydrogen implanted graphite fibers observed with TEM also saw a similar strain gradient in irradiated samples [88]. The strain gradient in TEM studies [89] was attributed to the chemical bonds forming between carbon and hydrogen atoms, increasing the radius of the graphite layer. While we are not sensitive to in-plane lattice changes, which could also change due to chemical bonding, we expect the interlayer spacing to see the largest lattice expansion as the interplanar bonding is the weakest in graphene/graphite. Given the effect of hydrogenation in graphite, it is expected that portions of the film with higher hydrogen content (near the interface) would have the largest interlayer spacing. Expecting hydrogen bonding to carbon to (in part) drive expansion and considering the (approximately) linear distribution of hydrogen peaking at the interface in samples having the dose centered at the graphene/SiC interface, shown in Fig. 5.1(a), we believe that the graphene nearest to the buried interface is likely to have the largest inter-layer expansion.

However, the expansion in graphene which comes with the LSG can be due to carbon interstitial atoms, hydrocarbon formation, or a combination of both. While the hydrogen ion distribution could not be measured for each sample, from NR we determined that the hydrogen remains in the film after implantation for films with the dose at the interface. For the sample shown in Fig. 5.8, the dose was $0.38 \pm 0.05 \text{H:C}$ (in graphene)

while the measured amount was $0.3 \pm 0.05 \text{H:C}$ which indicates the majority of the hydrogen remains in the film for the case of ion range near the SiC/graphene interface. While a gradient of hydrogen is more likely than a sample average (uniform hydrogen distribution), our model utilizes a sample average due to the small range in q which we can measure with NR. Due to this small range in q , the spatial distribution of hydrogen in the film is impossible to resolve.

The retention of hydrogen suggests that the ion, through chemisorption (hydrocarbon formation) or molecular hydrogen incorporation is partly responsible for the interlayer expansion. To address the question of whether molecular or bonded hydrogen is retained, annealing studies were done. From these studies, the expansion is found to not be reversible (observed from XRD where the position of the first order (001) graphene peak did not change) by annealing to 400°C in helium. This is substantiated by mobility calculations and diffusion experiments which show that molecular hydrogen moves quickly both in graphene and graphite even at room temperature – making it unlikely to remain in the film after ion implantation [103,104]. Therefore H_2 , which would leave the film at these temperatures, is not responsible for the expansion. XPS measurements (on sample 33MO6, where the ion distribution was at the graphene/SiC interface) also support the conclusion from NR that hydrogen remains in graphene. From the observed changes in the C1s peak, the changing sp^2/sp^3 peak intensity ratio suggests that the carbon in graphene was forming hydrocarbon and that hydrocarbon, at 550°C , can be removed by annealing in ultra-high vacuum. While further studies such as residual gas analysis and NR must be done to corroborate the removal of hydrogen with annealing, this result provides promising

evidence for hydrogen chemisorption rather than molecular hydrogen retention in our samples.

The change of the Si2p peak from XPS (sample 33MO6), however, is indicative of a change at the buried interface which we are not as sensitive to with NR. As we show in Chapter 4 this buried interface is extremely reactive and it stands to reason that ions can also bond to dangling bonds and other sites at the interface. While these results indicate changes of the SiC at the graphene/SiC interface, the complex chemical environment makes distinguishing the different features of the XPS difficult. However, the change in the chemical environment of Si suggests that H remains at the interface. The reversal of the change in Si2p peak with annealing (Fig. 5.12) shows these hydrogen atoms are mobile, as in graphene, and their chemisorption can be reversed.

Samples having the ion dose in graphene had an interlayer expansion which was smaller in comparison to samples with the dose at the graphene/SiC interface. In fact, we observed two regimes which depend on the ion range of expansion profiles, shown in Fig. 5.3, which vary with ion fluence (a) and ion density in graphene (b). This result, if considering the chemisorption of hydrogen to be the main driver of expansion as was suggested by studies on graphite [88,89], is surprising. The hydrogen density (for the same ion fluence) in the films with the dose entirely in graphene is much higher than in the case with the dose is centered at the interface. The nature of the expansion and the role of the ion in driving that expansion must be investigated further. Interestingly the samples having the dose at the graphene/SiC interface have a similar expansion profile with ion density, shown in Fig. 5.3(b), and not ion fluence (Fig. 5.3(a)). This suggests the role of

Fig. 5.15 shows the calculated atom and ion distribution from SRIM for each of the samples studied. The density of recoiled carbon atoms in graphene per ion is higher for samples C2, 33MO6, and 33MO7 which have the dose at the graphene/SiC interface. The ion distribution is shown with the open circles, demonstrating where the ions come to rest in the sample. Sample 33MO6 and 33MO7 were implanted with D while the remaining samples were implanted with H.

hydrogen/deuterium is important in the stabilization of the carbon interstitials formed during implantation.

To understand the different expansion profiles, SRIM calculations of defects density were considered. These calculations, done for the same number of ions and plotted for ion and carbon atom distributions for each sample is shown in Fig. 5.15. From these studies we find that interstitials density (averaged over the entire film) in graphene is higher in films with the ion distribution centered at the graphene/SiC interface. This suggests the

interstitial formation from ions passing through the film contribute more highly to the observed shift as compared to ions which come to rest in the film. Because of the dramatic difference in the expansion of the two conditions, we suggest that the role the hydrogen ions play in the graphene d-spacing change is a secondary effect to the interstitial formation caused by ions traveling through the film. Indeed it has been calculated that self-interstitials in carbon can be formed with low energies (few eV) and can cause a layer expansion [105], corroborating the idea that interstitials are contributing to the increase in graphene interlayer spacing.

It is important to note that both the ion and interstitial distributions in the samples are not uniform. We take a sample average of the densities of these distributions in order to compare to the sample average Bragg shift. While our data cannot distinguish where the shift is largest (in samples have LSG model) we suggest the shift is largest at the peak of the interstitial carbon distribution. Furthermore, the ion density profile is believed to be an important feature as it relates to the possible exfoliation of films. In samples with high density of hydrogen (i.e. dose all in graphene) the ΔN term which manifests itself might be due to the peak H:C ratio rather than the sample average. Indeed, the peak hydrogen content is higher near the surface (relative to the sample thickness) for samples with the ion distribution completely in the film.

