Interface Structure of Graphene on SiC for Various Preparation Conditions

Doctoral Thesis

May, 2012

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Abstract

In this thesis we study the preparation dependence of the interface structure of graphene on SiC. We compare epitaxial graphene grown in ultra-high vacuum (UHV), in an atmosphere of argon, and in a background of 10^{-4} Torr of disilane. Graphene growth is studied on both the polar faces of SiC – the SiC(0001) surface, also known as the Si-face and the SiC(0001) surface, also known as the C-face. We find that the quality of graphene and the interface of graphene on the substrate depend on which face of SiC is used, and also what environment it was prepared in. Characterization using atomic force microscopy (AFM), low energy diffraction (LEED) and low energy electron microscopy (LEEM) reveals that on the C-face the interface structure prior to graphitization sensitively depends on the preparation conditions. On the Si-face the interface structure prior to graphitization does not change for any of the three environments, however the quality of the graphene formed shows an improvement when prepared in disilane or argon compared to UHV.

When SiC is heated in vacuum the Si atoms preferentially sublimate leaving behind C atoms that rearrange to form graphene. In our prior work we found that compared to the Si-face graphitization of the C-face in vacuum results in thicker graphene films with a larger distribution of thicknesses. A reason for this could be the different nature of the graphene-substrate interface in the two cases. On the Si-face graphene growth is mediated through an interface layer that displays a $6\sqrt{3} \times 6\sqrt{3}$ -R30° LEED pattern (this interface layer is also known as the "buffer layer") which acts as a template for graphene growth, while on the C-face no such buffer layer is formed. This buffer layer on the Si-face is known to consist of basically a graphene monolayer, but with some of the carbon atoms bonded to the underlying SiC.

Graphene produced on SiC in vacuum conditions is quite inhomogeneous with small domain sizes and (we refer to an area with a constant thickness of multilayer graphene as a "domain") and numerous pits. On the Si-face it has been found by many research groups including our own that graphitization in an atmosphere of argon results in large monolayer domains with an elimination of pits. The argon decreases the Si sublimation rate, thus increasing the temperature required for graphene formation. The higher graphitization temperature results in an improved morphology of the graphene film. Some researchers use a background of disilane instead of an atmosphere of argon, and in this thesis we report our results for graphitization of SiC in a disilane environment. On the Si-face we find an improvement in the morphology of disilane prepared graphene films compared to those prepared in vacuum, consistent with other researchers. In terms of the interface structure prior to graphitization no difference was found for graphene produced in UHV, argon or disilane. For all three environments the LEED pattern from the interface prior to graphitization displayed $6\sqrt{3} \times 6\sqrt{3}$ -R30° ($6\sqrt{3}$ for short) symmetry.

In an attempt to controllably form thin layers of graphene on the C-face we previously tried graphitizing in an atmosphere of argon, however that led to inhomogeneous islands of thick graphene forming over the surface. It was found that due to an unintentional oxidation of the surface during graphitization, the surface became resistant to graphitization. In this thesis we present results for graphitization of the C-face in a background of disilane, which to our knowledge has not been attempted before. We are able to form graphene films that are thin and uniform relative to those prepared in vacuum or argon. We demonstrate that by graphitizing in a background of disilane we avoid the unintentional oxidation that inhibits graphene formation on the C-face in argon.

For C-face samples prepared in disilane, prior to graphitization we observe a $\sqrt{43} \times \sqrt{43} \pm 7.6^{\circ}$ ($\sqrt{43}$ for short) in situ LEED pattern that has never been observed in vacuum prepared samples. This $\sqrt{43}$ pattern is found to disappear after air exposure. The *ex situ* LEEM reflectivity curves of such a disilane prepared sample show unique features not seen in any vacuum prepared sample. By analyzing the LEED pattern and the LEEM reflectivity curves we associate the unusual reflectivity curves we observe on the C-face with a buffer layer, analogous to the $6\sqrt{3}$ layer that form on the Si-face. This buffer layer has the $\sqrt{43}$ symmetry due to bonding to the underlying SiC, but upon air exposure these bonds are broken (due to oxidation of the SiC) and the layer becomes "decoupled" from the SiC. This decoupling of the buffer layer on the C-face is analogous to what occurs upon oxidation or hydrogenation of the $6\sqrt{3}$ layer on the Si-face. We believe that the $\sqrt{43}$ layer does not form in vacuum prepared samples due to kinetic limitations but is able to form in Si-rich environments (such as disilane or furnace grown graphene) as the graphitization takes place with the Si sublimation rate closer to equilibrium. The schematic shown below summarizes the differences between Si-face and C-face SiC/graphene interface structures, depending on preparation conditions (vacuum or Si-rich). The right most figure shows the main result of this work, which puts graphene formation on the C-face on a similar footing as for the Si-face since the "buffer" layer provides a template for the graphene growth.



A separate project discussed in this thesis is scanning tunneling microscopy/spectroscopy (STM/S) on epitaxial graphene on the Si-face. Two different studies were performed. In the first study we performed STM/S on a Si-face graphene sample in which a large fraction of the area was covered by a secondary disordered phase. The disordered phase showed a graphene-like spectrum with additional features that could arise from dangling bonds or defects. On the basis of additional data from AFM and Auger electron spectroscopy we argue that this secondary phase is similar to the nanocrystalline graphite (NCG) phase that we observe on C-face samples. In the second study we performed STS on a graphene sample that was functionalized by hydrogen. Functionalizing graphene changes the nature of its bonding and can open up a band gap in it. Our STS results indicate that no band gap opened up in the graphene, however we found the presence of additional states in the spectra that indicate the nature of the bonds in graphene had changed due to the hydrogen functionalization.

In the last study of this thesis we perform LEEM on graphene samples prepared on Cu foil. The samples were made in a chemical vapor deposition (CVD) chamber under different growth conditions. LEEM was used to measure the reflectivity curves and perform selected area diffraction on the samples. The reflectivity curves allowed us to determine the graphene thickness, and the selected area diffraction allowed us to determine the orientation of the graphene and whether it was single-crystal or not.

Acknowledgements

Firstly I would like to wholeheartedly thank my advisor Prof. Randall Feenstra for investing so much of his time guiding, advising and going through the nuts and bolts of every experiment with me. It has been an honor to work with such a brilliant and thorough scientist. I especially admire his ability to come into the lab, understand and troubleshoot our experiments while also providing the vision to our group to explore new research avenues.

Next I would like to thank my extremely talented lab member Guowei He, who not only helped with sample preparation but cheerfully offered his time helping me troubleshoot any hardware, software or technical issues I have had in my own experiments. I am indebted to him for his selflessness and help.

I would like to thank my very supportive and insightful committee members Profs. Sara Majetich, Steve Garoff, and Dave Greve. Amongst the Physics staff I would especially like to thank Hilary Homer for going out of her way to help me out with paperwork issues. I would also like to thank Al Brunk for helping out with computer issues and Gary Wilkins for help with hardware issues. I would also like to thank the amicable Chuck Gitzen, Mary Jane Hutchinson and Donna Thomas.

I would like to thank Luxmi for always being an inspiration and a role model for me. I would also like to thank Patrick Mende for the many useful physics discussions we had on our research. I would like to wish Sergio de la Barrera good luck in his future endeavors in our research group, and would like to commend him on how fast he picked up the STM. Our research group has a truly wonderful environment, and I am lucky to have worked with such nice and smart scientists.

I would like to thank my countless friends in Pittsburgh who made my stay here so special. Finally and most importantly I would like to thank my mother, father and sister for I could not have finished grad school without them. **Chapter 1**

Introduction

1.1 Introduction

Graphene is a two dimensional sheet of carbon atoms arranged in a hexagonal lattice as shown in Fig. 1.1. It was experimentally isolated from graphite by Novoselov *et. al.* in 2003 [1]. Their electrical characterization revealed that graphene is a semimetal in which room temperature mobilities of ~ $10,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ could be induced by applying a gate voltage. Since then many other exciting properties of graphene have been discovered which are reviewed in Ref. [2, 3, 4, 5, 6]. Some examples include the anomalous quantum hall effect and existence of a Berry's phase [7, 8], Klein tunneling paradox [9], breakdown of Born Oppenheimer approximation [10], the observation of Andreev reflections [11] etc. These properties arise from the unique band structure of graphene which will be derived in Section 1.2. However a major challenge that remains before graphene based products become commercially viable is to make wafer scale high quality graphene reproducibly. The different techniques that researchers have come up with to produce graphene will be discussed in Section 1.3.



Fig. 1.1 (a) Carbon atoms arranged hexagonally in graphene. (b) Formation of in plane σ bonds and out of plane π bonds in graphene. From Ref. [12].

1.2 Electronic properties of Graphene

In this section we start by describing the hybridization of carbon orbitals, and then derive the band structure of graphene using the tight binding approximation for p_z orbitals. We then discuss how as a consequence of its unique band structure graphene can show phenomenon specific to quantum electrodynamics (QED).

1.2.1 Hybridization of Carbon orbitals A carbon atom has 6 electrons which can be represented as $1s^2 2s^2 2p^2$ in the ground state [13]. The 2 electrons in the 1*s* shell are called core electrons and they are tightly bound to the carbon nucleus. The 4 valence electrons in the next shell overlap with the valence electrons of surrounding atoms to form chemical bonds. The electrons in the second shell can get excited from their ground state configuration of $2s^2 2p^2$ to an excited state of $2s^1 2p_x^1 p_y^1 p_z^1$. The $2s, 2p_x$, $2p_y$, and $2p_z$ orbitals can then combine in different amounts to form sp^n hybridized orbitals, where *n* is the number of *p* orbitals involved in the mixing. Due to their shape these hybridized orbitals. This higher overlap makes it is energetically favorable to form hybridized orbitals even though it costs some energy for the carbon electrons to go from their ground state to an excited state. The carbon atom undergoes different kinds of hybridization in different allotropes which determines the geometrical arrangement of the atoms. In carbynes the atoms are *sp* hybridized.

Graphene is essentially a single sheet of graphite. In sp^2 hybridized graphite/graphene the 2s orbital mixes with the $2p_x$ and $2p_y$ orbitals which results in three different linear combinations of the s, p_x and p_y orbitals. These three sp^2 hybridized orbitals are rotated from each other by 120° in the x-y plane and overlap significantly with the sp^2 hybridized orbitals of the three neighboring C atoms as shown in Fig. 1.1(b) to form strong σ bonds. Due to the strong nature of these bonds the electrons residing in these do not contribute to conductivity significantly. The unmixed p_z orbital of the C atom sticks out of the plane and overlaps weakly with the p_z orbitals from the neighboring atoms to form π bonds, also shown in Fig. 1.1(b). The electrons in these π bonds are delocalized and are responsible for the conductivity and other interesting electronic properties of graphene.

1.2.2 Reciprocal Lattice of Graphene The unit cell of graphene is shown in Fig. 1.2(a) by vectors \vec{a}_1 and \vec{a}_2 . The unit cell has two carbon atoms, A (gray colored) and B (black

colored) from two interpenetrating triangular sublattices. The nearest neighbor distance between two carbon atoms is $a_{C-C} = 0.142nm$. The length of the unit cell is $a = |\vec{a}_1| = |\vec{a}_2| = 0.142nm \times \sqrt{3} = 0.246nm$. The real space unit vectors are $\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$ and $\vec{a}_2 = a(0,1)$. The corresponding unit vectors in reciprocal space

can be calculated as $\vec{b}_1 = \left(\frac{4\pi}{\sqrt{3}a}, 0\right)$ and $\vec{b}_2 = \left(\frac{2\pi}{a\sqrt{3}}, \frac{2\pi}{3a}\right)$ and are as shown in Fig. 1.2(b).

From the reciprocal lattice the first Brillouin zone can be obtained as the shaded hexagon also shown in Fig. 1.2(b).



Fig. 1.2 (a) A unit cell of graphene in real space formed by basis vectors \vec{a}_1 and \vec{a}_2 . (b) Reciprocal lattice of graphene formed by basis vectors \vec{b}_1 and \vec{b}_2 . The shaded hexagon is the first Brillouin zone with sides $\frac{2\pi}{a\sqrt{3}}$ from the center. From Ref. [12].

1.2.3 Tight binding calculation of graphene band structure The solution to Schrödinger's equation in a periodic potential, such as in a crystal lattice, should satisfy the Bloch condition [14]. An electronic wavefunction that satisfies the Bloch condition (called a Bloch function) can either be expanded in a basis set of free electron plane waves or in a localized basis set of functions centered on the atom (e.g. tight binding approximation). The advantage of the latter is that the number of basis functions is smaller than that used in the former. The localized basis set in the tight binding approximation can be a linear combination of atomic orbitals (LCAO) which is why the tight binding method is often referred to as the LCAO method. In the tight binding

model the electron is treated as tightly bound to the nucleus, which is the other extreme of the free electron model in which the electron is essentially treated as a free particle. The advantage of applying the tight binding approximation to graphene is that it is simple and provides analytical solutions that agree well with more sophisticated *ab initio* calculations. The calculation of the band structure of a single sheet of graphite was first done by Wallace in 1947 using the tight binding model [15]. The following tight binding treatment of graphene is taken from Ref. [13] and [16] with additional details from [17, 18, 19, 20, 21].

A tight binding wave function for the j th orbital that satisfies the Bloch condition is given by

$$\Phi_{j}(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}}^{N} e^{i\vec{k}\cdot\vec{R}} \varphi_{j}(\vec{r}-\vec{R}), \quad (j=1,\cdots,n), \quad (1.1)$$

where \vec{R} is the position of the atom, φ_j denotes the atomic wave function in state j, n is the number of atomic wavefunctions in the unit cell, and N is the number of unit cells in the crystal (~10²⁴). \vec{R} is summed over all N unit cells in the crystal.

A transfer integral matrix and overlap integral matrix, $H_{jj'}(\vec{k})$ and $S_{jj'}(\vec{k})$, are defined as

$$H_{jj'}(\vec{k}) = \left\langle \Phi_j \middle| H \middle| \Phi_{j'} \right\rangle, S_{jj'}(\vec{k}) = \left\langle \Phi_j \middle| \Phi_{j'} \right\rangle, \ (j, j' = 1, \cdots, n), \tag{1.2}$$

where *H* is the Hamiltonian of the solid. The energy dispersion relation can be obtained by solving the secular equation

$$\det[\boldsymbol{H}-\boldsymbol{E}\boldsymbol{S}]=0\tag{1.3}$$

where H is the Hamiltonian in the representation of the localized states and S is the matrix of overlaps between the localized states (which are not, in general, orthogonal). For graphene the only state φ_j we will consider here is the $2p_z$ state (since this state produces the important electronic bands near the Fermi energy). Since each unit cell has two atoms, one of type A and B, we will have two Bloch functions, thus H and S will form a 2×2 matrix.