From these results it is suggested that interstitials play a key role in the total interlayer expansion observed in the higher-energy (dose at the interface) implanted samples, however it was found that hydrogen remains in these implanted samples. What then is the role of hydrogen in samples? Sample C2 does not scale in the same way as samples 33MO6 and 33MO7 with ion fluence in Fig. 5.3(a). This suggests the mass of the

ion, having deuterium in the case of 33MO6 and 33MO7 or hydrogen in the case of C2, could influence the overall expansion. However, this assumption does not consider the ion energy whereas our SRIM calculations do. From our SRIM calculations we find the number of defects created per ion for the implantation conditions is equivalent for each of the samples (calculated 3 ± 0.5 vacancies or interstitials per ion). The creation of a high density of interstitial carbon and vacancies in combination with their stabilization by hydrocarbon formation is believed to be the main driver in the larger expansion seen in samples having the ion distribution at the graphene/SiC interface.

5.5 - Conclusions

In-situ XRD studies during ion implantation of many-layer epitaxial graphene grown on 4-H C-face SiC at various ion energies were performed in order to determine the structural changes of the film. The expansion profile with dose was dependent on the depth of the ion distribution in the sample. Samples having the dose only in the film saw minimal interlayer expansion but a significant change to the crystallinity of the graphene. This indicated a portion of the film was become highly damaged from the ion dose due to ion clustering and recombination – leading to the diminished crystalline size of graphene. Samples with the dose near the buried interface of SiC/graphene were revealed to have a non-uniform strain distribution and significant interlayer expansion which is believed to be due to the formation of a higher density of interstitial carbon which are stabilized by hydrocarbon formation. It was revealed from NR that hydrogen implanted into the films was retained which indicated indeed stable hydrocarbon formation plays a key role in the structural expansion seen in samples having hydrogen ion dose at the graphene/SiC interface.

6 – Helium Ion Implantation of Graphene

In order to better understand the structural changes in graphene we use the chemically inert ion helium for implantation. This offers the ability to understand the role of vacancies, interstitials, and strain while removing the complication of chemisorption. These results, in comparison to hydrogen implantation discussed in Chapter 5, will help to distinguish the role of the ion in creating defects in graphene. Ultimately, the results of this He implantation study will aid the understanding of how hydrogenation vs. carbon interstitial defects play a role in magnetism and structural changes observed in implanted films.

6.1 - Introduction

In graphite, a comparative study of the magnetism which arises from H and He implantation was performed for samples using ions implanted at very high (100s of keV) acceleration voltages [27,28]. From that study it was revealed that He implantation not only led to magnetism, but that magnetism exceeded the moment measured from H implanted films. That study also found that defects which occur in He implanted can create defect cascades in the sample which are more frequent than in H implanted samples due to the mass of the ion. However, those results were based on observations with only AFM and MFM and structural characterization of clustered interstitial and vacancy defects have yet to be completed. By unraveling the structural changes which occur during ion implantation in the present study, the differences between H and He implantation and how implantation leads to magnetism will be better understood.

In other studies, which were performed using He ion implantation at high (up to MeV) acceleration voltages, changes in the d-spacing of graphite was reported by electron microscopy studies [82,106]. From these it was seen that the generation of defects, which can be vacancies or interstitials, not only occurs but the global structure of these defects is energy dependent [28]. It was also shown that helium irradiation led to microstructures on the surface such as bubbles indicating ion atomic clustering and damage which is not uniform [82]. This damage from high energy implantation indicates that carbon is sputtered to form the blistered topology reported. By focusing on ions implanted at low energy, thereby minimizing sputtering, we aim to understand how helium implantation affects graphene on SiC, determine how carbon interstitials and vacancies are formed, and how these might change the electronic and magnetic structure of graphene.

Given our previous experience with hydrogen implantation showing the total expansion of the interlayer spacing was highly dependent on the location (tuned by ion energy) of the ion distribution, discussed in Chapter 5, we decided to focus on the case in which ions are implanted at the graphene/SiC interface. By focusing on samples of this type, direct comparison to the hydrogen implanted equivalent can be made. We first aim to understand how the helium implantation affects the graphene structure. Understanding how helium affects the graphene structure also will aide to understand whether hydrogen does indeed play a role though chemisorption in the expansion seen in previously studied samples. Comparison of results of helium and hydrogen ion implantation will drive the understanding of how to controllably affect the graphene structure in aims to control magnetism through defect generation.

6.2 - Experimental Methodology

6.2.1 - Ion Distribution Calculations

Like with H and D implantation studies, He ion distribution in samples was calculated using SRIM software using conditions outlined in Chapter 5 [94]. These calculations were used to determine ion distribution as well as the carbon atom distribution in implanted samples. The latter carbon atom distribution can be used to determine that distribution of interstitial carbon in the film – as this describes the final position of the carbon atoms which are displaced from their original position in the SRIM model (RANGE.txt output file). The carbon atom distribution is output with units of atom density/fluence. Using the total ion fluence (measured by time) for each of the samples and the fraction of carbon recoil which leads to an interstitial (direct result of SRIM, VACANCY.txt file) we can determine the approximate density of carbon interstitials (n) at any fluence for implanted samples, assuming minimal change to the graphene target.

By tracking the recoil cascades, SRIM can then reliably count displacement, vacancy, replacement and interstitial formation. Displacement collisions in the calculation is the total number of atoms in the sample which are moved by ions or the cascade of atoms creating damage in the sample. Carbon recoil describes all atoms knocked from their original site, not only those which create vacancies/interstitials. On the other hand, vacancies calculated by SRIM do not include replacements, or carbon atoms which fill a vacancy left behind by another carbon atom, as vacancy formation. More specifically, the total number of displacements is equal to the number of vacancies plus the number of replacements. In this context we count each interstitial as a recoiled atom which stops but does not replace a vacancy in the simulation. For an interstitial to occur the energy

transferred to the atom (E_I) must be enough overcome the energy to be ejected from the lattice site (E_L) so that it will not replace its own vacancy ($E_I > E_L$) and not too far that it replaced another vacancy.

The carbon recoil or vacancy distribution can equivalently be tracked in this case in order to estimate the (number) formation of interstitials. However, the final atom distribution (carbon atom distribution output from SRIM) is the best representation of carbon interstitial formation as it directly gives the density of carbon atoms at their final resting place (in comparison to vacancy distributions which show where carbon atoms left their sites). In order to determine the final interstitial density, the percentage of carbon recoiled atoms which create a vacancy (direct result of SRIM) is multiplied by the final carbon atom distribution output by SRIM (RANGE.txt file). Using the same method, utilizing now the ion distribution, an ion density (c) in the film can be extracted both to find the number of ions/carbon. Knowing n and c allows for the calculation of the number of interstitial carbons/ion (β).

6.2.2 - *In-situ X-ray Diffraction*

X-ray diffraction data was collected *in situ* during He ion implantation using X3B2, a rotating anode x-ray generator with a point beam from a Cu target discussed in Chapter 5 and in Appendix A2. Data was collected after each subsequent ion fluence was reached. Sample alignment did not change during the duration of the experiment allowing for direct comparison of changes in the first order graphene Bragg peak for sample C4MO5 (35L). The data resulting from this study is shown in Fig. 6.1. Ion flux was measured at $1.5 \pm 0.7 \mu\text{A}/\text{cm}^2$ for 1kV He acceleration voltage.

Fig. 6.1 shows the evolution of the first order graphene Bragg peak with in-situ XRD during He ion implantation. Solid lines are fits using the LSG model allowing also for a decrease in crystalline size.

6.3 - Results

In order to investigate how He implantation affects the graphene structure, in-situ studies of the graphene first order Bragg reflection were done. The implantation conditions which allow the ion distribution to be centered at the SiC/graphene interface. The sample, C4MO5, is a 35L sample. At each step of ion fluence, the graphene d-spacing is extracted by determining center of mass (COM) position of the 1st order graphene Bragg peak. This value is then compared to the interlayer spacing prior to implantation to calculate the film expansion via $\text{Expansion} = (d_{\text{final}} - d_{\text{initial}}) / d_{\text{initial}} = \Delta d / d$. From this study we see an interlayer expansion (Fig. 6.2), peak broadening, and an asymmetry in the graphene Bragg peak with increased fluence. This result, like the hydrogen implantation with the ion distribution at the graphene/SiC interface, required a non-uniform strain distribution to fit the data.

Fig. 6.2 shows the change in graphene interlayer spacing as a function of ion fluence. Expansion is calculated as $\Delta d/d^0\%$ as described in the text.

Fig. 6.3 shows the change in graphene $\Delta N/N$ (a) and α (b) as a function of ion fluence. Results are taken from best fits to the data from in-situ XRD studies. Also included are H (C2, C4, C6MO5) and D (33MO6, 33MO7) implanted samples which exhibited similar structural changes discussed in the previous chapter.

Table 6.1	Ion Energy (eV)	Fluence (10^{16} ions/cm ²)	Ion Type	Distribution of Ions	E^{Sat}	k_c (carbon per ion)	k_n (1/interstitial density)	γ ($\text{\AA}^3/\text{int}$)	β (int/ion)
C2	2000	34.2	H	Interface	4	3	$5.5\text{e-}24$	$2.2\text{e-}2$	4.82
C4	500	34.1	H	Graphene	0.85	3	$2.8\text{e-}23$	$2.4\text{e-}2$	0.97
33MO7	500	12.8	D	Interface	5.1	2.5	$4.5\text{e-}24$	$2.3\text{e-}2$	4.91
33MO6	500	3.8	D	Interface	-	-	-	-	-
C4MO5	1000	14.1	He	Interface	10	2.5	$1.6\text{e-}24$	$1.6\text{e-}2$	14.04
C6MO5	360	46.8	H	Graphene	0.53	2.5	$5\text{e-}23$	$2.6\text{e-}2$	0.44

Table 6.1 shows parameters describing the expansion behavior of each of the samples studied. 33MO6 was not possible to fit due to the low fluence, making extraction of the saturation expansion (E^{Sat}) impossible.

While the peak asymmetry could be described with the LSG model from Chapter 5, the peak broadening could not. To accommodate the peak broadening the graphene crystalline size, defined as ΔN , was refined in our fits. The ΔN and LSG term (α) are shown in Fig. 6.3(a) and (b) respectively and compared to H/D implanted samples which exhibited similar structural changes. The presence of ΔN (which did not appear for H and D implanted samples with the ion distribution at the interface) indicates the He implantation is doing more damage to the graphene than H or D. The LSG term is like that of H and D implanted films although, as shown in Fig. 6.3(b), the LSG term saturates for the He implanted film and not the others.

6.4 - Discussion

A striking result when comparing the ion implantation of He to H or D is the much larger expansion with increasing ion density (Ion:Carbon ratio), shown in Fig. 6.4(a). Viewed together it can be seen that Fig. 6.4(a) can be fit to a common exponential decay shaped curve (solid lines) according to:

$$E = E^{Sat} (1 - e^{-xk_x}) \quad (6.1)$$

Where x can be c (ion density) or n (interstitial density). k_x describes the $1/E$ -point of the expansion curve fit to Eq. 6.1. $1/k_c$ values are relatively constant for all samples suggesting the saturation region of the expansion curve is dominated by ion density in the film. Sample 33MO6 was excluded from this comparison as the low maximum fluence which the sample saw did not include the saturation regime, vital to fits using Eq. 6.1.

The helium expansion profile leads to greater maximum expansion, extrapolated from fitting the curve in Fig. 6.4(a) with Eq. 6.1. However, when normalizing the

Fig. 6.4 shows the comparison of expansion vs. ion density for hydrogen, deuterium, and helium implanted samples in (a). Here the solid lines are the best fit for the data described in the text. In (b) these curves are normalized by the maximum expansion approximated by fitting the corresponding curve in (a) with an exponential decay function. The saturation behavior for samples is similar given the results in (b).

expansion (E) by the saturation of the expansion (E^{Sat}), the compared shape of the profile between H, D, and He implanted samples is very similar, seen in Fig. 6.4(b). The curves all see initial linear expansion, a bend-over region where the expansion is not linear with ion density, and a saturation region at high ion density.

The question is then, how does the ion drive the value of the expansion in graphene? To understand this, we do SRIM calculations to approximate damage (carbon recoil) profiles in implanted samples. From these calculations we extract interstitial density and ion density of each film, assuming these are linear with ion fluence. For simplicity, we will first compare calculations done for samples C4MO5 (35L 1kV He implanted) and 33MO7 (20L 500V D implanted) directly. First, for C4MO5 the number of carbon recoils which occur per ion is found to be significantly greater than that of 33MO7, largely due to the mass difference of He and D. In SRIM, these carbon recoil events are classified either as a

displacement of a carbon atom creating an interstitial or an atom removed from the sample window (either sputtering or loss from the back of the sample) of the SRIM simulation.

The calculated carbon recoil profiles for 33MO7 (D implanted) and C4MO5 (He implanted) are shown in Fig. 6.5, where only the carbon interstitials generated from carbon in graphene are shown for simplicity. As shown the interstitial density peaks in graphene despite the ion distribution being centered at the graphene/SiC interface for both samples. In Fig. 6.5 the difference in interstitials/ion is demonstrated, where the number of defects per He ion is greater than 3x that of those generated by D ions due to difference in ion mass and implantation energy. Also plotted for reference in Fig. 6.5 are the ion distributions, showing the difference in where the ion and carbon recoil density peaks. The interstitial density of ions shown in Fig. 6.5 in graphene (by multiplying by the ion fluence) the density in He implanted films remains much higher than in H or D implanted films. The carbon interstitial atom distribution is determined by multiplying the percentage of vacancies found by SRIM to lead to an interstitial (100% for H and D and 90% for He) by the directly generated vacancy distribution. The 10% loss for He implanted films is due to defect cascades which penetrate the SiC substrate, seen in Fig. 6.5 for sample C4MO5. If carbon interstitials drive the structural expansion alone, we would expect the expansion to be related to this density.