From Eq. (1.1) the Bloch function for atom A can be written as

$$\Phi_{A}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_{A}}^{N} {}^{i\vec{k}\cdot\vec{R}_{A}} \varphi_{j}(\vec{r} - \vec{R}_{A}), \qquad (1.3(a))$$

where the summation is extended over all N coordinates that have carbon atoms of the type A. Similarly for atom B the Bloch function is

$$\Phi_B(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_B}^{N} {}^{i\vec{k}\cdot\vec{R}_B} \varphi_j(\vec{r} - \vec{R}_B).$$
(1.3(b))

An atom of type A (or B) has three nearest neighbors of type B (or A), and has six next nearest neighbors of type A (or B). We will assume that the maximum contribution to the Hamiltonian comes from nearest neighbors. The (2×2) Hamiltonian matrix can be obtained by substituting Eq. (1.3(a) and (b)) into Eq. (1.2). The first matrix element H_{AA} is evaluated as

$$H_{AA}(\vec{k}) = \left\langle \Phi_A \middle| H \middle| \Phi_A \right\rangle = \frac{1}{N} \sum_{\vec{R}_A, \vec{R}_A'} e^{i\vec{k} \cdot (\vec{R}_A - \vec{R}_A')} \left\langle \varphi_A(\vec{r} - \vec{R}_A) \middle| H \middle| \varphi_A(\vec{r} - \vec{R}_A') \right\rangle,$$

where \vec{R}_A is summed over all N carbon atoms of type A and \vec{R}'_A is summed over nearest neighbors. However there are no nearest neighbors of type A so the only term that survives is $\vec{R}_A = \vec{R}'_A$ and we get

$$H_{AA} = \frac{1}{N} \sum_{R_A} e^{i\vec{k} \cdot (\vec{R}_A - \vec{R}_A)} \left\langle \varphi_A(\vec{r} - \vec{R}_A) \middle| H \middle| \varphi_A(\vec{r} - \vec{R}_A) \right\rangle = \left\langle \varphi_A(\vec{r} - \vec{R}_A) \middle| H \middle| \varphi_B(\vec{r} - \vec{R}_A) \right\rangle = \varepsilon_{2p}$$

$$(1.4)$$

where ε_{2p} is the energy of the non hybridized $2p_z$ orbital. The same procedure as above can be used to calculate H_{BB} for atoms of type B. If atoms A and B are equivalent, $H_{BB} = \varepsilon_{2p}$. (In graphene and AA stacked graphite, the carbon atoms A and B see the same chemical environment and are hence equivalent. For AB Bernal stacked graphite the equivalence is broken.) For normalized wavefunctions $[\langle \varphi_A(\vec{r} - \vec{R}_A) | \varphi_A(\vec{r} - \vec{R}_A) \rangle = 1]$, so from Eq. (1.2) the diagonal overlap matrix elements are

$$S_{AA} = S_{BB} = 1.$$
 (1.5)

To calculate the off diagonal matrix element H_{AB} we will need to sum over the three nearest neighbor atoms of type B that surround atom A. The position of the three nearest black atoms (type B) relative to the gray atom (type A) in Fig. 1.2(a) will be represented by R_{11} , R_{12} , and R_{13} , or for short R_{1i} where i = 1,2,3. We get

$$R_{11} = \left(\frac{a}{\sqrt{3}}, 0\right), R_{12} = \left(\frac{-a}{2\sqrt{3}}, \frac{a}{2}\right), \text{ and } R_{13} = \left(\frac{-a}{2\sqrt{3}}, \frac{-a}{2}\right).$$
 (1.6)

The off diagonal matrix element is

$$H_{AB}(\vec{k}) = \frac{1}{N} \sum_{R_A R_B} e^{i\vec{k} \cdot (\vec{R}_B - \vec{R}_A)} \left\langle \varphi_A(\vec{r} - \vec{R}_A) \middle| H \middle| \varphi_B(\vec{r} - \vec{R}_B) \right\rangle.$$

Similar to what we did for H_{AA} , we will sum R_A over all N carbon atoms of type A, and then sum R_B over type B nearest neighbors of carbon atoms A. We get

$$H_{AB}(\vec{k}) = e^{i\vec{k}\cdot\vec{R}_{11}} \left\langle \varphi_{A}(\vec{r}-\vec{R}_{A}) | H | \varphi_{B}(\vec{r}-\vec{R}_{A}-\vec{R}_{11}) \right\rangle + e^{i\vec{k}\cdot\vec{R}_{12}} \left\langle \varphi_{A}(\vec{r}-\vec{R}_{A}) | H | \varphi_{B}(\vec{r}-\vec{R}_{A}-\vec{R}_{12}) \right\rangle + e^{i\vec{k}\cdot\vec{R}_{13}} \left\langle \varphi_{A}(\vec{r}-\vec{R}_{A}) | H | \varphi_{B}(\vec{r}-\vec{R}_{A}-\vec{R}_{13}) \right\rangle.$$

$$(1.7)$$

The φ s are radially symmetric in the graphene plane and depend only on the distance between A and B, so all $\langle \varphi_A(\vec{r} - \vec{R}_A) | H | \varphi_B(\vec{r} - \vec{R}_A - \vec{R}_{1i}) \rangle$ s are equal to each other. We can define

$$\gamma_{0} = \left\langle \varphi_{A}(\vec{r} - \vec{R}_{A}) \middle| H \middle| \varphi_{B}(\vec{r} - \vec{R}_{A} - \vec{R}_{1i}) \right\rangle \quad (i = 1, 2, 3)$$
(1.8)

where γ_0 represents the interaction between first-neighboring atoms in a graphene.

Substituting Eq. (1.8) in Eq. (1.7) gives

$$H_{AB} = \gamma_0 (e^{i\vec{k}\cdot\vec{R}_{11}} + e^{i\vec{k}\cdot\vec{R}_{12}} + e^{i\vec{k}\cdot\vec{R}_{13}}).$$
(1.9)

The same treatment as for H_{AB} gives

$$S_{AB} = s_0 (e^{i\vec{k}\cdot\vec{R}_{11}} + e^{i\vec{k}\cdot\vec{R}_{12}} + e^{i\vec{k}\cdot\vec{R}_{13}}), \qquad (1.10)$$

where $s_0 = \langle \varphi_A(\vec{r} - \vec{R}_A) | \varphi_B(\vec{r} - \vec{R}_A - \vec{R}_{1i}) \rangle$ represents the non orthogonality of the φ s. It can easily be shown that

$$H_{AB} = H_{BA}^{*} \text{ and } S_{AB} = S_{BA}^{*}.$$
 (1.11)

The sum of phase factors in Eq. (1.9) and (1.10) can be written as $e^{i\vec{k}\cdot\vec{R}_{11}} + e^{i\vec{k}\cdot\vec{R}_{12}} + e^{i\vec{k}\cdot\vec{R}_{13}} = f(k)$. Substituting for R_{1i} from Eq. (1.6) f(k) can be evaluated as

$$f(k) = e^{i_{kx}a/\sqrt{3}} + 2^{-ik_{x}a/2\sqrt{3}}\cos(\frac{k_{y}a}{2}).$$
(1.12)

Using the matrix elements calculated in Eq. (1.4), (1.5), (1.9), (1.10), and (1.11), H and S can be written out as

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{\varepsilon}_{2p} & \boldsymbol{\gamma}_0 f(k) \\ \boldsymbol{\gamma}_0 f(k)^* & \boldsymbol{\varepsilon}_{2p} \end{pmatrix}, \ \boldsymbol{S} = \begin{pmatrix} 1 & s_0 f(k) \\ s_0 f(k)^* & 1 \end{pmatrix}.$$
(1.13)

Substituting the above matrices into the secular equation (1.3) we get

$$\boldsymbol{H} - E\boldsymbol{S} = \begin{pmatrix} \varepsilon_{2p} - E & (\gamma_0 - s_0 E) f(k) \\ (\gamma_0 - s_0 E) f(k)^* & \varepsilon_{2p} - E \end{pmatrix} = 0.$$

Solving the above equation for E gives the well known dispersion relationship

$$E^{\pm} = \frac{\varepsilon_{2p} \pm \gamma_0 w(\vec{k})}{1 \pm s_0 w(\vec{k})} \text{ where } w(\vec{k}) = \sqrt{\left|f(\vec{k})\right|^2} = \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}.$$
(1.14)

The + signs in the numerator and denominator give the bonding π energy band, and the – signs give the antibonding π^* band. The tight binding parameters ε_{2p} , γ_0 , and s_0 are found by fitting experimental or *ab initio* data . The plot of the dispersion relationship surface defined by Eq. (1.14) is shown in Fig. 1.3(a).

At the boundary of the first Brillouin zone the dispersion surface is conical. Around these K and K' points the energy-momentum relationship is linear which implies the effective mass in this momentum range is zero. The K and K' points are also referred to as Dirac points because the dispersion relation around these points is like that of a relativistic massless particle. Most semiconductors have a dispersion relation that is parabolic about extrema of the conduction or valence bands. The unique dispersion relationship is responsible for graphene's exciting electronic properties, which will be discussed further in Section 1.2.3. Figure 1.3(b) shows a comparison of dispersion relations calculated from *ab initio* and nearest neighbor tight binding calculations [18].



Fig. 1.3 (a) A three dimensional plot of the surface represented by Eq. (1.14). The z axis is E^{\pm} , the x and y axes are k_x and k_y respectively. From Ref. [2]. (b) A comparison of dispersion relationship obtained from nearest neighbor tight binding approximation with that calculated from first principles. Tight binding parameters used were $\varepsilon_{2p} = 0$, $\gamma_0 = -2.7eV$, and $s_0 = 0$. From Ref. [18].

In the tight binding dispersion shown in Fig. 1.3(b) $s_0 = 0$ resulting in the conduction and valence bands being symmetric about the Dirac point unlike the *ab initio* dispersion relation which is asymmetric about the Dirac point. Using a finite value of s_0 makes the tight binding dispersion more asymmetric and gives a better agreement with the *ab initio* dispersion. Including interactions with more distant neighbors also improves the agreement between the two [18]. As more layers are included in the tight binding calculation the overlap between the conduction band and valence band starts to increase and the dispersion relationship becomes parabolic near the Fermi energy. For a thickness greater than 10 layers the band structure resembles that of graphite [19]. It should also be noted that if the equivalence between the carbon atoms A and B is broken, the site energy ε_{2p} would be different for the two atoms and the energy dispersion would show an energy gap between the conduction and valence bands. This provides a route for opening up a band gap in graphene.

The band structure for the $2sp^2$ hybridized orbitals and 3s orbitals in graphene can also be calculated in the tight binding approximation. These orbitals do not contribute significantly to the conductivity, but play a significant role in the electron reflectivity observed in Low Energy Electron Microscopy (LEEM) and will be further discussed in Section 2.4.2.

1.2.3 Quantum electrodynamics in graphene As discussed in the previous section monolayer graphene has a linear dispersion relationship similar to that of a relativistic massless particle. The electrons in graphene themselves do not have a relativistic velocity, it is only the dispersion relation of graphene that resembles that of a relativistic particle. Graphene can be thought of as being made of quasiparticles that are massless Dirac fermions. It is more appropriate to describe such relativistic quasiparticles by the Dirac equation from quantum electrodynamics, instead of the Schröedinger equation which is used for non-relativistic particles [2,9]. The Dirac Hamiltonian for a massless fermion is

$$\hat{H} = -i\hbar c \,\sigma \nabla \tag{1.15}$$

where *c* is the speed of light and $\sigma = (\sigma_x, \sigma_y)$ are the Pauli matrices. For graphene *c* is replaced by the Fermi velocity v_F (which is about 10⁶ ms⁻¹) and σ is replaced by a matrix that defines the relative contributions of the A and B type sublattices. σ is also referred to as pseudospin because in the Dirac equation for graphene quasiparticles it plays the role that real spin does in electrons. The exotic electronic properties of graphene arise from its linear dispersion and its pseudospin [4, 9,21]. In bilayer graphene the dispersion relation is parabolic near the K and K' points, implying a finite effective mass of low energy quasiparticles. Although the dispersion relation for bilayer graphene is unlike that of monolayer graphene, bilayer graphene also has unique properties not seen in a regular two dimensional electron gas. Bilayer graphene can be shown to have a pseudospin associated with the relative contribution of two inequivalent sublattices in each layer, forming a unique system of massive dirac fermions [22,23,24]. Monolayer and bilayer graphene thus form unique condensed matter systems where quantum electrodynamic effects can be observed. Figure 1.4 summarizes different systems and the corresponding dispersion relation, Hamiltonian and nature of the charge carriers. For detailed on the exotic electronic properties of graphene the reader is referred to Ref. [2,3,4,6,21,25, 26].



Fig. 1.4 Different systems and the corresponding dispersion relation, Hamiltonian, and nature of the charge carrier. (a) Most systems in condensed matter show a parabolic dispersion in which the electrons are described by Schrödinger's equation. (b) relativistic massless fermions have a cone like linear dispersion and are described by the Dirac equation of Eq. (1.15). (c) In graphene the charge carriers have a linear dispersion relation implying a zero effective mass. The quaisparticles of graphene are described by the Hamiltonian of Eq. (1.15) with *c* replaced by v_F . (d) In bilayer graphene the dispersion relation is parabolic and but the charge carriers have a pseudospin associated with them. The Hamiltonian combines features of both Schrödinger's equation. From Ref. [26].

1.3 Graphene synthesis

The three main techniques for graphene synthesis described in this section are mechanical exfoliation of highly oriented pyrolitic graphite (HOPG), chemical vapor deposition (CVD) growth on metals, and epitaxial growth on SiC. Exfoliating HOPG produces the highest quality graphene of the three techniques but can not be used to produce large scale graphene. Epitaxial graphene on SiC is a promising technique to produce high quality wafer scale graphene with the advantage that the SiC is an insulating substrate, so the graphene formed on it can directly be used in device applications without having to transfer to another substrate. This technique is however quite expensive due to the high cost of SiC wafers. CVD growth of graphene on Cu foils is an affordable technique to produce large scale graphene as Cu foil is quite cheap. However the graphene produced is not single crystal and has many grain boundaries that degrade the electrical properties of the graphene. Another disadvantage

in order to use the graphene for device applications. The etching away of the substrate and the transferring of graphene to an insulating substrate are tedious, and further degrade the quality of the graphene produced. In this section we will describe epitaxial graphene on SiC and CVD growth on Cu substrates in more detail as graphene samples made from such techniques will be studied experimentally in this thesis. For reviews on the different techniques to synthesize graphene the reader is referred to Ref. [5, 27, 28].

1.3.1 Mechanical exfoliation of graphite The researchers who first produced graphene did so by exfoliating it from graphite [1,29]. This technique is also known as micromechanical cleavage. The researchers used scotch tape to peel off the top layers of HOPG which leaves a thin layer of graphite on the scotch tape. By repeating this procedure several times the graphite is thinned down to a few ML or less. The graphene is then transferred to a Si substrate which has a 300 nm coating of SiO_2 . Graphene that rests on a substrate is called supported graphene; if the substrate is etched away and supported only on the edges it is called suspended graphene. Graphene supported on SiO_2 can be identified using an optical microscope. The interference of light from a 300 nm SiO_2 film results in a purple-blue color. The addition of a layer of graphene causes the contrast to change for two reasons [30], the addition of a path difference due to graphene and the opacity of graphene, which is 2.3% in the visible range. This optical contrast is crucial to identifying graphene domains, and using an even slightly different thickness of SiO₂ results in a decrease in the contrast of graphene [30]. For exfoliated graphene supported on SiO₂ and suspended graphene, mobilities as high as 15,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and 200,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively have been reported [28, 1, 31]. The high mobility indicates that exfoliated graphene is of high quality but this technique can not be used to produce graphene on a large scale.

1.3.2 Epitaxial graphene on SiC

Another technique to grow graphene is by the sublimation of SiC [32]. When SiC is heated to a high temperature in ultra high vacuum the Si preferentially sublimates leaving behind carbon atoms that rearrange to form graphene. Graphite formation on SiC was first studied by van Bommel *et al.* [33], but with the recent discovery of the exciting electronic properties of graphene there has been a renewed interest in

graphitization of SiC surfaces with the aim of reproducibly making graphene of a specific thickness.

We first briefly review the structure of SiC. The particular stacking sequence of a bilayer formed of a plane of Si and C atoms is known as a polytype. By changing growth conditions, SiC can be grown in various cubic and hexagonal polytypes. Graphene growth is mostly studied on *n*H polytypes of SiC where *n* is the number of SiC bilayers in the unit cell and H signifies that the polytype is hexagonal [12,34]. The most commonly used hexagonal polytypes for graphene growth are 6H and 4H SiC whose unit cells are shown in Fig. 1.5(a). The two polar faces of SiC are shown in Fig. 1.5(b). The [0001] direction is along the positive c-axis of the crystal, and the [0001] direction is along the negative c-axis. The (0001) surface is the basal plane of SiC that has an outward normal in the [0001] direction. The (0001) surface is also known as the *Si-face* and the (0001) surface also known as the *C-face*.



Fig. 1.5 Structure of SiC (a) Unit cell of 4H-SiC and 6H-SiC. Filled circles are carbon atoms and open circles are silicon atoms. $a_{siC} = 0.3nm$ and the distance between two successive SiC bilayers is 0.25 nm. For an *n*H unit cell $c_{siC} = n \times 0.25nm$. From Ref. [32]. (b) A 6H-SiC crystal showing the two polar faces, the Si-face and C-face. For a SiC crystal with a simple termination of the lattice at the surface as shown here, the Si-face refers to the face with Si atoms being outermost in the bilayer that terminates the surface, while the C-face refers to the face with C-atoms being outermost in the bilayer that terminates the surface. From Ref. [12].

The properties of epitaxial graphene on SiC depend heavily on whether it is grown on the Si-face or C-face. Graphitization occurs at a lower temperature on the C-face compared to the Si-face. The interface between graphene and SiC is different for the two faces and also depends on the preparation conditions. The nature of the interface influences the properties of the graphene and will be discussed in more detail in Section 3.1. For Si-face samples prepared in vacuum a $6\sqrt{3}\times6\sqrt{3}$ reconstruction at the interface of graphene and SiC acts as a precursor to graphene formation [35, 36, 37, 38, 39, 40]. This $6\sqrt{3}$ layer (also known as a 'buffer layer') provides a template for further graphene growth and forces the graphene layers to be azimuthally aligned with respect to the underlying substrate. On the other hand vacuum prepared C-face samples do not show such a buffer layer, but show a 2×2 or 3×3 reconstruction at the interface [41, 42]. The lack of a buffer layer is believed to be the reason C-face graphene shows rotational disorder. Other differences in morphology and electronic properties between films grown on C-face and Si-face are also believed to be a result of the different interfaces on the two faces and will be examined in more detail in Section 3.1.