To investigate this relationship the average density of carbon interstitials in graphene for each of the implanted films (calculated from SRIM) is compared to E^{Sat} or, equivalently the expansion at the $1/k_n$ -point. The expansion behavior vs. average interstitial density (n) is shown in Fig. 6.6 where the expansion (a) and the normalized (b) expansion ($\text{expansion}/E^{\text{Sat}}$ from Eq. 6.1) are plotted. Here we see an initial linear region common to

Fig. 6.5 shows the calculated carbon interstitial distribution in He (C6MO5, solid blue circles) and H (33MO7, solid red triangles) implanted samples. Also shown are the ion distributions, shown for each sample with unfilled symbols (red triangle for 33MO7 and blue circles for C4MO5) are plotted to demonstrate the distribution is at the graphene/SiC interface.

Fig. 6.6 shows the comparison of expansion vs. interstitial density for hydrogen, deuterium, and helium implanted samples in (a). Here the solid line shows the linear region in the limit of low interstitial density. In (b) these curves are normalized by the maximum expansion approximated by fitting the corresponding curve in (a) with an exponential decay function, shown here the interstitial density does not drive the saturation region seen for all samples.

all samples. k_n and volume expansion per interstitial (γ) can be extracted from the number of interstitials created per ion (β) and k_c (from fits to Eq. 6.1) via:

$$\gamma = E^{Sat} k_n \quad (6.2)$$

$$\beta = k_c/k_n \quad (6.3)$$

The values for the k-points, γ , β , and additional sample information is given in Table 6.1.

γ describes the slope of the line in Fig. 6.6(a) which is found to be $1.9 \pm 0.3 \text{ \AA}^3/\text{int}$ for all samples (or ranging from 1.6 for He to $2.6 \text{ \AA}^3/\text{int}$ for H when using Eq. 6.2 to calculate). This is a constant term for all samples, showing that the initial region in the expansion profile is dominated by the interstitial density. The volume expansion per interstitial, however, saturates at high fluence, evident in Fig. 6.6(b) which shows the normalized expansion curve is not uniform. Knowing interstitials cause expansion, the saturation region of the expansion curve can be explained by investigating the ion density in the film.

First, stabilizing carbon self-interstitials does not require passivation by ions in graphite. In fact, carbon dangling bonds can be stabilized by carbon from other vacancy sites or by inter-sheet bonding [107]. To investigate if bonding is playing a significant role in the saturation of the expansion of H or D implanted films, we investigate the role of β which is a metric for the efficiency of ions in creating interstitials. In Fig. 6.7 the saturation expansion (E^{Sat}) as a function of β (interstitials/ion). From this result we see that by maximizing ions/interstitial, one can effectively increase the saturation expansion. This

Fig. 6.7 demonstrates the relationship between ion to interstitial (calculated) and calculated saturation expansion (E^{Sat}) in He implanted and H implanted graphene films. The solid line is linear best fit to the data.

shows that the ion, not the interstitial, controls the saturation region of the expansion curve. The dependence of the expansion on the efficiency of the ion in creating an interstitial defect can allow for the engineering of strain in graphene by providing an indicator of what shift, energy and ion mass leads to the desired structural change. However, the comparative values of γ , in combination with NR reflectivity results showing retention of H presented in Chapter 5, supply compelling evidence for the chemisorption of hydrogen/deuterium in implanted films. γ for H/D implanted films are higher than from He implantation. This volume expansion difference is further evidence for the presence of chemisorption in H/D implanted many-layer graphene films.

6.5 - Summary

The structural implications of hydrogen and helium implanted at low (100s of eV) energies are investigated using in-situ XRD. He implanted films were found to have a much steeper expansion profile with ion fluence. These results were fit and detailed

SRIM studies were performed to understand what is driving the differences in the expansion profiles and saturation expansion (E^{Sat}) of samples with different ion types and implantation energies. From these results we see the density of interstitials formed from implantation drives the expansion seen regardless of where the distribution resides in the sample or at the interface. Knowing the interstitial density is key to engineering the strain distribution in the samples, we aimed to determine how E^{Sat} in samples could be modified. It was found that the saturation expansion heavily relies on the efficiency of the ion in creating defects in the film (β).

7 – Magnetism Resulting from Low-energy Hydrogen Ion Implanted Graphene

Studying defects induced by implantation has been focused around the central goal of creating and understanding magnetism in graphene. From Chapters 5-6 we understand the ion distribution, fluence, and type heavily impact the structural implications of ion implantation. In Chapter 7 we discuss how hydrogen implantation of graphene films not only become magnetic but how this magnetism is controlled by the tuning of the carbon interstitial density with combined magnetometry and structural (XRD) measurements.

7.1 - Introduction

High energy ion implantation of graphite has been of interest since the 1980s due to the use of graphite in nuclear applications. In those studies, the structural changes of graphite upon implantation were studied via Raman scattering, electron microscopy, and other techniques. Until recently, however, the electrical and magnetic modification of graphite upon implantation was not studied. Magnetism was found to occur in proton irradiated graphite – exhibiting novel p-orbital ferromagnetism in a metal free carbon system [5,29,31]. These studies concluded that ferromagnetism occurred due to hydrogenated carbon atoms creating sp^3 and sp^2 networks via hydrogenated graphite sheets, citing the Lieb's theorem picture of an orbital driven magnetism in a bi-partite lattice [5,25]. From this it is postulated that in graphene, which is completely decoupled layer by layer, magnetic modification of this nature can be achieved.

Using the experience of the semiconductor industry, which has advanced the science of ion implantation in efforts to dope materials for development of devices, control of graphene's properties via ion implantation can be attempted. However, due to the 2D nature of the crystal, the mobility of the atoms and the energy of the ions needs to be thought through. While high-energy implantation of substrates like HOPG has been shown to lead to magnetism, potentially more interesting in the case of the atomically thin graphene samples is the use of low (10s-100s of eV) energy ion implantation. This caters to device fabrication utilizing the unique properties of graphene. The use of ion beam patterning also can allow for creating regions of functionalized/doped graphene using a process which has been highly developed for the semiconductor industry.

Ion implantation of graphene is also being investigated as a potential avenue to modification of electronic properties through p or n type doping [108]. Boron and nitrogen doping via implantation at ultra-low energies (10s of eV) have been shown to create substitutional defects in the graphene lattice of up to 1% [108–110]. From these studies both ion beam damage and substitutional atoms were observed with STM. The treatment, however, leads to higher sheet resistance and lower electron mobility compared to samples treated with carbon ion implantation. This suggests that the defects created from implantation do not significantly affect the graphene electronic properties via doping, rather the chemical substitution drives functional changes observed from nitrogen and boron doping through creating damage to the graphene lattice [110].

Upon further analysis of the carbon K edge with EELS it was revealed [111] that by changing the dopant, the substitutional process leads to localized sigma bonding states in the graphene akin to the type of defect which is expected to yield magnetism in the

Lieb's theorem picture described in Chapter 1. Recently, the magnetic properties of nitrogen doped graphene have been investigated theoretically [112]. However, the presence of magnetism from N defects remains difficult to manipulate and control. Further study of carbon magnetism is dependent on the understanding of carbon vacancy magnetism at the macroscopic scale, where the defect abundance can exceed the reported 1% in nitrogen doped graphene.

Heavy atoms such as phosphorous, germanium, and xenon have also been used in ion implantation of graphene sheets [81,111,113]. Phosphorus, much like N and B, should behave like a dopant in the graphene sheet. Because of the atomic radius of the atom however, the substitution of a carbon atom also creates a buckling or strain effect which can also contribute to the changes in the electronic properties of the material [111].

Germanium implantation, like carbon implantation, is not expected to dope the graphene sheet. Upon Ge implantation, direct substitution of a carbon atom is observed. This leads to a significant strain of the graphene sheet again creating a buckled shape, distorting the graphene from its 2D sheet, about the Ge defect [81]. This buckled shape is comparable to the expected effect of the addition of carbon interstitials, leading to an expansion of the c-axis of graphene similar to what is discussed in Chapters 5-6. However, Ge implantation is subject to a large degree of contamination making the study of the structural, electronic, and especially magnetic changes due to the implantation process difficult.

In order to investigate the role of vacancy and chemisorbed defects (rather than adding the complication of substitutional defects) on carbon magnetism we use hydrogen ion implantation. Hydrogen/deuterium implantation was previously (Chapter 5)

Table 7.1	Thickness (N)	Ion Energy(eV)	Ion Fluence (10^{16} ions/cm ²)	Sat. Moment (10^{-6} e.m.u.)	Coercive Field (Oe)	Remanence (10^{-7} e.m.u.)
C2	78	2000	34.2	2.2	200	9.4
C6MO3	20	500	85.8	6.0	175	15.8
C6MO4	22	500	28.6	12.1	175	20.2
C4	60	500	34.1	7.9	100	13.0
C6MO5	50	360	29.3	2.1(RT)	N/A	N/A

demonstrated to controllably induce carbon interstitial vacancies in many-layer graphene grown on 4H SiC. Previously completed neutron reflectivity experiments revealed that hydrogen ions remain in the implanted film, playing the role of mediating the carbon interstitials formed upon implantation. Here we address the question of if magnetism arises from hydrogen implanted films and, via combined XRR, XRD, and magnetometry measurements, the relationship of structural and magnetic properties of the samples.

7.2 - Experimental Methodology

7.2.1 - Ion Distribution Calculations

Ion distributions in samples was calculated using SRIM software [94] which approximates the ion distribution, density, and carbon vacancy density in our samples. Ion flux was measured for each implantation condition: $3 \pm 1.5 \mu\text{A}/\text{cm}^2$ for 2kV acceleration voltage, $1.1 \pm 0.6 \mu\text{A}/\text{cm}^2$ for 500V, and $0.3 \pm 0.05 \mu\text{A}/\text{cm}^2$ for 360V acceleration voltage. Implantation energy and ion type for each of the samples studied are shown in Table 7.1.

7.2.2 - X-ray Measurements

The sample studied with incremental ion dose (C6MO5) was measured ex-situ after each ion dose using a four-circle high-resolution x-ray diffractometer (X'Pert Pro, Panalytical with $\text{Cu}\alpha_1$ radiation). XRD was obtained in this way by measuring intensity along the specular condition and subtracting a background from an off-specular scan along the same range in q_z .

Fig. 7.1 shows magnetometry data from four hydrogen ion implanted graphene samples. The coercive field for these samples ranged from 100-150Oe. Inset shows the entire range of the measurement to moment saturation. Data taken at 10K. Plotted are samples C6MO3 (black), C4 (red), C6MO4 (blue), and C2 (green).

7.2.3 - MPMS Measurements

Magnetization measurements utilized two Quantum Design MPMS3 SQUID magnetometers. Field dependent diamagnetic component from the substrate was subtracted. Samples were measured at fixed temperature, varying field and at fixed field varying temperature in both the zero-field cooled and field cooled conditions. The sample sizes for MPMS measurements were 4x6mm in order to fit in the standard plastic straw sample holder.

7.3 - Results and Discussion

After hydrogen ion implantation, four samples with different thickness and ion dose/energy were studied with magnetometry to determine the magnetic properties of the graphene film. In order to understand the magnetic behavior magnetization vs. field loops were measured at 10K. These samples thickness, saturation moment, coercive field,

remanence, ion energy, and ion dose are given in Table 7.1. From these results, shown in Fig. 7.1 with the linear diamagnetic background from the substrate subtracted, we observe ferromagnetic behavior with a small coercive field of between 100-200 Oe for every implanted sample. In our sample with the highest magnetic moment (a saturation moment of 1.2×10^{-5} e.m.u.) the moment was calculated to be $0.14 \pm 0.05 \mu_B/\text{hexagon}$, far exceeding high-energy proton irradiated graphite at room temperature [5].

Given the varying degree of magnetism for the four samples, we aimed to understand the relationship of the saturation moment with the ion dose in the graphene film, in the SiC substrate, and the entire sample. This could help us determine, if hydrogen content is driving magnetism, whether magnetism is coming from a specific component of the sample. In order to calculate the dose in each portion (substrate or film) of the sample, SRIM calculations were completed, allowing for an estimation of the fraction of the dose in the SiC and graphene via partial integration of the calculated ion distribution. From these fractions of the overall dose, we can determine the amount of hydrogen in each portion of the sample. With this result we did a comparison of the magnetism arising from each sample, shown for the four samples in Fig. 7.2. As shown in Table 7.1, these samples vary in fluence, in thickness, and in ion implantation energy. These differences in treatment conditions and sample properties lead to different structural changes and ion densities in graphene and SiC. In Fig. 7.2, the total saturation moment for each sample is attributed to either the SiC, the graphene film, or the total sample to understand what is driving the differences in magnetism we are seeing between samples.