Graphene films prepared by vacuum annealing of SiC have domains that are limited in size. For multilayer graphene a domain refers to a region of constant graphene thickness and a grain refers to an area with only one crystal orientation. To increase the domain size a background gas such as disilane or argon is introduced during graphitization [43,44,45]. The background gas decreases the sublimation rate of Si from SiC bringing the graphitization closer to equilibrium which is expected to improve homogeneity and morphology of the graphene films. This improvement is indeed is seen on the Si-face for both argon and disilane. However on the C-face many research groups observe inhomogeneous graphene formation in argon [46,47,48]. This is believed to be due to an unintentional oxidation of the surface during graphitization [46]. In Section 3.3 we describe our studies on the graphitization of C-face in a disilane background, which to our knowledge has not been done before. We find an improvement in the morphology compared to samples prepared in vacuum or argon. We also find the existence of a new interface structure identified as a $\sqrt{43} \times \sqrt{43} \pm 7.6^{\circ}$ reconstruction which is not seen in vacuum formed C-face samples. We believe this $\sqrt{43}$ reconstruction represents the equilibrium structure of the interface, and is similar to the buffer layer seen on the Si-face.

1.3.3 CVD growth of graphene on metals

There are two main techniques to produce graphene on metal surfaces [49, 50]. The first is by surface segregation of carbon dissolved in the bulk and the second is by directly decomposing a hydrocarbon on a metal surface. Both these techniques were known 40 years ago, but then the graphene formation was an unwanted byproduct, produced when annealing and cooling a metal surface resulted in diffused carbon impurities segregating to the surface [51] or when the metal catalyst in a hydrocarbon reaction got deactivated due to deposition of graphitic carbon. With the discovery of graphene in 2004, there has been a renewed interest in these previously unwanted byproducts, and current research is on optimizing the quality of graphene produced on such surfaces.

The segregation technique is used for metals with a high solubility of carbon. The sample is either doped with carbon at a high temperature or the intrinsic carbon impurities in a clean metal are used. When the metal is cooled down the solubility of carbon decreases, as a result the carbon precipitates out. The graphene film can be thought of as an equilibrium phase that lowers the surface energy of the system. The equilibrium between carbon on the surface and bulk depends on the temperature and concentration of carbon in the bulk, so either of these parameters can be used to control the thickness of graphene formed [50].

In the decomposition technique either the hydrocarbon is adsorbed on a metal at room temperature and then heated to decompose the hydrocarbon, or the hydrocarbon is directly heated over the metal and the carbon atoms directly adsorbed onto the metal surface. The metal acts as a catalyst for the hydrocarbon decomposition, so when the metal gets covered by a layer of carbon there are no more active sites to further catalyze the reaction and the decomposition stops. This automatically self limits the growth of graphene to monolayer thickness.

The electronic properties of graphene and its interaction with the substrate depend highly on which metal substrate is used as discussed in Ref. [50]. As of now no theory fully explains which metals will interact strongly or weakly with graphene. Graphene on Co, Ni, Re, Ru, and Rh are examples of a strong interaction with the substrate. General properties of a strong interaction are formation of a single domain structure, strong alteration of the π band of graphene, and a separation between graphene and substrate that is less than the 0.33 nm separation between graphite layers. On metals like Co and Ni there is no lattice mismatch so the graphene has the same registry with the metal atoms throughout the surface. However on metals like Re, Ru, Rh there is a lattice mismatch between graphene and the metal so the position of the carbon atoms relative to the metal varies across the surface. This mismatch between the graphene and metal lattice results in a moiré-pattern. In strongly interacting metals the moiré-pattern has a large corrugation because the separation between the graphene and substrate depends strongly on the position of the carbon atoms relative to the metal atom. Examples of weakly interacting metals are Cu, Pt, Ir, Ag, and Au. Characteristics of graphene on weakly interacting metals are rotational disorder, a π band that is undisturbed with the Dirac points almost intact, and a graphene substrate separation that is close to the 0.33 nm separation of individual layers in graphite.

In metals like Ni, the high solubility of carbon at high temperatures can result in a segregation of multilayer graphene on the surface when the samples are cooled down to room temperature. The advantage of growing graphene on Cu compared to other metals is the limited solubility of carbon in Cu, because of which the growth can easily be limited to 1 ML over a large area. In this thesis we will examine graphene samples on a Cu foil substrate. Because of the limited solubility of carbon in Cu, the segregation technique is not used but rather carbon is deposited directly on the surface either by decomposing a hydrocarbon or using some other carbon source. Controllable graphene growth on Cu was first demonstrated by Li et al. who heated Cu foil at temperatures of 1000°C in a mixture of methane and hydrogen, in a CVD growth chamber [52]. The standard procedure to clean the Cu foil is to heat it in a mixture of Ar and H₂ at 1050°C for 30 min, this cleaning helps promote the growth of large graphene domains. In the carbon deposition stage the growth mechanism and kinetics depend on preparation conditions. The three main growth conditions are UHV ($\sim 10^{-10}$ Torr), low pressure CVD (10⁻³ Torr), and ambient pressure CVD (1 atm). Some groups use UHV conditions to deposit carbon on Cu. Under UHV conditions the pressure of the hydrocarbon is not sufficient to adsorb carbon on the Cu surface, so researchers in Ref. [53] heat a graphite rod to deposit carbon onto the Cu surface. They obtain four-lobed graphene islands which ultimately combine to form a continuous polycrystalline sheet of graphene. For low pressure CVD growth similar lobed islands are also observed [52], but several other groups report hexagonal, single crystal islands [54, 55]. For ambient pressure growth most groups report the formation of hexagonal crystal domains of multilayer graphene [54, 56]. Graphene domain size and thickness thus depend sensitively on growth conditions. In this study we use LEEM to study the thickness and orientation of graphene grown on Cu foil in ambient CVD growth.

1.4 Overview of the thesis

In this thesis the main work is a comparison of the interface structure of epitaxial graphene on SiC, for different preparation conditions. We primarily study the interface structure for samples prepared in a disilane environment, and compare it to our previous results from samples prepared in UHV or an atmosphere or argon. We find that the interface and quality of graphene depends on the environment and which face is used for graphitization.

In the previous part of this chapter we introduced graphene and derived the bandstucture of the π bands using the $2p_z$ orbitals as basis functions. The unique bandstructure of graphene is responsible for its exciting electronic properties. We also discussed the various techniques used to prepare graphene. The main preparation technique we are concerned with in this thesis is the annealing of SiC to form epitaxial graphene.

In Chapter 2 we describe the main experimental techniques used in this thesis. We first describe our graphene preparation chamber. We then describe three important surface science tools used in this study, Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and low energy electron microscopy (LEEM). In LEEM the intensity variation of low energy electrons reflected from the surface allows us to determine the number of graphene layers at any point of the surface. These reflectivity curves are an important part of our data analysis, and so we discuss the origin of these reflectivity curves and their relation with the higher lying bands in the bandstructure of graphite. To help understand the bandstructure of graphite we perform our own tight

binding calculations for the higher lying bands and compare it with first principles calculations in the literature.

In Chapter 3 we discuss our results for graphitization of SiC in a disilane environment, and compare these results with those obtained from graphitization in a vacuum or argon environment. We first introduce graphene on SiC, and briefly review prior literature on graphene growth on the Si-face and C-face. The pre-graphitization reconstructions are different for the two faces. Notably the Si-face shows a $6\sqrt{3} \times 6\sqrt{3}$ R30° reconstruction also known as the buffer layer which acts as a template for further graphene growth. On the other hand for the C-face the pre-graphitization structure is a 3×3 or 2×2 reconstruction which is not believed to act as a template for future graphene growth.

We then present results for graphitization of the Si-face in a disilane pressure of about 10⁻⁴ Torr. We see an improved morphology compared to vacuum formed films, however the monolayer domains are not as large as those obtained with graphitization in an argon environment. On the C-face we start by presenting results for graphitization in a relatively low disilane pressure of 10^{-6} Torr. The AFM and LEEM results are not significantly different from a vacuum prepared sample. However for higher disilane pressures near 10^{-4} Torr we find that we are able to produce graphene samples that are thinner and more uniform than those formed in vacuum. We also start to see a qualitative difference in the LEEM and LEED results compared to those formed in vacuum. The LEEM reflectivity curves from such samples show unique features not seen in vacuum prepared samples. These unique features are similar to what is seen in the reflectivity curves of graphene samples lying on a buffer layer on the Si-face decoupled by hydrogenation or oxidation. The in situ LEED of such disilane prepared samples shows a $\sqrt{43} \times \sqrt{43} \pm 7.6^{\circ}$ structure prior to graphitization which persists for thin graphene samples. After air exposure of a few days this $\sqrt{43}$ reconstruction disappears and in some cases is replaced by a $\sqrt{3} \times \sqrt{3}$ R30° reconstruction. An intensity vs. voltage analysis of the $\sqrt{3}$ diffraction pattern agrees well with that of a silicate layer, implying that the surface is oxidized. Along with additional data from selected area diffraction we conclude that the $\sqrt{43}$ layer is similar to the $6\sqrt{3}$ buffer layer seen on the Si-face, and the unusual reflectivity curves observed in LEEM arise when the $\sqrt{43}$ layer gets decoupled from the substrate due to oxidation.

To further confirm this theory of the $\sqrt{43}$ layer being a buffer-like layer on the Cface that gets oxidized with air exposure, we prepare a sample with a $\sqrt{43}$ diffraction pattern and study it in LEEM prior to any possible oxidation. We then allow the sample to get oxidized by exposing it to air. The LEEM reflectivity curves before and after oxidation look quite different, with the oxidized samples displaying the same unusual features seen in the oxidized samples discussed in the previous paragraph. We are thus confidently able to associate the $\sqrt{43}$ layer with a buffer-like layer, that gets decoupled from the substrate by oxidation. At the end of the chapter we discuss why the $\sqrt{43}$ layer forms when prepared in a disilane environment, but not when prepared in vacuum. We also discuss how by graphitizing in disilane we avoid an unintentional oxidation process that inhibits graphene growth on the C-face in an argon environment.

In Chapter 4 we present results from two separate STM/S studies on epitaxial graphene on the Si-face. In the first study we perform STM/S on a graphene sample that shows a high coverage of a secondary disordered phase. The STS from such disordered regions shows additional features in the spectrum compared to that from ordered regions of graphene. With the help of additional AFM and AES data on this sample, we argue that the disordered phase is nano-crystalline graphite that is also seen on the C-face. In the second study we perform STS on a graphene sample that has been functionalized with hydrogen. Functionalizing graphene is expected to change the carbon hybridization from sp² to sp³ type and possibly open up a band gap in the normally semi-metallic graphene. Our STS measurements reveal that the functionalization did *not* in fact open up a bandgap in the graphene, but rather, the spectra reveal additional states near the Fermi energy that are indicative of the nature of bonding changing from sp² to sp³.

Chapter 5 is a LEEM study of graphene on Cu substrates. LEEM reflectivity curves allow us to determine the graphene thickness at any point on the surface, and additionally selected area LEED patterns acquired in the LEEM allow us to determine the orientation of the graphene domains on Cu. We end the chapter by discussing the variation in LEEM reflectivity curves that we see when studying graphene on different substrates. The interface between graphene and the substrate varies for different substrates and affects the nature of the reflectivity curve obtained from the graphene.

Chapter 2

Experimental Techniques

2.1 Graphene preparation chamber

We prepare epitaxial graphene by annealing SiC in a home-built ultra high vacuum (UHV) preparation chamber [57]. The preparation chamber is pumped by a 150 l/s turbo molecular pump backed by a scroll pump, and has a base pressure of 1×10^{-9} Torr. In the preparation chamber a 1 cm \times 1 cm SiC sample is placed on a bowtie shaped graphite strip heater as shown in Fig. 2.1. When current flows through the strip heater, it heats up resistively and radiatively heats the sample placed on it. The graphite heater is held on either side by copper clamps which connect outside the chamber to water-cooled copper feedthroughs. A transformer supplies the current that runs through the copper feedthroughs and into the graphite heater.





The sample is first H-etched to remove polishing damage [58]. To perform Hetching we flow 99.9995% pure hydrogen in the chamber at the rate of 10 lpm and heat the sample to 1600°C for 3 minutes. A gate valve between the chamber and turbo pump protects the pumps from the hydrogen. In some cases we clean our SiC samples by heating it in 5×10^{-5} Torr of disilane at 850°C. The disilane is flowed in through a leakvalve which can be used to accurately control the pressure of the disilane in the chamber. While flowing disilane into the chamber, the pumps are kept running at their normal operation. After the cleaning procedure the sample is graphitized by annealing in either vacuum or in 5×10^{-5} Torr of disilane. The temperature of the sample is monitored by a disappearing filament pyrometer which is calibrated as described in Ref. [34,57].

A newer preparation chamber with *in situ* LEED capability was built by in 2010 by another student in the group, Guowei He, and is now routinely used for sample preparation. Guowei He prepared some of the samples in this thesis, and also acquired all the LEED patterns in this thesis.

2.2 Auger electron spectroscopy (AES)

AES is a popular technique to determine the chemical composition of a surface. A primary electron beam a few keV in energy ionizes a core level electron of an atom, as a result of which secondary Auger electrons are emitted. The kinetic energy of the emitted Auger electrons strongly depends on the atomic number Z of the atom, thus allowing the atom to be identified. Due to the low mean free path of Auger electrons, the main contribution comes from electrons emitted 1-3 nm below the surface [59].



Fig. 2.2 Nomenclature for different transitions that result in production of Auger electrons, as explained in the text. From Ref.[59].

Figure 2.2(a) shows a schematic that explains the production of Auger electrons [59]. A primary electron ionizes a core level (K shell). The resultant hole in the core level is unstable, so an electron from a higher energy shell (L_1) drops into the core level. The energy released from the transition of the electron from the higher shell to the core

level either results in the production of a characteristic x-ray photon or results in a radiationless ionization of another electron in the same or higher shell, this ionized electron is called the Auger electron. For core levels with binding energies less than 2000 eV the de-excitation is more likely to be a radiationless Auger transition [60]. The nomenclature of Auger transitions is similar to that used in X-ray spectroscopy. As shown in Fig. 2.2(a) the KL₁L₂ transition arise when the primary beam ionizes a core level K shell, after which an electron from the L₁ level 'drops' into the K core level accompanied by the emission of an Auger transitions possible.

In our lab we use a primary beam energy of 5 keV to excite the sample. A VG Scientific Clam 100 hemispherical analyzer is used to detect the emitted Auger electrons [12]. The detected electrons are multiplied by a channel electron multiplier (chaneltron) to enhance the Auger signal. By sweeping the voltage at the detector during data acquisition, one can get the Auger signal as a function of kinetic energy. From the energies at which Auger peaks are seen, the chemical composition of the surface can be identified. In addition to Auger electrons the collected signal detected has a large contribution from other secondary electrons produced by the excitation. To clearly distinguish the small Auger signal riding on this large structureless secondary electron signal, one can take a derivative of the total signal, and the change in the derivative will correspond to the Auger signal. AES is usually performed in derivative mode. A small oscillatory voltage is applied to the signal, and lock-in amplifier is used to detect the in phase output signal which corresponds to the derivative of the signal.

2.3 Low energy electron diffraction (LEED)

LEED is a technique used to determine the crystal structure of a surface, similar to how X-ray diffraction is used to determine the crystal structure in the bulk of a solid. Diffraction techniques allow us to visualize the reciprocal lattice structure of a crystal, from which one can calculate the structure and periodicity in real space. To probe an inter-atomic spacing of 0.1 nm it can be calculated that an X-ray photon needs to have an energy of around 10 keV while an electron needs an energy of only 100 eV. Due to their higher energies X-ray probe deeper into the surface, while low energy electrons are surface sensitive. Low energy electrons used in LEED have an energy of 10 - 100

eV and are able to penetrate only the top few layers of the sample. Another difference is that while X-rays undergo simple kinematic scattering (one scattering event), low energy electrons undergo dynamic scattering (multiple scattering events) due to their low mean free path.