These results became the first indication that hydrogen content (through chemisorption) may not be the only driver of magnetism seen in graphene. The moment

Fig. 7.2 shows the lack of a trend with regards to hydrogen in graphene (blue triangle), hydrogen in SiC (red x), and total ion dose (black circles).

does not scale with ions in graphene (blue triangles in Fig. 7.2), SiC (red x), or the total fluence in the film (black circles) for these four samples. From the Lieb's theorem picture for graphene magnetism we would expect the moment to scale with the dose in graphene (effectively the H:C ratio) and saturating at a high fluence. However, it is clear from these results that this is not the case for H implanted films.

The absence of a trend with ion dose leads to the question of the source of the ferromagnetism seen in graphene: if hydrogen ions in the film are not the main indicator what change is occurring during implantation which leads to magnetism? Given the results discussed in Chapter 5, we know the structural changes vary with ion dose, energy, and mass. In order to ascertain the effect of the structural changes observed and reported in Chapter 5, a single sample was studied with multiple successive hydrogen doses with constant ion energy. In this sample, the entire ion distribution remained in graphene. At

Fig. 7.3 shows the change in saturation moment for multiple doses on sample C6MO5. Dose is entirely in graphene. The gap which appears in the spectra are due to residual field in the magnet prior to measurement.

each dose magnetometry data and XRD were collected and fit. This 50L sample (C6MO5) was treated with a low acceleration voltage of 360V, which was calculated by SRIM to allow the ions to stay in the film. Simultaneously, a bare SiC sample was also treated to determine if any magnetism arose from the substrate as has been found in other studies [114].

Magnetometry data for the bare SiC substrate after implantation gave no measurable moment. In graphene, however, we observe a magnetic moment which changes as a function of dose. The magnetometry data for room-temperature magnetization vs. field is shown in Fig. 7.3. From these field loops, which show an opening due to an instrumental effect (not observed in Fig. 7.1 as it was run on another MPMS system without this effect from a residual field in the magnet), we extract a saturation moment as an indicator of the

ferromagnetic behavior for each dose. The saturation moment is taken to be the average of the measured moment for each data point for fields exceeding ± 2 tesla (20kOe).

The diffraction data, shown in Fig. 7.4(a), was modeled for the sample using the ΔN model discussed in Chapter 5. From this model, which only allowed for the variation of number of layers and d-spacings, the expansion of the film was extracted. Evident from prior work in Chapters 5-6, the expansion is an indicator of carbon interstitial formation. From the extracted structural features of the sample after each dose we can begin to investigate how the moment is influenced by the formation of these interstitial defects. The SiC Bragg peak of the graphene sample did not vary, shown in Fig. 7.4(b), indicating the SiC crystallinity was not affected.

In Fig. 7.5 we see the dependence of the saturation moment of the sample (at 300K) for the ion density in graphene (black) and the graphene interlayer expansion (blue). From the curve relating ion density to saturation moment it is clear that the moment does not scale with ion density in graphene (or equivalently ion fluence), as it increases initially but then saturates after an ion density of 1H:C. Contrary to this the expansion of the film (determined from XRD) relates linearly (blue line in Fig. 7.5 shown to guide the eye) to the saturation moment in the film. This relationship to the expansion is an indicator of carbon interstitial formation, and therefore this result clearly shows that carbon interstitial formation from ion implantation, rather than hydrogen chemisorption to the graphene sheet, is the primary source of the ferromagnetic domains in our films.

From this result we conclude that the formation of carbon interstitials leads to magnetism in implanted graphene samples. Next, we aim to discuss the potential avenues

Fig. 7.4 shows XRD data which was taken at various ion fluence iterations in the graphene sample. Shown is the graphene 1st order Bragg peak (a) and the SiC 004 peak (b).

by which an interstitial can exhibit magnetism. When a proton creates an interstitial there might be two potential sources of magnetism: the interstitial vacancy pair where a carbon atom is knocked completely from graphene sheet and the interstitial defect where 1-2 sigma (in-plane) carbon bonds are broken creating carbon dangling bonds. As hydrogen ions come to rest after creating this damage, they can stabilize these defects through bonding, effectively creating a mix of sp^2 and sp^3 carbon. We know that hydrogen chemisorption does occur because neutron reflectivity shows the retention of hydrogen in implanted films (Chapter 5). However, the nature of the disorder in the system makes the determination of its effect difficult to interpret. Hydrogen can quench the magnetism if every carbon becomes sp^3 hybridized, leading to the conclusion that there is an ideal H:C ratio which can maximize the dose. To further examine the relationship of hydrogen to magnetism in implanted samples, polarized neutron reflectivity experiments which can determine simultaneously the hydrogen and magnetic sample profile are planned on BL-4A at the ORNL SNS.

Fig. 7.5 shows the relationship of ion fluence and graphene interlayer expansion with the saturation moment measured for a single sample with sequential doses. As shown the moment increases linearly with expansion.

7.4 - Summary

We show room-temperature ferromagnetism arising from low-energy hydrogen ion implantation of many-layer graphene grown on C-face 4H-SiC. From magnetometry on many samples we see a weak remanence and a coercive field of 100-200Oe. We see that ion density in graphene or total ion fluence is not an indicator of the magnetism of the film. From structural analysis we find that carbon interstitial density, indicated by interlayer expansion, drives the magnetism resulting from implantation. Potential mechanisms for the formation of localized moments though clustering of defects and different interstitial conformations are shown to be potential avenues to the magnetism observed in hydrogen implanted films. The moment which we measure from our most magnetic film ($0.14 \pm 0.05 \mu_B/\text{hexagon}$) far exceeds the moment measured from high-energy implanted graphite films.

8 – Outlook and Continuation

8.1 – XRR and NR of Hydrogen Implanted Graphene

Reflectivity studies of epitaxial graphene have been inherently difficult due to the large roughness of samples. The added complication of disorder from ion implantation has compounded this problem. Nevertheless, ongoing work includes the interpretation of XRR data from sample C6MO5, shown in Fig. 8.1 at multiple ion fluences. The change in the XRR is indicative of a dramatic increase in thickness. This sample, which had the dose entirely in graphene, should not have any ions in SiC. Therefore, it is not known what is causing the oscillation suggesting a thickness change. At the present, the fitting of the XRR from C6MO5 seems to suggest two effects – a change in the buried interface (like in Chapter 4) between graphene and SiC and a change in the graphene roughness. However, quantitatively addressing these changes requires additional measurements to corroborate the graphene thickness and possible buried interface change.

Neutron reflectivity, which is ongoing at BL-4A at the ORNL SNS, has revealed the presence of hydrogen in implanted samples C2 and C6M10 (~80L sample). Sample C6M10, which is planned to be measured using PNR, has been measured before and after H ion implantation at the buried SiC/graphene interface. The results of this measurement are shown in Fig. 8.2(a). The corresponding profiles, shown in Fig. 8.2(b) demonstrate that the SLD of the graphene and the transition layer (interface) of this sample, implanted with the ion distribution centered at the graphene/SiC interface, decreases which is indicative of the presence of hydrogen. Because we were able to measure this sample prior to implantation, a direct comparison allowed for determination of hydrogen content in the graphene/SiC interface. Given the high quality of the sample,

Fig. 8.1 shows the change reflectivity for sample C6MO5 as a function of ion dose. The change in the fringe position indicates a thicker layer forming.

Fig. 8.2 shows the change neutron reflectivity for sample C6M10. In (a) the best fit to the data (solid lines) is shown both before and after implantation. In (b) the resulting profiles are shown, where the incorporation of hydrogen at the interface and in graphene lower the SLD of these layers.

we plan to measure PNR to attempt to correlate the ion distribution with the magnetization profile in C6M10.

Fig. 8.3 shows the calculated spin asymmetry (SA) for a sample having 3.5emu/g (green) and 0.9emu/g (magenta). In order to illustrate our ability to measure SA, the open black circles with error bars shows data taken on BL-4A from virgin 80L sample C6M10 proposed to be measured after H implantation.

Fig. 8.3 demonstrates that we expect to observe spin-asymmetry from PNR on BL-4A using our current best sample magnetization applied to sample C6M10. The error bars for the spin-asymmetry (SA) measured on BL-4A (~24 hrs) were obtained from a non-magnetic virgin sample that will be H-implanted for the proposed beam time. Also shown are calculations of the SA using Ref1D for the two sample magnetizations of 5-50emu/g. The lower magnetization is just above the detection limit whereas our new higher magnetization sample leads to a measurable SA. Our calculations give an expected sensitivity to see moments down to ~ 1 emu/g.

8.2 – Analysis of the SiC Bragg Change by Implantation of Graphene Samples Centered at the Graphene/SiC Interface

Fig. 8.4 shows the asymmetry which appears at the SiC Bragg reflections (004 shown here). Fitting of the SiC Bragg reflections in graphene samples which are implanted with the dose at the graphene/SiC interface will provide insight into the ion damage to the substrate. Shown is data from sample C6MO4.

Much like the analysis of the Bragg reflections of graphene, the SiC Bragg reflections can be fit to determine the structural changes which occur to the crystal with low energy hydrogen ion implantation. From measurements of the SiC Bragg we see a peak asymmetry, shown in Fig. 8.4, for samples with the ion dose centered at the graphene/SiC interface. The tail, going to low q is indicative of an expansion in some portion of the SiC near the interface. To better understand this change, in hopes to relate it to both the NR and XRR data, fitting of the SiC Bragg reflections is underway.

Fig. 8.5 shows the M vs. T (zero-field cooled condition) for sample C6MO5 at multiple ion fluences.

8.3 – MPMS Measurements of H Implanted Graphene

MPMS data has two main issues which we aim to understand: the possible change in shape of the M vs. T curves with high fluences and the instrumental broadening of the gap in the M vs. H data, as in Fig. 7.3.

From the MPMS measurements of sample C6MO5, we find the shape of the M vs. T changes at high fluence. The emergence of two features at these high fluences is not well understood but the feature at 50K in Fig. 8.5 is attributed to molecules like oxygen on the surface of graphene, which is a possibility indicated by XPS. These organic molecules can stick to the surface and contribute to the magnetization of the sample. Particularly, oxygen has a contribution which begins around 50K. While the emergence of these features is potentially interesting, we do not observe similar features in samples implanted at similar doses (up to 3H:C, $\sim 10^{18}$ ions/cm² with dose centered at the graphene/SiC interface) making the determination of the significance of this feature in magnetism from graphene convoluted.

The gap in M vs. H data measured on C6MO5 (Fig. 7.3) is of concern. However, it is a well-known issue for samples having complex backgrounds in SQUID measurements (voltage plots) [115]. Because we are measuring a weak magnetic response on a large diamagnetic background from the substrate, the treatment of the voltage vs. position scans and understanding of possible systematic errors is important in retrieving the true magnetic signal from the substrate. The latter issue is being investigated by running samples at multiple conditions. Residual fields in the magnet or current in the power supply can be quenched prior to measurements in order to test their effect on the M vs. H data obtained on known samples. Additionally, sample mounting can be an important factor especially if the magnetic signal we are seeing is not isotropic. In order to investigate this, sample mounting to a quartz rod and Cu rod is being tested in addition to measurements of the out of plane component of magnetization to determine if there is any magnetic anisotropy are planned.

8.4 - Continuation of He Implantation Studies

Chemical modification of graphene (chemisorption) has been discussed in detail in prior chapters. While the chemical modification of graphene has been demonstrated to lead to functional changes such as magnetism, Chapter 6 calls into question the role of chemical modification vs. self-interstitial carbon in the magnetism in which we observe in graphene from hydrogen ion implantation. In addition to the PNR measurements, other studies of He implanted samples are ongoing. First, x-ray photoelectron spectroscopy measurements are being done in order to compare He and H implanted samples. Presumably, a change in functionality by chemisorption as compared to vacancy formation could be distinguished by investigating the C1s spectra. Tandem with this study is the investigation of He retention

via residual gas analysis during sample annealing. Knowing if He is retained is important to understanding the expansion, we see in He implanted samples as compared to H, which we know from NR is retained after implantation.

Also ongoing are the studies of magnetism as a function of He ion dose in graphene. Understanding and comparing these results to the H implanted study will aid in the understanding of how different defect types lead to magnetism in graphene. He implantation studies have been shown to have dramatic structural effects on the graphene film and, from preliminary measurements, lead to a magnetic moment. We intend to compare directly the magnetism arising from both He and H implanted films with the dose centered at the graphene/SiC interface. By continuing these studies, it is our hope to better understand the driving cause for magnetism in graphene via implantation.

Appendix – Experimental Setup

A1 - Atomic treatment chamber

In order to test the possibility of chemisorption of hydrogen to graphene by atomic hydrogen treatment, a UHV chamber utilizing a tungsten (W) filament to crack molecular hydrogen was prepared. The requirements of the chamber were having ultimate pressure $\sim 5 \times 10^{-10}$ Torr, having the ability to heat and measure the temperature of the sample, the ability to vary the sample to filament distance, the ability to isolate the pumping station, and pressure control and measurement capabilities. In order to reach ultimate pressure, the chamber was baked for 24 hour period.