In a three dimensional lattice the Bragg diffraction condition (such as in X-ray or netron diffraction) is $\Delta \mathbf{k} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$ where **k** is the wavevector of the incident beam, \mathbf{k} ' is the wave vector of the diffracted beam, and \mathbf{G} is a reciprocal lattice vector in the crystal. The Ewald construction shown in Fig. 2.3(a) allows us to visualize the Bragg condition [14]. A sphere of radius $|\mathbf{k}|$ is drawn such that it intersects at least one point in reciprocal lattice points of the crystal. A diffracted beam will form where the sphere intersects any other reciprocal lattice point. To understand the diffraction pattern that arises in the case of LEED we next consider a surface structure periodic in two dimensions [59]. For qualitative purposes it is sufficient to consider a simple kinematic treatment. The Bragg condition for a structure periodic in two dimensions is $\Delta \mathbf{k}_{II} = \mathbf{k}'_{II} - \mathbf{k}_{II} = \mathbf{G}_{II}$, where \mathbf{k}_{II} and \mathbf{k}'_{II} are the wave vector components parallel to the surface, and G_{II} is a surface reciprocal lattice vector. The constraint on the wavevector in the direction perpendicular to the surface no longer applies as the periodicity is broken in this direction. To visualize the Bragg condition we can again make an Ewald sphere construction shown in Fig. 2.3(b). The reciprocal lattice is periodic in the same two dimensions as the surface structure. If we want to extend this lattice to three dimensions we can draw rods perpendicular to the surface, passing through every reciprocal lattice point on the surface. An Ewald sphere of radius \mathbf{k}_{II} is drawn such that it intersect the (0 0) reciprocal lattice point. The diffraction condition is satisfied everywhere a reciprocal rod intersects the Ewald sphere. As can be seen in Fig. 2.3(b) this is actually satisfied at every reciprocal lattice point as long as it lies within a radius vector \mathbf{k}_{II} . By increasing \mathbf{k}_{II} higher order diffraction spots can be seen. Thus the diffraction condition in two dimensions is much less severe than in three dimensions and can be satisfied for every scattering geometry and electron energy.



Fig. 2.3 Ewald sphere construction in three dimensions and two dimensions respectively. (a) The dots represent the reciprocal lattice points of a bulk crystal and extend in three dimensions. The incoming wavevector is \mathbf{k} , the diffracted wavevector is \mathbf{k} 'and \mathbf{G} is any reciprocal lattice vector. All points in the reciprocal lattice that lie on the Ewald sphere give rise to a diffraction spot. (b) Cross section of the reciprocal lattice of a surface along the \mathbf{k}_x direction. The dots are reciprocal lattice points on the surface indexed by their coordinates in k-space (h k). The rods represent the \mathbf{k}_x values of the reciprocal lattice and are drawn through all the reciprocal lattice points normal to the surface. The Ewald sphere is drawn through the (0 0), and all points where it intersects the reciprocal lattice give rise to a diffraction spot. This actually occurs for every reciprocal lattice point that lies within the Ewald sphere, thus the diffraction pattern from a lattice periodic in two dimensions is a map of every reciprocal lattice point on the surface.

The LEED diffraction pattern is simply a map of the surface reciprocal lattice from which the periodicity of the crystal in real space can be calculated. The above treatment of LEED was a simple kinematic one. For a more rigorous treatment that can quantitatively explain the intensity variation of the diffraction spots with beam energy one would need to do a full dynamical LEED calculation that takes into account the finite penetration depth and multiple scattering events that the low energy electron undergoes. Such an intensity *vs*. energy analysis can then give information about the exact locations of the atoms in the unit cell.

Figure 2.4 shows a schematic of an experimental LEED set-up in a vacuum chamber [60]. The electron gun consists of a filament and a Wehnelt electrode. The electrons emitted by thermionic emission from the filament are controlled by the Wehnelt which is held at a negative potential relative to the filament. The electron gun is at a negative potential V compared to the sample, which in this case is grounded, as a result the electrons accelerate towards the sample. To prevent inelastically scattered secondary electrons from reaching the screen S a retarding grid G₂ is held at a negative potential

with respect to grid G_1 . This retarding grid is held at such an energy that blocks the lower energy secondary electrons, but allows the elastically backscattered electrons to pass through. The elastically scattered electrons that pass through G_2 are attracted to the phosphor screen S which is held at a large positive voltage, where they form the diffraction pattern. The pattern on the screen is recorded by a detector such as a CCD camera. In modern LEED instruments the set up as shown in Fig. 2.4 is slightly modified such that the LEED pattern is viewed on the rear of the screen. The viewport window and detector would then be kept to the left of the electron gun in Fig. 2.4. Such a set-up where the diffraction pattern can be viewed on the same port as the electron gun is called a rear-view LEED. The advantage of a rear-view LEED is that the same port is used to both mount the LEED optics assembly and to view the LEED, whereas in the set up shown in Fig. 2.4 two separate ports facing each other are required for mounting and viewing [61].



Fig. 2.4 An experimental set up of a LEED apparatus optics assembly. From Ref. [60].

2.4 Low energy electron microscopy (LEEM)

LEEM is the microscopy counterpart of LEED [62]. In this technique, low-energy electrons in the range 0-100 eV are directed towards a surface to be studied. The electrons are elastically reflected or diffracted from the surface, and those exiting electrons are collected with a series of electromagnetic lenses. The diffraction pattern of

the electrons can be measured, and a spatial image of the reflected intensity (with lateral resolution of ≈ 10 nm) can also be observed. For graphene in particular, LEEM is a very powerful tool since it allows a direct determination of the number of graphene layers on a surface. The number of graphene layer can be determined from the intensity variation of the reflected electrons and will be discussed later in this section.

2.4.1 Instrumentation Figure 2.5 shows a schematic of the electromagnetic lenses in the instrument in our lab, LEEM III manufactured by Elmitec [63]. The electron gun is kept at a potential of -20 kV with respect to the objective lens, as a result electrons accelerate towards the objective. The electrons are collimated by a series of condenser lenses CL₁, CL₂, and CL₃ along the path to the objective lens. The sample is kept at the same potential as the electron gun, so that after passing through the objective the electrons decelerate and reach the sample with a much reduced energy. The low energy electrons are elastically backscattered by the sample and then re-accelerate up to the objective lens. The objective acts on the incoming and outgoing beam in the same manner, so a magnetic deflector is used to separate the two beams from each other [64]. These back scattered electrons form the diffraction pattern of the sample in the focal plane of the objective lens [65] and form an image of the sample in the image plane which is in the center of the beam separator. A transfer lens (TL) is used to transfer the diffraction pattern or image in front of the intermediate (IL) lens. A contrast aperture can be inserted at this point in front of the intermediate lens to select a particular beam in the diffraction pattern for image formation. Depending on the strength of the intermediate lens either the diffraction pattern or the image of the sample is projected onto the channel plate using two projector lenses $(P_1 \text{ and } P_2)$ [34].

An illumination aperture can be inserted between CL_3 and the objective lens. This aperture blocks out a fraction of the incoming beam allowing only a certain area of the sample to be illuminated. The diffraction pattern formed on the channel plate will only arise from the specifically illuminated area of the sample, and this allows us to find the diffraction pattern from any selected region on the sample. This is called microdiffraction (µLEED) and is similar to selected area diffraction done in transmission electron microscopy (TEM). We will make use of this capability to perform microdiffraction in the studies of Chapter 3 and 5.



Fig. 2.5 Arrangement of electromagnetic lenses in LEEM. From Ref. [63].

As discussed above the electron gun and sample are held at -20 keV with respect to the objective. Such an arrangement where the sample is at a high voltage with respect to the objective is called a cathode lens. This arrangement is unlike a regular electron microscope like TEM where it is not necessary to slow down the electron before they reach the sample. The advantage of using an electron beam that first accelerates then decelerates to a high voltage (called beam deceleration) instead of simply using a low voltage is that the resolution is much better and aberration is reduced [66].

2.4.2 Graphene thickness determination

It was shown by Hibino et al., that the intensity of the electron beam reflected from a graphene sample depends on its thickness [67]. The number of minima in the reflectivity curve between 2-7 eV equals the number of graphene layers at that point. A study of reflectivity curves is a significant topic in this thesis so in this section we discuss in detail the the relation between bandstructure and LEEM reflectivity curves.


Fig. 2.6 Structure of graphene and graphite in different stacking arrangements. Unit cells are shown shaded in gray. In graphite the individual graphene layers stack on top of each other along the c-axis. In AA stacked graphite the individual graphene layers are placed directly on each unrotated. In AB stacking (also called Bernal stacking) the second graphene layer is rotated by 60° relative to the first. From Ref.[32].

To understand the reflectivity spectra from the LEEM, and how these related to graphene thickness, we must consider the energy bands of graphite. The unit cell of graphene, and different stacking arrangements of graphite, are shown in Fig. 2.6. The energy bands of graphite are shown in Fig. 2.7, taken from the work of Hibino et al. [67] (together with some additional labeling of the states, as discussed below). This band structure determined by a first-principles local-density-functional method, yielding a realistic (albeit complicated) view of the bands. The bands circled by the red dashed line in Fig. 2.7(a) are the ones that were identified by Hibino et al. to be responsible for the LEEM reflectivity spectra of graphene (both single layer and multilayer). These bands are shown in an expanded view in Fig. 2.7 (b). To understand the origin of these bands, we have performed tight-binding computations for a number of simple situations, as shown in Fig. 2.8. It is important to realize that the bands of Fig. 2.7 refer to graphite, i.e. with 2 graphene layers per unit cell in the c-direction whereas the bands of Fig. 2.8 are only for a single layer of graphene. Hence, to associate bands from Fig. 2.8 to those in Fig. 2.7, we must double the number of the bands in Fig. 2.7 (with splitting between these doubled bands, in cases where significant dispersion of the states exists in the c-direction).

The simplest bands to understand in Fig. 2.7(a) are the ones associated with the $2p_z$ orbitals of the carbon atoms, labeled π and π^* for in-plane bonding and antibonding combinations, respectively. These are the bands that form the valence and conduction bands in graphene, meeting at the Dirac point (0 eV in Figs. 2.7 and 2.8). A tight-binding computation, with a single $2p_z$ orbital per atom, can be done to provide an approximate model for these bands. Our method for performing this computation is identical with that described by Saito et al. [13], which was also used in Section 1.2 to calculate the π bands of graphene. This treatment explicitly includes terms arising from nonorthogonality of the basis functions (i.e. $2p_z$ orbitals on neighboring atoms in the present case). The result is pictured in Fig. 2.8(a), using tight-binding parameters chosen to approximately match the first-principles results. These π and π^* bands can easily be associated with the corresponding bands in Fig. 2.7. A doubling of the bands occurs there (since graphite, not graphene, is being considered), and for the π band significant dispersion in the c-direction occurs, as further discussed below.



Fig. 2.7(a) Electron band structure of graphite, taken from Ref. [67]. In-plane directions for the wavevector are from Γ (the zone center) to K or M. The out-of-plane direction is shown on the far right of the diagram, from Γ to A. (b) An expanded view of the portion of panel (a) delineated by the red dashed line. The dispersive states originate from an in-plane bonding combination of 3s atomic orbitals on each carbon atom. From [67].



Fig. 2.8 Results of tight-binding computations of graphene bands, considering: (a) $2p_z$ orbitals, (b) 2s, $2p_x$, and $2p_y$ orbitals that form hybrids directed along lines joining nearest-neighbor atoms, and (c) 2s, $2p_x$, $2p_y$, and 3s orbitals. The bands of (a) are orthogonal to those of (b) or (c), so they can simply be added together [i.e. the results of (a) can simply be added to those of (b) or (c)]. Tight-binding parameter values are chosen to yield bands that approximately match the first-principles results of Fig. 2.7.

Other bands in graphite (and graphene) that are easy to understand are those derived from the in-plane $2sp^2$ hybrid orbitals These hybrids are composed of linear combinations of the 2s, $2p_x$, and $2p_y$ atomic orbitals, directed along the lines joining nearest-neighbor carbon atoms. Figure 2.8(b) shows the resultant bands, labeled σ and σ^* for in-plane bonding or antibonding combinations, respectively. In contrast to the π bands of Fig. 2.8(a), these σ bands reveal a single band at the lowest or highest energies, and bands that are two-fold degenerate at Γ at intermediate energies. These two-fold bands correspond to "partially" bonding (or antibonding) states, i.e. with bonds forming only in the [2 1], [1 1] and [1 1] directions in the lattice shown in Fig. 2.6, whereas the highest/lowest energy states form bonding/antibonding combinations in all three symmetric directions in the lattice. Comparing Fig. 2.8(b) to Fig. 2.7(a), the σ bands are easily identified in the first-principles results. However, it is not obvious how to identify the higher-lying σ^* bands. Of course, in the first-principles results there is no assumption about the number of states at high energies in the computations. Therefore, to more fully understand the first-principles bands, we must consider additional state(s) in our tight-binding treatment.

Figure 2.8(c) shows tight-binding results including 2s, 2p_x, and 2p_y orbitals, together with an additional 3s atomic orbital. The energy of the latter is assumed to be considerably higher than for the $2sp^2$ hybrid composed of the 2s and 2p states, so that, at least at the Γ -point, the states can be reasonably characterized as having either 3s character or $2sp^2$ character. Also, it should be noted that the 3s states can mix with states having 3p character (i.e. forming $3sp^2$ hybrids), but, at the Γ -point, the lowest lying state composed of a combination of 3s and 3p states is a totally symmetric combination, so that the 3p character cancels out (i.e. equals zero) for that state. Thus, our assumption of only using 3s orbitals for additional states is reasonable for describing the character of the lowest-lying additional state at the Γ -point. Examining the bands shown in Fig. 2.8(c), we have chosen our energies so that the band composed primarily of 3s character lies slightly below the two-fold σ^* bands. This ordering is chosen to match the first-principles results of Fig. 2.7(a). Examining those closely, we see a two-fold band labeled σ^* , which we associate with our tight-binding bands also labeled σ^* . On either side of the σ^* energies in Fig. 2.7(a) we see other states, which we label by σ_{3s} . Importantly, examining the out-of-plane dispersion of those states on the right-hand side of Fig. 2.7(a), we see that these two bands converge to a single energy at the A-point. Therefore, these two states comprise a single band in graphene, and the only possibility for this band is the σ_{3s} band shown in Fig. 2.8(c). It is this band that is central to the interpretation of the LEEM reflectivity curves, and we thus identify it has having primarily 3s character around each carbon atom.

To fully understand the graphite bands, we must also consider the out-of-plane dispersion. This feature is seen on the right-hand side of Fig. 2.7(a), with the wavevector varying from Γ to the A-point. Consider the situation for the 2p_z orbitals, highlighted in Fig. 2.7(a) by the blue dashed line. A moderately large dispersion exists for these states, with the lowest and highest energy states (both at the Γ -point)

corresponding to the out-of-plane bonding and antibonding combinations, respectively. This moderately large dispersion occurs because the $2p_z$ orbitals in neighboring graphene planes have substantial overlap. In contrast, for the σ and σ^* states discussed above (composed of combinations of 2s, $2p_x$, and $2p_y$ orbitals), they have substantially less overlap between neighboring graphene planes, so that their dispersion is practically zero.

Finally, for the states that we have associated with the 3s orbitals, the extent of these states is much greater than for the $2sp^2$ hybrids, and it is also greater than for the $2p_z$ orbitals (i.e. since the 3s orbitals have higher principal quantum number). Thus, relatively large out-of-plane dispersion results in the band formed from the 3s orbitals. This dispersive band is the one marked by the red dashed line in Fig. 2.7(a). An expanded view of this portion of the band structure is shown in Fig. 2.7(b). It should be noted that an actual 3s atomic orbitals will have considerable structure (nodes in the wavefunction) around the carbon atoms, but nevertheless, an *envelope function* for the states can be constructed, and that will be a simply oscillatory function.

The wavevector for this dispersive σ_{3s} state will vary from 0 (Γ -point) for the lowest energy state, to π/c at the midpoint of the band (A-point), and back to 0 (Γ -point) for the highest energy state. This "folding" of the band at its midpoint occurs, of course, because in the c-direction graphite has two graphene planes per unit cell. If we consider a vertical unit cell length of b = c/2, then we would have just a regular non-folded band extending from wavevector of 0 up to π/b , as pictured on the right-hand side of Fig. 2.9. The dispersive σ_{3s} states are expected to couple well to incident electrons with the same values of out-of-plane wavevector, since the states are composed of a *bonding* combination of the 3s orbitals (i.e. without wavefunction nodes between neighboring carbon atoms).

Hibino and co-workers have associated this dispersive band with the observation of features in the LEEM reflectivity curves from graphene. Their argument is direct, and produces very good agreement with experiment: the dispersive band is a property of an infinite number of graphene layers, one atop the other. It can therefore be viewed at a tight-binding band for an infinite 1-dimensional (1D) chain. Considering a chain of

finite length, the resultant energies will change in a well-known way, as pictured in Fig. 2.9. A formula to describe this set of energies is given by [67]



Fig. 2.9 Energy levels for a 1D chain containing *m* atomic sites, in a tight-binding treatment. The index *n* labels the states. For an infinitely long chain, a band of states is formed, as shown on the right-hand side. The wavevector k varies from 0 to π/b , where *b* is the separation of atoms in the chain (for graphite, with two graphene planes per unit cell, c = 2b where *c* is the unit cell height).

Thus, within the model of Hibino et al., the local minima (dips) observed in the reflectivity spectra of graphene correspond directly to the energies in this simple tightbinding model. In a more sophisticated treatment, they take the band energies, E(k), from a first-principles computation such as Fig. 2.7(b). They then evaluate that E(k) curve at values of wavevector corresponding to the argument in Eq. (1), i.e.

$$k^{TB} = \frac{\pi n}{(m+1)b} \tag{2}$$

where, again, *m* refers to the number of graphene layers in the film, *n* is the index for the states (n=1,2,...,m), and *b* is the separation of graphene planes. In this way, the energetic location of all dips in the reflectivity curves, for any thickness of graphene

film, are known. The subscript TB here refers to the fact that this formula arises from a tight-binding treatment.

2.4.3 Data analysis

To obtain reflectivity spectra in the LEEM at each pixel within a spatial image, the following procedure is used: A sequence of images is recorded starting with beam energy of 0 eV and incrementing it by 0.1 eV as we go from one image to another. This sequence of images is analyzed to obtain the reflectivity spectra (which provide the local graphene coverage) by the following procedure [34,57]:

(i) At each pixel a reflectivity curve extending between about 2.0 and 6.5 eV is extracted from the data



(ii) A quadratic (or sometimes just a linear) background is subtracted:



(iii) A sinusoidal function with adjustable frequency and phase, $A\sin(kE+\phi)$, is fitted to the curve. The process is repeated for all pixels and a scatterplot of the phase *vs*. frequency is constructed, with reflectivity curves associated with different number if monolayers (ML) occupying distinctly different regions in the plot.



(iv) The number of counts in the different regions of the scatterplot then gives the fraction of the surface covered with different integer ML of graphene. From this we can calculate the average graphene thickness for a given sample. Also, we can construct a color map of the local graphene thickness by assigning each pixel in the image a specific color associated with the region that its reflectivity curve falls in.

Chapter 3

Graphitization of SiC in a Disilane Environment

Graphitizing SiC in vacuum results in significant inhomogeneity in the graphene film, including pit formation on the surface and small graphene domain sizes (areas of constant thickness of multilayer graphene). In an effort to improve the quality of graphene on SiC researchers have started using a background gas such as argon or disilane during graphitization, instead of graphitizing in vacuum. In this chapter we present results for graphitization of SiC in a disilane environment. On the Si-face we find disilane-prepared samples show an improvement in morphology compared to those prepared in vacuum. On the C-face we find an improved morphology, larger grain size and the existence of a new $\sqrt{43} \times \sqrt{43} \pm 7.6^{\circ}$ interface structure. This interface structure shows properties similar to the so-called "buffer layer" on the Si-face. We will then discuss why we find it possible to form uniform, thin graphene in a disilane environment and not in vacuum or argon environments. Before presenting our new results we first review prior research done on epitaxial graphene on SiC.

3.1 Introduction

When SiC is heated in vacuum the Si atoms preferentially sublimate, and the excess C atoms rearrange to form graphene. One graphene layer contains three SiC bilayers worth of carbon (a SiC bilayer is a unit that contains a plane of Si atoms and a plane of C atoms as shown in Fig. 1.5(a)). Thin films of graphite have been studied on SiC surfaces by various research groups since 1975 [33, 68, 69]. In 2004 deHeer's group in Georgia Tech verified the 2D electron gas behavior of such thin graphite films on SiC and proposed its use for nanoelectronics [70]. Since then significant progress has made in reproducibly forming graphene on SiC of a specific thickness, making epitaxial graphene on SiC a promising candidate for large scale graphene production [32].

As discussed in Section 1.3, SiC{0001} has two inequivalent surfaces – the (0001) face, also known as the Si-face, and the ($000\overline{1}$) face also known as the C-face. The graphene growth mechanisms and properties are quite different for the two faces. On the Si-face growth proceeds in a nearly layer by layer manner (for $\ge 2ML$ graphene coverage) whereas on the C-face it proceeds in a more three-dimensional manner [71,46]. This difference in the growth modes for two faces is surely influenced by the different temperatures used in the two cases in vacuum, about 1150°C for the C-face but

1300°C for the Si-face [72, 73]. As mentioned in Section 1.3.2 another contributing factor is the different interface structures for the two faces: a $6\sqrt{3}\times6\sqrt{3}$ -R30° interface layer forms between Si-face SiC and the graphene. This layer, also known as a "buffer layer" acts as a template for the formation of graphene. However, on the C-face there are 2×2 and 3×3 structures that variously occur, but these are not believed to act as templates. (This difference in interface structures likely affects the formation temperatures of the graphene on the two surfaces). In Sections 3.1.1 and 3.1.2 we review prior results on the growth and stacking of graphene on the Si-face and C-face respectively. In Section 3.1.3 we outline the organization of the remaining chapter.

3.1.1 Epitaxial graphene on the Si-face When Si atoms start to desorb from the SiC surface due to heating, the remaining surface atoms rearrange their positions and bonds to minimize the surface energy. This rearrangement of a surface is called a reconstruction and compared to the original surface it can have a different periodicity. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) are popular techniques to study surface reconstructions. When the Si-face is heated it undergoes various intermediate reconstructions till it finally forms graphene. The different reconstructions on the Si-face have been studied by many research groups, and they show slight variations with different preparation conditions [32, 39, 42, 74]. Figure 3.1 shows the LEED pattern of the main reconstructions seen on the Si-face when prepared in ultra-high vacuum (UHV) conditions by our group [12, 57, 75]. A side view of the atomic arrangement associated with the LEED pattern is also shown. After H-etching to remove polishing damage on the sample the surface shows a 1×1 pattern along with a weak $\sqrt{3} \times \sqrt{3}$ -R30° reconstruction as shown in Fig. 3.1(a). This $\sqrt{3}$ pattern is associated with an oxidation of the surface [76, 77]. With mild heating the surface the weak $\sqrt{3}$ spots disappear and the 1×1 pattern becomes stronger. On further heating to 900°C the 1×1 structure is replaced by a strong $\sqrt{3}\times\sqrt{3}$ -R30° phase as shown in Fig. 3.1(c). This $\sqrt{3}$ phase is not due to an oxide phase as in Fig. 3.1(a), but rather is a silicon rich phase with a Si adatom per $\sqrt{3}$ unit cell [78]. On further heating to 1200°C this Si-rich $\sqrt{3}$ reconstruction develops into a $6\sqrt{3}\times6\sqrt{3}$ -R30° ($6\sqrt{3}$ for short) structure as shown in Fig. 3.1(e), and subsequently into graphene as shown in Fig. 3.1(g).



Fig. 3.1 LEED patterns at 100 eV and corresponding atomic arrangement of reconstructions on the Si-face with the following steps : (a) LEED pattern acquired from a sample after 3 min of H-etching. In addition to the SiC(1,0) spot, we have marked the (1/3,1/3) and (2/3,2/3) spots associated with a $\sqrt{3} \times \sqrt{3}$ -R30° arrangement, that arises from residual oxidation of the surface. (b) The weak nature of the $\sqrt{3}$ spots suggests the corresponding silicate (oxidized surface) is not fully formed. (c) LEED pattern acquired after heating the sample for 1 min at 900°C. The strong $\sqrt{3}$ pattern in this case is not from oxidation, but rather from a Si-rich reconstruction with a Si

adatom as shown in (d). (e) LEED pattern acquired after 10 min annealing at 1200°C shows the development of a 6 fold satellite spot arrangement around the SiC and $\sqrt{3}$ spots. This is the $6\sqrt{3}$ reconstruction and it arises from a graphene like layer bonded to the substrate as shown in (f). The $6\sqrt{}$ layer is also referred to the zeroth graphene layer or 'G₀'. (g) LEED pattern acquired after heating further at 1350°C for 20 min. Additional 1×1 spots associated with graphene are marked, they are rotated from the SiC 1×1 by 30°. The 6-fold satellite spots from the underlying $6\sqrt{3}$ layer surround both the graphene and SiC 1×1 possibly due to a distortion of the graphene from the underlying layer. The graphene layer on top of the $6\sqrt{3}$ layer is sometimes referred to as 'G'₁ as shown in (h).

The $6\sqrt{3}$ reconstruction that appears prior to graphene formation, also known as the buffer layer, plays an important role in the subsequent graphene formation. Emtsev *et. al.* mapped out the valence bandstructure of the $6\sqrt{3}$ layer using angle resolved photoemission spectroscopy (ARPES) [40, 79]. They found that the σ bands (formed by in-plane sp² hybridized orbitals) were identical for the $6\sqrt{3}$ layer and graphene, implying that the in-plane geometrical arrangement of the two layers was identical. However the π bands (formed by the out of the plane p_z orbitals) are different for the $6\sqrt{3}$ and graphene, implying the out of plane bonding is different for the two cases. Also unlike graphene, the $6\sqrt{3}$ reconstruction was found to be non-metallic since there were no states at the Fermi level. Combining these ARPES observations with x-ray photoelectron spectroscopy (XPS) data they concluded that in one-third of the C atoms the p_z orbitals of the buffer layer formed strong covalent bonds with the substrate, unlike in graphene where the p_z orbitals only weakly interact with the underlying layer.

The buffer layer acts a template for subsequent graphene growth and enforces the subsequent graphene layers to be Bernal (AB) stacked. After the formation of the buffer layer, further heating leads to a sublimation of Si atoms below the buffer layer. The excess C atoms beneath the original buffer layer rearrange to form covalent bonds with the substrate, and become the new $6\sqrt{3}$ layer, and concomitantly the original buffer layer decouples from the substrate to form the first graphene layer. This is represented in the schematic of Fig. 3.2. Every graphene layer starts out as a $6\sqrt{3}$ layer with an arrangement determined by the covalent bonds to the substrate.



Fig. 3.2 Schematic of graphene formation on the Si-face. Heating the SiC to 1150°C causes Si atoms to desorb and a graphene like $6\sqrt{3}$ layer is formed. The $6\sqrt{3}$ layer is bonded to the underlying substrate (also shown as 'G₀' in Fig. 3.1(f)). Further heating to 1300°C causes more Si atoms to desorb from below the original $6\sqrt{3}$ layer, and a new $6\sqrt{3}$ layer is formed with bonds to the substrate. The out of plane bonds of the original $6\sqrt{3}$ layer are released and it becomes the first graphene layer ('G₁' in Fig. 3. 1(h)). From Ref. [34].

When the buffer layer forms, it is found to be quite rough with deep thermal etchpits that form due to kinetic limitations in the mobility of the atomic steps. These pits persist in the graphene layers that form over the buffer layer [38]. Graphitizing in the presence of a background gas such as argon or disilane decreases the sublimation rate and hence increases the temperature required for graphene formation [43,44,45]. The increased temperature results in a much improved morphology of the graphene and an elimination of etch pits. It was suggested that the reduced Si sublimation rate in the presence of a gas such as argon is because the argon atoms act around the SiC as a diffusion barrier for sublimating Si atoms [45,80]. The diffusion barrier can cause the sublimating Si atoms to get reflected back, and get deposited on the surface, resulting in a decrease in the net Si sublimation rate. Graphitization in the presence of a Si containing gas such as disilane causes the disilane to dissociate into Si and H, thus increasing the partial pressure of Si atoms over the surface which decreases the net Si sublimation rate from SiC. It was found that graphitizing in argon led to increased room temperature hall mobilities of around 1000 cm² V⁻¹s⁻¹ compared to vacuum prepared samples which had mobilities of around 500 cm² V⁻¹s⁻¹[45]. Graphitization in an atmosphere of argon is now becoming the standard technique to produce large area graphene on the Si-face of SiC.

The influence of the buffer layer is responsible for the intrinsic doping and somewhat low mobilities of Si-face graphene. Eliminating the covalent bonds between the interface and buffer layer would result in quasi-free standing graphene with superior electronic properties. To eliminate the buffer layer some research groups intercalate their samples with hydrogen by heating their samples to about 1000°C in an atmosphere of hydrogen [81]. The hydrogen breaks and saturates the bonds between the buffer layer and the substrate, thus structurally and electronically decoupling the buffer layer. The decoupled buffer layer when studied with ARPES showed the π bands of graphene, confirming that it had become the first graphene layer. In general *n*-layer graphene on the Si-face transforms to *n*+1-layer graphene after intercalation as shown in Fig. 3.3. It was found that the mobility of a decoupled buffer layer on the Si-face (also called quasi-free monolayer graphene) was around 3000 cm² V⁻¹s⁻¹ while that of a monolayer of graphene on Si-face (prepared in argon) is around 1000 cm² V⁻¹s⁻¹[82]. Since the original work on hydrogen intercalation, it has been shown that a decoupling of the buffer layer can also be achieved with other elements like oxygen [83], lithium [84, 85], germanium [86], silicon [87], gold [88], etc.



Fig. 3.3 Buffer layer before and after H-intercalation. (a) Prior to H-intercalation a graphene layer rests on the $6\sqrt{3}$ buffer layer which is bonded to the substrate. (b) After H-intercalation the bonds between the buffer layer and the substrate are broken, and saturated by H atoms. Now the buffer layer in (a) becomes the first graphene layer.

3.1.2 Epitaxial graphene on the C-face When the C-face is heated in vacuum it goes through a series of reconstructions which are different from those seen on the Si-face

[70,68,89]. The LEED patterns and atomic arrangement and of the main reconstructions on the C-face are shown in Fig. 3.4. After the H-etching cleaning procedure in our group we see a $\sqrt{3} \times \sqrt{3}$ -R30° structure due to residual oxidation as shown in Fig. 3.4(a) [75]. This $\sqrt{3}$ seen on the C-face after H-etching is faint compared to the SiC 1×1 suggesting that the silicate layer is not fully ordered. In our work we find that the $\sqrt{3}$ on the C-face forms more readily than on the Si-face. On further heating to 1000°C we see a 3×3 reconstruction as shown in Fig. 3.4(b). The atomic arrangement of this structure is not yet known. Some groups report seeing a 2×2 in addition to the 3×3 reconstruction [89,90,91]. When the sample is further heated to 1100°C a graphitic phase is formed. This graphitic phase shows up in LEED as ring-like diffraction pattern as shown in Fig. 3.4(c), indicative of azimuthal disorder which will be discussed later in this section.



Fig. 3.4. LEED patterns at 100 eV and corresponding atomic arrangement of reconstructions on the C-face with the following steps : (a) LEED pattern acquired from a sample after 3 min of Hetching of C-face. In addition to the SiC(1,0) spots we see a $\sqrt{3} \times \sqrt{3}$ -R30° arrangement that arises from residual oxidation of the surface. LEED pattern obtained following heating C-face in vacuum to 1130°C for 15 min shows a 3×3 pattern whose exact atomic arrangement is not yet known. Faint graphene streaks are also seen indicating the start of graphitization. (c) LEED pattern acquired after heating C-face to 1270°C for 15 min. The sample thickness was found to be 15 ML using AES, however in (f) we just represent the first 2 layers of graphene G₁ and G₂.

An STM study found that the 2 \times 2 and 3 \times 3 structure survive also at the interface between graphene and the SiC (i.e in analogy to the $6\sqrt{3}$ structure for the Si-face) [40,41,42]. Even so, it is not expected that the 2×2 or 3×3 structure would act as a template for the graphene, since there is no simple coincidence between their unit cell size and that of graphene. The existence of rotated domains can be seen as an indication of a lack of a strongly bonded first layer that acts as a buffer layer. The higher mobilities seen on C-face graphene compared to the Si-face for vacuum preparation could be due to a difference in the interface structures, with room temperature mobilities of around 2000 cm² V⁻¹s⁻¹ observed on the C-face [92]. However the existence of a buffer layer on the C-face is a much debated issue. ARPES [40], transmission electron microcopy (TEM) [93] and STM studies [41, 42] from some groups suggest that the interface is weakly bound to the underlying substrate, while density functional theory calculations [94,95] inverse photoemission studies [91] and xray reflectivity studies [96] suggest a strong interaction between the first graphene layer and SiC substrate. The sample used in the latter studies differed from those in of the former in terms of its preparation (furnace-growns vs. vacuum-prepared) so as suggested by Hass et al. it is possible that their interface structures could be different [96]. In this chapter our main new result is that we find that the interface structure does indeed depend on preparation conditions. For disilane prepared samples we show existence of a buffer layer, not seen in our vacuum prepared C-face samples.