In order to accommodate for the filament, which required the W to heat to $>1600\text{K}$, a high voltage feedthrough was needed. Nickle feedthroughs were used as they allowed for spot-welding of the filament to the Ni posts and met the requirement for voltage/current feedthrough to the filament to reach the desired temperature. Filament to sample distance was regulated by mounting the filament on a bellow which allowed distances to vary from $\sim 2\text{-}30\text{cm}$. Sample temperature was controlled by an electrical feedthrough to two rod heaters in series which allowed for temperatures up to $\sim 1000\text{K}$ and temperature was measured using thermocouple feedthrough. A standard ($4\frac{1}{2}$ ") gatevalve was used to isolate the turbopump/pumping station during the exposure to atomic hydrogen. Pressure regulation was controlled by a leak valve which allowed for leaking hydrogen gas to pressures between $10^{-3}\text{-}10^{-7}$ Torr. Pressure was measured using both a convectron and ion filament gauge allowing for access to pressure measurements from $10^2\text{-}10^{-10}$ Torr. A schematic of the chamber is shown below in Fig. A.1.

Fig. A.1 is a schematic of the atomic hydrogen source chamber built by A. R. Mazza at the University of Missouri. Components are: 1. Turbo/backing pump, 2. Gate valve, 3. Leak valve, 4. High voltage feedthrough with tungsten filament to crack atomic hydrogen, 5. bellow to adjust sample to filament distance, 6. Thermocouple feedthrough for sample temperature, 7. Sample holder with feedthrough for heating, and 8. Ion and convection gauges for pressure reading.

A2 - X-ray instrumentation

X-ray measurements performed at MU utilized two instruments. Both instruments are controlled with Spec software for data acquisition and motor control. The first which will be discussed will be referred to as the Mo instrument. The Mo instrument uses a rotating anode x-ray generator with a line beam from a Mo target. A Ge(111) monochromator is used in conjunction with a slit to produce a high-resolution beam

Fig. A.2 is a schematic showing the scattering plane of the Mo instrument at MU. Here the specular condition of the sample is demonstrated.

containing only $\text{MoK}_{\alpha 1}$ radiation with a wavelength of $\lambda = 0.70926 \text{ \AA}$. In the scattering plane the beam width is 0.12 mm with an angular divergence of 0.003° . The angular divergence out of the scattering plane is several degrees. A schematic of the instrument is shown in Fig. A.2.

The high resolution of the Mo instrument allowed for careful analysis of transverse (to the specular rod) scans. This allowed for, amongst other findings, determination of true specular scattering from rough samples at grazing angles and domain sizes exceeding $10\mu\text{m}$. The four-circle diffractometer which controls the rotation of the sample is a Heuber goniometer (sample stage) which allows for customization of the sample holder environment. A picture of the instrument is shown in Fig. A.3, showing the sample stage and other components. This ability to customize the sample environment was important in studying graphene samples, which are sensitive to x-rays in air due to formation of ozone in the beam.

Fig. A.3 is a picture of the Mo instrument at MU which shows the sample stage on the Heuber goniometer as well as the other components discussed in the text.

Fig. A.4 shows pictures of the vacuum furnace used on the Mo instrument for graphene samples in both the closed (a) and open to air (b) configurations.

Fig. A.5 shows the flightpath (in red) of the x-rays, monochromator, and source for the X3B2 instrument used in in-situ ion implantation studies.

In order to accommodate graphene samples, vacuum furnace which can be mounted onto the sample position of the instrument was used. This furnace was built for in-situ high temperature studies on the Mo instrument but was used only at room temperature as a vacuum chamber for the graphene samples. The furnace, pictured in Fig. A.4, has a KF 25 valve which was used as a port to pump with a turbo pump station. The x-rays travel through a thin aluminum window (seen in Fig. A.4(a)) and scatter from the sample which is mounted with a standoff. The standoff allows for the alignment of the sample at grazing angles to be straightforward. In order to reduce background, steel shim stock (seen in Fig. A.4(b)) was used to block the beam spill off in the vertical direction.

The second x-ray instrument used at MU, henceforth referred to as X3B2, utilizes a rotating anode x-ray source with Cu radiation. Here, rather than a conventional monochromator, a multilayer elliptical mirror monochromator was used. This utilizes a superlattice of Si/W and, because like a conventional monochromator, only reflects x-rays which satisfy Bragg's law, also serves as a filter for Cu K_{β} . This leaves us with an average

Fig. A.6 shows the flightpath (in red) into the sample chamber as well as the Auger, metal deposition, and ion gun used for in-situ studies in the chamber.

Cu K_{α} (mixing of α_1 and α_2) x-rays. The elliptical shape of the mirror allows for a point focus of the beam. The point focus both improves intensity at the sample location and allows (in principal) for in-plane studies of thin film samples. In order to avoid air scattering attenuating the beam, the flightpath of the x-rays is evacuated using a roughing pump. The monochromator and flightpath to the sample chamber are shown in Fig. A.5.

The sample environment on this source is the UHV chamber previously at Brookhaven National Lab. After it was decommissioned it was sent to Missouri and adapted to fit the source described above. X3B2 chamber is a chamber with capabilities such as ion implantation, metal deposition, Auger, and LEED seen in Fig. A.6. These allow for detailed in-situ x-ray studies of materials – lending eyes to crystallographic changes of graphene upon treatment via ion implantation. The sample stage on the chamber is on a probe arm (Fig. A.7) which inserts into a load lock allowing for quick changing of samples

Fig. A.7 shows the probe arm (in red) holding the sample stage inserted into the load lock. The main chamber is labeled, separated from the load lock by a gate valve.

Fig. A.8 shows the insert (first seal) of the load lock as well as the sample holder plate.

while maintaining UHV in the main chamber. This probe arm allows for sample translation in xyz, θ rotation, and χ rotation allowing for the alignment of the sample. The sample mount is pictured in Fig. A.8. Because this stage has an isolated filament and heat shield the ion current from the ion implantation can also be determined by measuring the current to ground from this isolated heat shield. The diffraction plane is in the vertical, contrary to the Mo instrument, and data is collected by a detector on a virtual 2θ elevator stage shown in Fig. A.9. The beam path enters and exits the chamber through a beryllium window.

Fig. A.9 shows beam path into the detector hutch (in red). The detector, elevator stage, Del rotation (allowing for a virtual 2θ arc, and Be window from the chamber are shown.

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