The ring-like diffraction pattern of C-face graphene was initially believed to be due to polycrystalline graphite on the surface [33, 90]. However, Hass et al. from Georgia Tech found that the diffraction pattern showed certain preferential orientations and was not due to random rotational disorder different [97]. According to them adjacent graphene layers were not necessarily AB stacked but rather showed stacking fault

boundaries because each graphene layer was formed of interleaved rotated phases. In their C-face graphene most successive layers showed stacking faults with a minority of layers showing AB-stacking. Through first principles calculations they showed that the bandstructure of multilayer graphene with rotational faults was identical to that of a single layer of graphene. This could explain why ARPES measurements on multilayer graphene on the C-face reported by various groups gave results very similar to that of an isolated graphene sheet [40,98]. However recently, this picture of rotational faults in multilayer graphene has been challenged. Siegal et. al. studied the multilayer C-face graphene samples prepared by the Georgia Tech research group in a different ARPES setup and found a single monlayer like dispersion relation but surprisingly a majority of the layers were AB stacked [99]. Results similar to Siegal et. al. were also found by Weng et. al. when they studied their argon prepared C-face samples using TEM [93]. In yet another study Johansson et. al. performed selected area LEED on their argon prepared C-face samples and found that adjacent graphene layers did not show rotational disorder in stacking, and that the apparent rotational disorder seen in previously reported diffraction patterns was because the area probed was too large [48]. The Georgia Tech research group has revisited their bandstructure calculations for multilayer graphene with rotational stacking faults and found serious inconsistencies between theoretical and experimental data which would need to be investigated further [100].

For vacuum-prepared C-face films the distribution of thickness is significantly larger than for the Si-face, particularly for relatively thick films [46]. We believe that this thickness variation in the film occurs both because of the relatively low temperatures used and because of the lack of a stable low energy interface between the graphene and the C-face SiC. Planarization of the films is inhibited, at least until temperatures of about 1250°C at which point very thick films are produced. To increase the formation temperature for graphene on the C-face, one can try the same method used for the Siface of performing the annealing in an argon atmosphere. Unfortunately instead of getting large area monolayer domains, for heating the C-face in argon [47,48] it is found that relatively thick islands of multi-layer graphene form, and the reason for this phenomenon was demonstrated in our prior work to be unintentional oxidation of the C- face surface in the argon environment [46]. The oxidation occurs when argon is flowed into the chamber due to an impurity in the argon or/and due to the pumps of the chamber being turned off during argon flow. Compared to a vacuum environment the effect of oxidation is more pronounced in an argon environment, since the argon is continuously flowing through the chamber during graphitization. The oxidized C-face is a disordered silicate layer as shown in Fig. 3.4(d). This oxidized surface is resistant to graphitization indicative of a lower surface energy for the C-face. The thick graphene islands arise from either from areas of the surface where the oxide decomposed or from dislocations as discussed by Camara *et. al.* [101, 102] (This oxidation is found not be an issue on the Si-face, apparently due to the relative stability of that surface under the inert gas environment). For heating in disilane, no prior studies have been performed to our knowledge on the C-face. In this chapter we show that by graphitizing in a disilane environment chamber we avoid unintentional oxidation that occurs in an argon environment and are able to use higher graphitization temperatures than in vacuum, allowing us to form relatively thin uniform films of graphene on the C-face.

Section 3.1.3 Outline The remaining chapter is organized as follows. In Section 3.2 we present experimental details. In Section 3.3 we present our atomic force microscopy (AFM), low energy electron microscopy (LEEM), LEED, and Raman results for graphitization of SiC in a disilane background. In section 3.3.1 we present our results on the Si-face where we see an improvement in morphology compared to vacuum prepared films. On the C-face the results for samples prepared in a low pressure of disilane (10^{-5}) Torr) are similar to results obtained for vacuum-prepared samples as discussed in Section 3.3.2. In Section 3.3.3 we show that for samples prepared in a high disilane pressure (10^{-4} Torr) the high temperature allows us to form thin graphene films with better uniformity than what we have found for vacuum preparation. We also start to see qualitative differences in the LEEM and LEED compared to vacuum-prepared samples. The LEEM reflectivity curves of a typical sample show unusual features not observed in vacuum- prepared samples. The in situ LEED of such samples shows a $\sqrt{43} \times \sqrt{43} \pm 7.6^{\circ}$ ($\sqrt{43}$ for short) interface not seen in vacuum-prepared samples, and this pattern disappears due to oxidation when exposed to air. We associate this $\sqrt{43}$ interface with a buffer like layer similar to that seen on the Si-face. The oxidation of the surface

decouples the buffer layer which can explain the unusual features observed in the reflectivity curves. To confirm our theory of a buffer layer on the C-face that decouples with oxidation, we prepare a sample in disilane, and rapidly transfer it to the LEEM set up to study it before it gets oxidized. We then oxidize the sample and study it again in LEEM. The change in the LEED pattern and reflectivity curves after oxidation is as we expected for a decoupled buffer layer on the C-face.

In Section 3.4 we discuss two aspects of graphene formation in disilane. We first discuss how by graphitizing in a background of disilane in our ultra high vacuum system we avoid the unintentional oxidation that occurs in an argon environment or in the moderate vacuum conditions used by some other research groups The cleanliness of our system when using a disilane background allows us to prepare large area thin films of graphene not possible in other environments. Secondly we discuss our interpretation of the structure of the buffer layer and the conditions for its formation. We believe the $\sqrt{43}$ buffer layer represents the equilibrium structure of the interface while the 3×3 interface forms due to kinetic limitations.

3.2 Experiment

Our experiments are performed on nominally on-axis (unintentional miscut $\leq 0.2^{\circ}$), *n*type 6H-SiC or semi-insulating 4H-SiC wafers purchased from Cree Corp, with no apparent differences between results for the two types of wafers. The wafers are normally 2 or 3 inch in diameter, mechanically polished on both sides and epi-ready on either the (0001) surface or the (0001) surface. These wafers are cut into 1×1 cm² samples and the samples are chemically cleaned in acetone and methanol before putting them into our custom built preparation chamber which uses a graphite strip heater for heating the samples. The ultimate base pressure of the chamber (after a thorough bake) is 1×10^{-10} Torr, although under normal operating conditions, employing a load-lock for sample introduction, it is used at a base pressure of about 2×10^{-9} Torr. To remove polishing damage samples are either heated in 1 atm of hydrogen at 1600°C for 3 minutes or 5×10^{-5} Torr of disilane at 850°C for 5 minutes. For the studies in a disilane environment reported below, the wafers were cleaned in disilane rather than by Hetching since this procedure is more straightforward than the H-etching. The samples are then graphitized by heating in $10^{-6} - 10^{-4}$ Torr of disilane at $1200 - 1400^{\circ}$ C for 10 to 30 min. It should be noted that when the disilane is flowed in the chamber, the regular pumping of the chamber is maintained. Temperature is measured using a disappearing filament pyrometer, with calibration done by using a graphite cover over the sample and measuring its temperature [103]. Characterization by LEED can be performed *in situ* in a connected ultrahigh-vacuum chamber using a conventional VG Scientific rear-view system.

Following graphitization our samples are transferred through air to an Elmitec III system for LEEM and LEED measurements. Samples are initially outgassed at 700°C, and then as part of the alignment procedure in the LEEM a few ML of Pb are deposited on the sample to enable photoemission electron microscopy (since Pb has a relatively low work function). This Pb is then removed from the sample by heating it to 1050° C prior to the LEEM measurements. For Si-face graphene this heating does not produce any observable effect on the sample, but for C-face graphene the heating is found to generate a small amount of additional carbon on the surface. During LEEM, the sample and the electron gun are kept at a potential of $-20 \,\text{kV}$ and LEEM images are acquired with electrons having energy set by varying the bias on the sample, in the range of 0-10eV. The intensity of the reflected electrons from different regions of the sample is measured as a function of the beam energy. As discussed in Section 2.4 these LEEM reflectivity curves shows oscillations, with the number of graphene MLs (38.0 carbon atoms/nm² in each ML) being given by the number of local minima in the curve [67]. From sequences of images acquired at energies varying by 0.1 eV, color-coded maps of the graphene thickness are generated using the method described in Section 2.4.3.

The surface morphology of the graphene films was studied in air by AFM, using a Digital Instruments Nanoscope III in tapping mode. Raman spectra were measured on a Raman microscope (Renishaw, inVia) with excitation wavelengths of 514 nm. All spectra were measured using a 100× microscope objective to focus the laser excitation (10 mW) onto the samples as well as to collect the scattered light.

3.3 Results

We first present our results for graphitization on the Si-face in a high pressure of disilane in Section 3.3.1. In section 3.3.2 we present results for graphitization of the C-face in a low pressure of disilane which is qualitatively similar to the results for C-face graphitization in vacuum. In Section 3.3.3 we present results for graphitization in a high pressure of disilane where we start to see qualitative differences from vacuum prepared samples.



Fig. 3.5. Results for graphene on 6H-SiC(0001) prepared by annealing under 5×10^{-5} Torr of disilane at 1380°C for 20 min, producing an average graphene thickness of 1.3 ML. (a) AFM image, displayed using gray scale range of 3 nm. (b) LEEM image acquired at electron beam energy of 4.0 eV. (c) Intensity of the reflected electrons from different regions marked in (b) as a function of electron beam energy. (d) Color-coded map of local graphene thickness; blue, red, or yellow correspond to 1, 2, and 3 ML of graphene, respectively. Small white or black crosses mark the locations of reflectivity curves.

3.3.1 Graphitization of Si-face in a disilane environment In general, annealing at elevated temperatures and/or increased times leads to greater uniformity in the graphene surface morphology and its thickness, albeit with an increase in the average thickness. The use of a disilane background during the annealing permits the use of a higher temperature without an increase in the average thickness since the sublimation rate is decreased by the presence of the disilane. Higher temperature then permits a more equilibrium form of the surface structure, i.e. more uniform thickness and few, if any, of the surface pits. Results for graphene formation on the Si-face of SiC under a 5×10^{-5} Torr environment of disilane are shown in Fig. 3.5. Compared to vacuum-prepared surfaces, the graphene thickness [34, 104]. Comparing to prior work from our group in Ref. [104], the surface morphology is somewhat smoother for the disilane-prepared film and the thickness homogeneity of the graphene is also better. The reflectivity curves displayed in Fig. 3.5(c) are used to calculate the graphene thickness as discussed in

Section 2.4.3. The 2-ML-thick areas of graphene in Fig. 3.5(b) display less of the smallscale mottling seen for vacuum preparation. As discussed above, even for vacuum preparation, the uniformity of the graphene films improves considerably for preparation temperature above about 1320°C, although it is difficult to prepare films thinner than about 2 ML at those temperatures because of the short annealing times that would be required. With the disilane background, the annealing time can be raised without an associated increase in the Si sublimation rate. Thus, with the higher temperature, improved uniformity is achieved.



Fig. 3.6. Results for graphene on 6H-SiC($000 \overline{1}$) prepared by annealing in 1×10^{-6} Torr of disilane at 1290°C for 15 min, producing an average graphene thickness of 4.2 ML. (a) AFM image, displayed using gray scale range of 4 nm. (b) LEEM image acquired at electron beam energy of 2.3 eV. (c) Intensity of the reflected electrons from different regions marked in (b) as a function of electron beam energy. (d) Color-coded map of local graphene thickness; red, yellow, green, cyan, magenta, gray and white correspond to 2 - 8 ML of graphene, respectively. Small white or black crosses mark the locations of the reflectivity curves.

3.3.2 Graphitization of C-face in low pressure of disilane To increase the formation temperature for graphene on the C-face, one can try the same method used for the Siface of performing the annealing in an argon atmosphere. Unfortunately, this technique is found *not* to be successful for the C-face. Rather, we observe only the formation of isolated, thick graphene islands [46], the reason for which was found to be unintentional oxidation of the C-face in the argon environment. As an alternative to the graphene preparation under argon, we formed graphene under disilane on the C-face. Typical results are shown in Fig. 3.6. A relatively low pressure of disilane was used there, 1×10^{-6} Torr, but even so the annealing temperature needed for graphene formation was about 100°C higher than in vacuum. A moderately thick film was formed for the sample of Fig. 3.6, with average thickness of 4 ML. The large range of thicknesses seen in Fig. 3.6(d) are similar to that found for vacuum preparation [46]. However, one notable

difference between the results of Fig. 3.6 compared to a vacuum-prepared film such as Fig. 5 of Ref. [75] is the network of raised (white) lines prominently seen in Fig. 3.6(a) but that are not present (or only faintly seen on a smaller length scale) in Fig. 5 of Ref. [75]. We attribute these ridges to the strain-induced features arising from the different thermal expansion coefficients between the graphene and the SiC. As emphasized by Hass et al., the presence of such features is an indicator of a structurally ideal graphene film [32]. An additional feature of our disilane-prepared samples is that, unlike the case for vacuum preparation, they do *not* display nanocrystalline graphite (NCG) on their surface. NCG is a secondary disordered carbon phase that is found to occur both on the Si-face and C-face for vacuum prepared samples, but more abundantly on the latter [71]. The presence of the additional Si on the surface probably acts to provide an incorporation mechanism for that carbon.



Fig. 3.7. Raman spectroscopy from graphene on C-face SiC, obtained from the sample shown in Fig. 3.6 prepared in disilane (upper curve) and a sample prepared in vacuum (lower curve). The vacuum-prepared graphene is thicker, so that the graphene-derived peaks labeled D, G, and 2D are more intense for that spectrum relative to the SiC peaks (one of which is labeled). The origin of the peak marked by "?" at 1419 cm⁻¹ is not known.

A Raman spectrum of the graphene film of Fig. 3.6 is shown in Fig. 3.7, where it is compared to a spectrum of the vacuum-prepared film shown in Fig. 3 of Ref. [71]. The vacuum-prepared film is thicker than the disilane-prepared one, so that the graphenederived peaks labelled D, G, and 2D are correspondingly weaker for the latter. Other than that, the spectra appear quite similar, except that the disilane-prepared sample displays a large peak at 1419 cm⁻¹. We do not know the precise origin of this peak, although as discussed in Ref. [103] it is seen more intensely in some substrates compared to others and it appears to be related to some sort of defect or damage in the substrate itself.



Fig. 3.8. Results for graphene on 6H-SiC($000\overline{1}$) prepared by annealing in 6×10^{-5} Torr of disilane at 1310°C for 10 min. (a) AFM image, displayed using gray scale range of 5 nm. (b) LEEM image acquired at electron beam energy of 4.1 eV. (c) Intensity of the reflected electrons from different regions marked in (b) as a function of electron beam energy. (d) Color-coded map of local graphene thickness; blue corresponds to 1 ML of graphene, sitting on top of an interface layer denoted by white. Red corresponds to 2 ML of graphene sitting on the interface layer. Yellow corresponds to 3 ML of graphene (likely on the interface layer, and gray denotes an ill- defined surface structure. Small white or black crosses mark the locations of reflectivity curves.

3.3.3 Graphitization of C-face in low pressure of disilane Results for a C-face film prepared under a higher pressure of disilane, 6×10^{-5} Torr, are shown in Fig. 3.8. A thinner film was formed in this case as compared with Fig. 3.6. The surface morphology measured by AFM in Fig. 3.8(a), displays islands of graphene as revealed again by the presence of the raised (white) lines on the surface, surrounded by featureless areas that apparently contain no graphene. The electron reflectivity curves in Fig. 3.8(c) contain a number of new features compared to those in Figs. 3.5(c) or 3.6(c). Considering first the curves B, C, and D of Fig. 3.8(c), they contain 1, 2, or 3 minima in the reflectivity over the energy range 2.0 – 6.2 eV, as expected for 1, 2, or 3 ML of graphene respectively [67], but they also contain a new minimum near 6.8 eV. This new feature is even more intensely seen (at 6.3 eV) in the reflectivity curve from regions like A which shows a broad maxima over 2.0-6.2 eV. Typical samples prepared in vacuum or low disilane pressure display simple oscillations between 2.0-6.2 eV as in Fig. 3.6(c), so the unusual

minimum that occurs between 6.2-7.0 eV in the reflectivity curves of Fig. 3.8(c) indicates that the structure of the graphene/SiC interfaces has changed.

It should be mentioned that the pits seen in the AFM of Fig. 3.8(a) are not typical of disilane prepared samples. This particular sample was prepared by re-using an existing graphene sample. The pre-existing graphene was first H-etched off and and then the sample was graphitized in the disilane in the conditions mentioned above. In our work we have found that re-used samples are more susceptible to pit formation irrespective of the environment used. As shown in the next figure (Fig. 3.9) our other disilane prepared samples are pit-free, and still show the unusual reflectivity curves of Fig. 3.8(c).

Figure 3.9 shows the LEEM results from another sample which was prepared in 5×10^{-5} Torr of disilane. The reflectivity curves B-D in Fig. 3.9(b) also show an unusual minimum between 6.2 eV-7.0 eV similar to the curves in Fig. 3.8(c). To investigate the structure of the regions diplaying these unusual reflectivity curves we performed selected area diffraction (also called μ -LEED) studies using an aperture size of 2 μ m. Notably, µ-LEED acquired from both bright (like B) or dark (like D) areas both display diffraction spots with wavevector magnitude equal to that of graphene, as shown in Figs. 3.9 (c) and (d). Thus, a graphene (or graphene-like) layer apparently extends over the entire surface. Based on the results we presented so far we tentatively associate this new reflectivity curve B and C of Fig. 3.9(b) with a graphene-like layer in contact with the SiC, i.e. the base or "buffer" layer of graphene. There are several reasons for this identification: (i) this curve appears only on samples with very thin (sub-ML) films of graphene films, consistent with it being the layer nearest the SiC, (ii) the reflectivity curve itself resembles that found for the $6\sqrt{3}$ buffer layer found on the Si-face of SiC [67], albeit with the extra minimum near 6.3 eV which we explain later in this section, is associated with oxidation of the underlying SiC, (iii) the reflectivity minimum near 6.3 eV also appears in the curve of some overlying graphene, i.e. curves D of Fig. 3.9(b) [albeit shifted up to 6.8 eV], consistent with our identification of this layer being the base layer, and (iv) electron diffraction of this layer reveals spots identical with those found on the overlying graphene layer, demonstrating that this base layer does indeed have the graphene structure. Later in this chapter through more detailed LEED and

LEEM studies we provide a compelling case to prove that the reflectivity curves B and C of Fig. 3.9 arises from a buffer layer in contact with SiC.



Fig 3.9 Results for graphene on 6H-SiC($000\overline{1}$) prepared by heating in 5×10^{-5} Torr of disilane at 1270°C for 15 min (a) LEEM image acquired at electron beam energy of 4.5 eV. (b) Curves B – E show the intensity of the reflected electrons acquired from the circular areas marked in (a), and curve A shows data from a different sample with less graphene coverage prepared by heating in 6×10^{-5} Torr at 1310°C for 10 min. (Regarding curve E ,this curve appears to arise from a combination of areas with characteristics as in curves A – D. (c) and (d) Selected-area patterns acquired with a 2-µm aperture at 44 eV in the LEEM, from locations indicated by B and D, respectively, in panel (a). The thin black lines indicate two 30° ranges of angles, for reference.



Fig. 3.10 LEED results obtained at 100 eV from the same 6H-SiC($000\overline{1}$) sample shown in Fig. 3.9 (a) *in situ* LEED pattern with LEED spots marked (see text), (b) same sample as (a) but after air exposure, (c) and (d) intensity vs. energy of the spots indicated in (b). The thin black lines in (b) and indicate two 30° ranges of angles, for reference.

It should also be noted that the precise locations of the graphene diffraction spots shown in Fig. 3.9 are found to vary from point to point over the surface, indicating a grain size on the order of 2 μ m. This result is in contrast to the vacuum prepared C-face

sample of Fig. 5 of Ref.[75] where no variation was found in the μ -LEED patterns, indicating grain size smaller than 2 μ m. Use of the disilane environment is thus found to lead to much large grains and thinner films compared to vacuum preparation.

The µ-LEED measurements that we presented in Fig. 3.9 were performed in the LEEM instrument itself. This instrument is only capable of energies of around 44 eV or lower, for reasons which are discussed in Section 3.4. To obtain LEED patterns at higher energies we use the dedicated LEED instrument that is attached to our preparation chamber, however this is not capable of selected-area LEED measurements. With this conventional LEED instrument (using 100 eV) we find that the in situ LEED pattern from a sample prepared in a high disilane pressure is quite different from the 3×3 LEED pattern of a sample prepared in a low disilane pressure or vacuum. Figure 3.10(a) shows the *in situ* LEED pattern from a typical disilane prepared sample right after it was made. Weak graphene streaks are visible along with the primary SiC spots, as marked, and a complex arrangement of additional spots is apparent. This complex arrangement of diffraction spots is unlike the 3×3 pattern shown in Fig. 3.4(b) of a vacuum prepared sample. Figure 3.10(a) also shows an analysis of the diffraction spots. The pattern can be perfectly indexed using a supercell on the SiC with edges extending along (6,1) and (-1,7) of the SiC 1×1 cells. In conventional notation this structure would be expressed as a matrix with columns (6,1) and (-1,7), and in a more compact notation we denote this structure as $\sqrt{43} \times \sqrt{43} \cdot R \pm 7.6^{\circ}$ (or $\sqrt{43}$ for short) with the $7.6^{\circ} =$ $\tan^{-1}(\sqrt{3}/13)$ being the rotation of the supercell relative to the SiC. Approximately 8×8 unit cells of graphene fit within this super cell (with 2.4% mismatch, using room temperature lattice constants asic=0.3080 nm and agraphite=0.2464 nm). To perform LEEM studies it is necessary to transfer our sample through air. Air exposure causes the $\sqrt{43}$ pattern to disappear, being replaced by a $\sqrt{3} \times \sqrt{3}$ -R30° pattern as shown in Fig. 3.10(b). Intensity vs. energy characteristics of the $\sqrt{3}$ spots, e.g. Figs. 3.10(c) and (d), agree semi-quantitatively with those for the well-known Si₂O₃ silicate structure on the ($000\overline{1}$) surface [105]. The samples from both Fig. 3.8 and 3.9 showed this $\sqrt{3}\times\sqrt{3}$ -R30° pattern when studied ex situ implying that the surface was oxidized when their reflectivity curves were acquired.

The results of Fig. 3.10 demonstrate that different surface structures exist for disilane-prepared SiC($000\overline{1}$) compared to a vacuum-prepared surface. The $\sqrt{43}$ is quite similar to the $6\sqrt{3}$ structure in that both structures are complex large area superstructures that form prior to graphitzation. The similarity between the two structures suggests that the $\sqrt{43}$ layer might also act like a buffer layer just as the $6\sqrt{3}$ on the Si-face does. The disappearance of the $\sqrt{43}$ diffraction pattern from air exposure is not at all surprising for for a surface reconstruction, although it differs from that of the $6\sqrt{3}$ structure of the SiC(0001) that survives when exposed to air. In any case the modification of the ($000\overline{1}$) surface from air exposure provides an explanation for the shape of the reflectivity curves observed in Figs 3.8 and 3.9. The unusual minimum that occurs between 6.2 and 7.0 eV in the reflectivity curves of Figs. 3.8(c) and 3.9(b) is very similar to what has been previously reported for the SiC(0001) surface, associated with a *decoupling* of the $6\sqrt{3}$ buffer layer from the underlying SiC due to oxidation or hydrogenation [81,83,106]. The decoupled buffer layer then assumes a diffraction pattern identical to that of graphene, i.e. it becomes a graphene layer. We interpret our results for the $(000\overline{1})$ surface in exactly the same way: The unique reflectivity curves A of Fig. 3.8(c) or B and C of Fig. 3.9(b) are attributed to a buffer-like layer on the surface, and we associate the $\sqrt{43}$ diffraction pattern to this same layer. In the above results we have not been able to observe that pattern in the LEEM, since that part of the surface becomes oxidized during transfer to the LEEM. However, we do find a clear correlation between the intensity of the $\sqrt{43}$ LEED pattern from various samples and the prevalence of the surface areas with reflectivity curves like A of Fig. 3.8(c) or B and C of Fig. 3.9(b). To conclusively show that the reflectivity curves of Figs. 3.8 and 3.9 arise from a buffer layer decoupled due to oxidation, we next discuss a $\sqrt{43}$ sample that employed a rapid transfer of the sample between our graphene preparation system and the characterization system, thus enabling study of the graphene buffer layer before any oxidation occurs underneath that layer (i.e. decoupling it from the SiC). It should be clarified that the oxidation of the buffer layer in disilane prepared surfaces is due to air exposure i.e it occurs *after* the graphene formation, and should not be confused with the in situ oxidation that inhibits graphene formation in an argon environment.



Fig. 3.11 Results for graphene on 6H-SiC($000\overline{1}$), prepared by heating at 1220°C for 10 min in 5×10^{-5} Torr of disilane. (a) in situ LEED at 100 eV. (b) LEEM image at beam energy of 3.8 eV. (c) Intensity of the reflected electrons from different locations marked in (b).

Figure 3.11 shows results obtained from a sample prepared by heating in disilane $(5 \times 10^{-5} \text{ Torr})$ at 1220°C for 10 min. The conventional LEED pattern in Fig. 3.11(a) was acquired *in situ* after preparation and displays the $\sqrt{43}$ pattern. The LEEM results were obtained after a relatively short transfer time of ~ 10 minutes. The LEEM image at 3.8 eV shown in Fig. 3.11(b) consists predominantly of two types of areas, one with bright and the other with dark contrast. The reflectivity characteristics from the dark region, curves C and D of Fig. 3.11(c), reveal a single minimum near 3.7 eV, as is typical for single-ML graphene The reflectivity from the bright region, curves A and B of Fig. 3.11(c), show behavior that we have never observed previously on any C-face or Si-face sample. Small areas of this surface consist of thicker graphene, as in curves E and F, which reveal 2 and 4 ML of graphene respectively.

After the LEEM study of Fig. 3.11, the sample was removed from the LEEM instrument and was exposed to air for several days. This procedure caused the $\sqrt{43}$ spots to disappear, as shown in Fig. 3.12(a) (for this sample we do not observe the formation of $\sqrt{3}\times\sqrt{3}$ -R30° spots for the oxidized surface). LEEM results from the air-exposed surface are shown in Fig. 3.12(b) and(c). We don't have LEEM images from the same location of the surface as in Fig. 3.11(b), since it is hard to find exactly the same location of the surface after talking out the sample from the LEEM instrument and then loading it back. A LEEM image at 3.8 eV, Fig. 3.12(b), is again found to consist

predominantly of dark and bright area, as for Fig. 3.11(b), although the dark areas now appear with two slightly different contrasts. Reflectivity curves from these dark regions, curves C and D of Fig. 3.12(c), reveal single-ML behavior (curve D) for the darkest contrast and single-ML plus an additional minimum near 7 eV (curve C) for the slightly lighter contrast areas. These reflectivity curves are exactly the same manner as in Figs. 3.8 and 3.9 with the minimum near 7 eV interpreted as forming because of "decoupling" of the buffer layer that is below the single-ML graphene (i.e. release of the covalent bonds between the buffer layer and the underlying SiC, as in Refs. [83] and [106], due to oxidation of the SiC in the present case).



Fig. 3.12 Results for the same sample as in Fig. 1, after oxidation. (a) LEED pattern at 100 eV (b) LEEM image at beam energy of 3.8 eV. (c) Intensity of the reflected electrons from different locations marked in (b).

The reflectivity curves from the lighter-contrast areas in Fig. 3. 12(b), curves A and B of Fig. 3.12(c), reveal the same behavior as we previously associated with the oxidized buffer layer on the C-face. Thus we can now identify the reflectivity characteristic of the *unoxidized* buffer layer as being that of curves A and B of Fig. 3.11(c). Additional information is contained in the μ -LEED results of Figs. 3.13(a) and (b). These patterns were acquired with a 5 μ m aperture, centered around the points A and C in Fig. 3.11(b). The size of that aperture is slightly larger than the areas of buffer or ML graphene, respectively, surrounding those points, but data with a 2 μ m aperture reveal the same diffraction spots (albeit with worse signal-to-noise) at these locations and at many other locations studied on the surface. In all cases, the pattern reveals spots

with wavevector magnitude precisely the same as for graphene. This occurs both for the buffer layer and for the single-ML graphene on the buffer layer.



Fig. 3.13 μ -LEED patterns acquired at 44 eV in the LEEM, using a 5 μ m aperture centered at location A in Fig. 3.11(b) (the buffer layer) and location B in Fig. 3.9(b) (the 1-ML graphene area) respectively

We thus find that the unoxidized buffer layer has essentially the structure of graphene, consistent with our interpretation as this layer being a precursor of a graphene layer and converting to graphene when the covalent bonds to the underlying SiC are released. In Fig 3.9 we observed a graphene-like diffraction pattern from the oxidized buffer layer, but now we find this pattern from *both* the unoxidized and the oxidized buffer layers. We thus deduce that the buffer layer consists of a carbon layer with structure close to that of graphene, but with some distortions of the layer due to bonding (with $\sqrt{43} \times \sqrt{43}$ -R±7.6° symmetry) to the underlying SiC. It should be noted that the $\sqrt{43}$ spots that appears in the conventional LEED patterns acquired at 100 eV from these unoxidized samples are not seen in the LEED patterns acquired in the LEEM. We attribute that discrepancy to a reduced sensitivity of the diffraction in the LEEM, as further discussed in Section 3.4. Figure. 3.14 shown below summarizes our understanding of graphene formation in a Si-rich environment such as disilane.



Fig. 3.14. Graphene formation on the C-face in a disilane environment. (a) The graphene formation occurs on a graphene like $\sqrt{43}$ 'buffer' layer bonded to the interface whose structure is not yet known. (b) After the sample gets oxidized by air exposure a silicate layer forms on the substrate thus decoupling the $\sqrt{43}$ 'buffer' layer and turning it into the first graphene layer.

3.4 Discussion

In this section we will discuss two aspects of graphene formation in a disilane environment. First we will discuss the different growth conditions used by different research groups to grow graphene on the C-face. We demonstrate that by graphitizing in a disilane background we avoid the unintentional oxidation that prevents that prevents the formation of thin, uniform graphene films on the C-face in moderate vacuum conditions or an argon atmosphere. Secondly we discuss the structure and bonding of the buffer layer, and the reason it forms when graphitizing in a disilane environment but not in vacuum.

The reproducibility between research groups regarding growth mode or growth morphology of the graphene is somewhat limited. Inhomogeneous formation of the graphene on the C-face has been reported by several groups, although the details differ between groups. Early work of Hass et al. reported poor results for C-face graphene formation in vacuum, but much improved results using an rf-induction furnace at pressure of 3×10^{-5} Torr [107]. A relatively extensive study has presented by Camara et al., in which they demonstrate that under vacuum conditions of 10^{-6} Torr the graphitization of 6H-SiC consists of both an extrinsic process in which an existing structural defect creates a nucleating center and an intrinsic process in which the graphitization occurs everywhere on the surface [101, 102]. To control these processes they cover the SiC with a cap which reduces the Si sublimation rate and quenches the intrinsic growth process, thereby enabling the growth of graphene ribbons at step bunches due to the extrinsic process [108].

Work of other groups revealed either islanding in the initial stages of the C-face graphene formation, or an apparent inhibition in the initial growth followed by rapid growth at temperatures above some critical temperature, with these works performed at pressures between 10^{-6} and 10^{-5} Torr [47,109]. An important factor for graphene formation on the C-face is, we believe, the cleanliness of the surface (and surrounding environment). We have previously reported the presence of a silicate layer (Si₂O₃) on the C-face of SiC formed under argon, i.e. due to unintentional oxidation [46]. A number of the vacuum systems used by other groups for graphene formation under vacuum have only moderate base pressures, and as further discussed in the following section we believe that unintentional surface oxidation of the SiC (making it resistant to graphitization) is a significant factor in many of the previous reports.

As discussed in Section 3.1.2 increasing the formation temperature for graphene on the C-face should result in a planarization of the film and towards this goal one can performing the annealing in an argon atmosphere. Unfortunately, this technique is found not to be successful for the C-face. Rather, we observe only the formation of isolated, thick graphene islands. The islanding we see for C-face graphitization in argon is similar to that seen by Tedesco et al. [47]. However, unlike us, they also see a similar islanding for samples made in vacuum. We believe this likely arises from unintentional oxidation of their surfaces, since their background pressure is only 10^{-5} Torr. Prakash et al. report difficulty in forming thin (ML-thick) graphene on the C-face in vacuum, with nearly no graphene forming for temperatures up to 1450°C, and then at 1475°C a film with thickness of 5 ML is observed (for constant annealing time of 10 min) [109]. The background pressure is about 4×10^{-5} Torr in their case, so again, we consider it likely that some oxidation of the surface occurs, inhibiting the graphene formation at the lower temperatures. The electrical properties of the few-layer graphene formed on the C-face by both of these groups are good, with mobilities $>10,000 \text{ cm}^2/\text{Vs}$ [110,111] but nevertheless, the formation of thin (~ML-thick) graphene that uniformly covers the Cface surface has not been achieved. The work of Camara et al. displays rather inhomogeneous graphene formation on their C-face surfaces, although this inhomogeneity is used to advantage to form well-defined nanoribbons on the surface and producing larger areas of single-ML graphene on stepped surfaces [101, 102,112].

Again, we believe that this anisotropic growth is related to the moderate vacuum conditions in their graphitization chamber. Finally, it is important to note the good thickness uniformity and the relatively high mobilities ($\geq 15,000 \text{ cm}^2/\text{Vs}$) of the ML-thick graphene on the C-face reported by Wu et al.,[113] although the precise formation conditions for that graphene are not well understood due to the confined geometry employed for the growth.

The role of oxygen in our own observations of C-face graphene formation is established by its characteristic signature in the intensity vs. voltage measurements of the $\sqrt{3}\times\sqrt{3}$ -R30° LEED patterns [46]. When we employ disilane for the surface cleaning rather than H, we find that the resulting LEED patterns from the surface do *not* reveal any significant $\sqrt{3}\times\sqrt{3}$ -R30° LEED spots. This is the case even when restricted pumping of the preparation chamber (i.e. prior to, and during the disilane cleaning) is employed. Of course, during the disilane cleaning (pressure of 5×10^{-5} Torr) the pumping of the chamber is maintained, unlike the 1-atm H (or Ar) environments for which the pumps are valved off. Thus, it is perhaps not surprising that no significant surface oxidation occurs during the disilane cleaning. Of course, the disilane itself is effective in removing any surface oxide, likely by the formation of volatile products such as SiO.

Disilane has a significant effect on the surface chemistry not only for the surface cleaning but also during the graphitization. For C-face (or Si-face) samples graphitized in disilane, we find a total absence of NCG on the surface. (In contrast, we find that samples cleaned in disilane but graphitized in vacuum still show very significant amounts of NCG, demonstrating that the absence of NCG found during graphitization in disilane is *not* related to the presence or absence of a surface oxide). The NCG that we commonly observe during graphitization has not been widely reported by other groups, and we believe this difference is due to the presence (oftentimes unintentional) of Si in those other growth environments. Perhaps the Si acts to combine with surface C and allows that C in incorporate into the SiC (e.g. at step edges).

In any case, for our usual vacuum conditions, we are able to form continuous, thin graphene on the C-face, although the thickness of the resulting film is still much less uniform than for the Si-face (at ≤ 2 ML coverage the nonuniformity is similar on the C-

face and Si-face, but for thicker films the thickness uniformity of the Si-face improves whereas that for the C-face continues to be poor). We attribute this inhomogeneity to kinetic limitations arising from the relatively low temperature of the formation process. Under argon, severe islanding is found, which as described above we attribute that to unintentional oxidation of the surface. Finally, to overcome that oxidation, we employed a disilane environment. In that case, thin graphene layers on the C-face surface are indeed achieved, with thickness variation significantly reduced compared to our vacuum-formed films. Our observations that the C-face is more susceptible to oxidation than the Si-face, is consistent with prior reports that find that the C-face is more reactive than the Si-face [72]. The C atoms of the graphene on the other hand do not oxidize readily. The ease with which a surface gets oxidized depends on the ease with which the O atom can form twofold coordinated bridge bonds with the atoms of the surface. The O atoms in the silicate layer on the Si-face and C-face of SiC do form such bridge bonds [105], however it is not possible to form such bridge bonds with the p_z orbitals of graphene without distorting them.

The reflectivity curves of the pristine buffer layer [curves A and B of Fig. 3.11(c)] appear quite different than after oxidation has occurred [curves A and B of Fig. 3.12(c)]. The general effect of the oxidation is seen to be the formation of a prominent minimum in the reflectivity near 6.4 eV. This minimum also occurs for graphene on top of the buffer layer, albeit shifted to about 7.0 eV, as seen for 1-ML-thick graphene on the buffer layer [curve C of Fig. 3.12(c)]. For the pristine buffer layer, we find that μ -LEED reveals diffraction spots with the *same* wavevector magnitude as for perfect graphene. Thus, we conclude that the buffer layer is essentially a graphene layer, but one that is most likely covalently bonded to the underlying SiC. This situation is thus completely analogous to the $6\sqrt{3}$ buffer that forms on the Si-face [94,81,83,37] it should be noted, however, that the angle-resolved photoemission experiments that directly reveal the bonding and subsequent decoupling of the buffer layer from the Si-face SiC [81] are not yet available for the C-face; such data would provide more complete evidence for our interpretation of our C-face results).
When oxidation of our C-face samples occurs, μ -LEED results from the buffer layer are unchanged, as expected since that layer is essentially graphene. As noted in Section 3.3.3, those μ -LEED results are acquired at energies of around 44 eV or below. For the conventional LEED patterns displayed in this work at 100 eV, a change *is* observed before and after oxidation of the sample, namely, the $\sqrt{43}$ spots are present in the former case but absent in the latter. We attribute this difference between the diffraction results of the LEEM compared to the conventional apparatus simply to the energy-dependence of the diffraction intensities (and also considering instrumental effects in the LEEM at the higher energies). Indeed, using the conventional LEED apparatus at lower energies we find the $\sqrt{43}$ spots diminish in intensity as energy is lowered from 100 eV, becoming very faint close to 60 eV. The disappearance of the $\sqrt{43}$ spots upon oxidation is interpreted, as already mentioned above, in terms of a release of the covalent bonds between the buffer layer and the underlying SiC.

Regarding the *reason* for the different interface structures in a Si-rich environment compared to vacuum, the graphene formation conditions in the former case are expected to be closer to equilibrium, as argued by Tromp and Hannon [43] so that kinetic limitations may lead to the absence of the $\sqrt{43}\times\sqrt{43}$ -R±7.6° structure in vacuumprepared C-face graphene. Complete geometrical determination of the $\sqrt{43}$ structure (as well as the C-face 3×3 structure) is needed before a full understanding of its formation can be achieved. In any case, the fact that we obtain the same $\sqrt{43}$ interface structure using either disilane or a purified neon environment [114, 115] (and it was also seen previously in small areas on an argon-prepared surface) [46] demonstrates that the hydrogen from the disilane is unimportant. Separately, it is interesting to note that in Figs. 3.9(c) and (d) most of the graphene diffraction spots (both the buffer layer and the overlying graphene) are rotationally misaligned from the SiC spots by angles in the range ±10°, the same range as found in studies of thick graphene on C-face SiC [46, 48, 97]. Thus, the $\sqrt{43}$ buffer structure observed here may play a role in the origin of this commonly observed rotational misalignment [116].

3.5 Summary

To summarize we find that graphene formation depends on the growth environment. On the Si-face disilane prepared samples show an improved quality compared to those prepared in vacuum, however the monolayer domains are not as large as those produced in an argon atmosphere. The interface structure between the graphene and Si-face is a $6\sqrt{3}$ buffer layer for all three environments (vacuum, disilane, and argon).

On the C-face for vacuum prepared samples the interface structure between graphene and the substrate is a 3×3 reconstruction which is not believed to act as a buffer layer. The graphene formed is quite non-uniform and has a small domain size. When graphene is prepared in an argon atmosphere the surfaces gets unintentionally oxidized and is covered by a stable $\sqrt{3} \times \sqrt{3}$ -R30° silicate layer which is resistant to graphitization. Thus the graphene forms in islands on the regions of the surface that are not covered by a silicate layer. In a disilane environment for low pressures no significant difference is seen from vacuum prepared films. For higher pressures we do see a difference from vacuum prepared samples. We are able to form thin uniform films of graphene and the interface between the graphene and the C-face is a graphene like $\sqrt{43}$ layer. Upon air exposure the $\sqrt{43}$ layer decouples from the substrate due to oxidation of the substrate, and the decoupled $\sqrt{43}$ layer becomes the first graphene layer. Chapter 4

STM/S on Epitaxial Graphene on SiC(0001)

Scanning tunneling microscopy (STM) is a very useful tool to image atoms and also to simultaneously perform spectroscopy measurements. The spectra collected in scanning tunneling spectroscopy (STS) measurements contain information about the density of states of the sample above and below the Fermi energy. In this chapter we present results for two different STM/STS studies on graphene on SiC(0001). In the first study we perform STM/S on a graphene sample with a fairly large coverage of a secondary disordered graphitic phase. The spectra from the disordered phase contain additional features compared to the ordered graphene. We argue that this disordered secondary phase is the nano-crystalline graphite (NCG) that we also see on the C-face. In the second study we examine graphene that has been functionalized by hydrogen. On comparing the spectra from pristine graphene with that from the functionalized graphene we find that the functionalized graphene shows additional features in its spectrum near the Fermi energy, suggesting the carbon atoms in graphene have changed character from p^2 hybridized to sp^3 .

4.1 NCG on graphene on SiC

We briefly review our prior work on the formation of a secondary disordered phase identified as nano-crystalline graphite (NCG) [71]. Before graphitizing our samples we first H-etch our SiC samples to eliminate polishing damage. H-etching generally results in a well ordered step terrace arrangement, but we sometimes see less well ordered step arrays. Surfaces that do not display a regular step-terrace array following H-etching are found to form significant amounts of NCG when graphitized. NCG is seen as a rough, disordered phase in AFM, both on our Si-face and C-face samples, but with a heavier coverage on the latter. We acquired spatially resolved Raman spectra on a C-face graphene sample with a large fraction of the surface covered with NCG [71]. The Raman results revealed that, compared to the ordered graphene, the areas with NCG showed a larger defect related D peak at 1360 cm⁻¹ and a graphite related G peak that was shifted by 10 cm⁻¹ to 1596 cm⁻¹. This type of shift is known in the literature to be associated with the occurrence of NCG. In the STM/S study in this chapter we perform spatially resolved STS on a Si-face graphene sample that shows a large fraction of a

secondary disordered phase on its surface, and present evidence that this phase is NCG similar to that seen on the C-face.

4.2 Experiment

The sample used in this study was cut from a nominally on-axis, *n*-type 6H-SiC wafer purchased from Cree Corp. The sample preparation is as discussed in Section 3.2. The sample was chemically cleaned in acetone and methanol, after which it was etched in a 10 lpm flow of pure hydrogen for 3 min at a temperature of 1600°C. Before annealing, hydrogen was pumped away from the chamber until a desired pressure of 10^{-8} Torr was reached and then the sample was annealed for 40 min at 1350°C in vacuum.

The thickness of the graphene sample was measured by Auger electron spectroscopy (AES) using a 5 kV electron gun and VG Scientific Clam 100 hemispherical analyzer. For routine determination of graphene thickness by AES we use the ratio of the 272 eV KLL C line to the 1619 eV KLL Si line. This ratio is analyzed with a model involving the escape depths of the electrons [117], with the overall magnitude of the ratio being calibrated to graphene thicknesses determined by LEEM. For the Si-face, the $6\sqrt{3}\times 6\sqrt{3}$ -R30° "buffer" layer between the graphene and the SiC is taken to contain 1 ML worth of carbon [38] and this amount is subtracted from the carbon coverage determined from AES to yield the graphene coverage values given below. The surface morphology of our graphene films were studied by AFM using a Digital Instruments Nanoscope III in tapping mode.

The STM/STS measurements were performed in a home built system maintained at a base pressure of 2×10^{-10} Torr. The images are acquired at a constant current of 0.1 nA. Pt-Ir tips are employed and are cleaned thoroughly by electron bombardment using a constant emission current of 3 mA at 500 V for 5 minutes. For the spectroscopy measurements the method of variable tip-sample separation was employed [12, 39, 118], typically using a ramp of 0.1 nm/V and with broadening parameter of 1.0 V to compute the normalized conductance $(dI/dV)/(\overline{I/V})$ (the results are only weakly dependent on these parameters). The conductance spectra were acquired using a lock-in amplifier with 50 mV modulation at a frequency of typically 1 kHz.

4.3 Results

Many AFM images of our Si-face graphene sample display a faint "snowflake-like" pattern suggestive of some sort of secondary phase other than regular, ordered

graphene. In an early work of ours we speculated that this phase might be associated with excess Si and/or C atoms present at the graphene/SiC interface [103] but here we present additional data indicating that this phase probably exists on the top *surface* of the graphene. Below we argue that the disordered secondary phase that we observe on the Si-face is NCG similar to what we see on the C-face, and we discuss possible origins of this carbonaceous surface layer.



Fig. 4.1 Images of graphene on SiC(0001), prepared by annealing in vacuum at 1350°C for 40 min. (a) AFM image, (b) STM image acquired at sample voltage of +2.0 V, and (c) STM image acquired at +0.4 V. Images are displayed with gray scale ranges of 2.2, 0.04 nm, and 0.025 nm, respectively. Arrows on the side of (a) indicate the locations of cross-sectional cuts, shown in Fig. 4.3. Black lines in (c) indicate the two dominant corrugations in the image.

Fig. 4.1 shows AFM and STM images obtained from a Si-face sample that was annealed in vacuum at 1350°C for 40 min. This sample was found from AES measurements to be covered with an average of 6.2 ML of graphene (a remarkably thick layer, as further discussed below). As seen in Fig. 4.1(a) there are two types of morphologies existing on the surface, one labeled A that is relatively flat and smooth and another labeled B that is rougher and has higher topographic height than A. An STM image of a flat, smooth area is shown in Fig. 4.1(b). The particular pattern found there can be definitely identified as the $6\sqrt{3}\times 6\sqrt{3}$ -R30° structure associated with the C-rich SiC(0001) surface;[39] this same pattern is found by STM imaging of other SiC(0001) surfaces, *both with or without* the presence of overlying graphene layers. Furthermore, from low-bias imaging, Fig. 4.1(c), a hexagonal corrugation with period

consistent with that of graphene, $\sqrt{3}(0.246 \text{ nm})/2=0.213 \text{ nm}$, is seen (the two dominant corrugations are marked by black lines in Fig. 4.1(c), with the third corrugation being very faint in the image). From this hexagonal arrangement we can identify the presence of graphene covering the $6\sqrt{3}\times6\sqrt{3}$ -R30° structure, *i.e.* the usual surface phase for vacuum-annealed SiC(0001) surfaces.



Fig. 4.2 Upper: STM image acquired from same sample as in Fig. 4.1, with a sample voltage of +2.0 V and displayed with gray scale range of 2.2 nm. Lower: Tunneling spectra from the locations indicated, with individual spectra are shown by thin lines and the average by a thick line. The sample voltage corresponds to the energy of a state relative to the Fermi-level (0 V). The normalized conductance $(dI/dV)/(\overline{I/V})$ is proportional to the density of states of the sample, and is computed as described in Section 4.2.

An STM image over a larger range is shown in the upper part of Fig. 4.2, now including both an area of the graphene-covered $6\sqrt{3}\times6\sqrt{3}$ -R30° structure (on the left) and a portion of the rough, disordered region (on the right). Tunneling spectra acquired at the points indicated are shown below the image. The spectra from the graphene-covered $6\sqrt{3}\times6\sqrt{3}$ -R30° region are very similar to each other, and they closely resemble

that known for graphene on SiC [39]. The spectra reveal nonzero conductance at 0 V, but nevertheless with a distinct conductance minimum at 0 V, indicative of semimetallic behavior (these measured spectra actually have a somewhat lower conductance at 0 V than that found for single- or bilayer-graphene [39], but in measurements of very thick graphene layers, *i.e.* graphite, we have observed similar low conductance at 0 V and we associate it with the presence of the semi-metallic graphitic band structure [119]). On the disordered region the *average* spectrum is quite similar to that from the graphene, but we find significant variation from point to point. Some points display a large conductance maximum near -1.1 or -0.5 V, others shown distinct features at positive voltages, and some curves are smoothly varying without any clear peaks. Although it is certainly not possible to identify the chemical composition of the disordered layer based solely on these tunneling spectra, we can nevertheless conclude that this material has an average spectrum quite similar to graphene but with additional features at specific locations, perhaps arising from extra dangling bonds and/or defects.



Fig. 4.3 Topographic height profiles at the locations of the arrows in the AFM image of Fig. 4.1(a), with the blue (red) line corresponding to the upper (lower) cut. Dashed lines in the surface height indicate intervals of 0.75 nm, the half-unit-cell height of 6H-SiC(0001), with dotted lines showing half that amount.

The fact that the spectra acquired on the disordered region can be, locally, quite different than that from the ordered graphene region indicates that the disordered region does not exist at the *interface* of the graphene and the SiC (since a tunneling spectrum

of that would be smoothly varying, like the spectrum from the ordered region, at least for ≥ 2 ML of overlying graphene [39]). Rather it appears that the disordered material exists on the graphene *surface*. Cross-sectional cuts from the image of Fig. 4.1(a) are shown in Fig. 4.3. The disordered layer can be seen to have two different levels [see e.g. the arrow in Fig. 4.1(a) showing a transition between the levels], and from Fig. 4.3 it appears that the height of each level is about 0.37 ± 0.02 nm, close to the half-unit-cell height of 6H-SiC, 0.375 nm. This latter agreement is coincidental, however, since from measurements made on 4H-SiC (not shown) we find a value for the height of the disordered layer of 0.35 ± 0.03 nm, in agreement with the results from 6H-SiC.

We interpret the disordered surface layer on this Si-face sample, as well as the prior snowflake-like patterns seen on other Si-face samples [103], in the same way as the disordered layers seen previously on C-face SiC, namely, as being NCG. The tunneling spectra we observe in Fig. 4.2 are consistent with this interpretation. The layer heights just mentioned are slightly larger than the expected 0.34 nm for NCG, but still close to that. AES results for the sample of Fig. 4.1 produced an intensity ratio of the C KLL line to the Si KLL line of 130. The intensity of the Si peak in this case was very low (almost unobservable), indicative of little or no Si content in the disordered surface layer. Taking the Si content to be zero, then the observed intensity ratio corresponds to a graphene+NCG coverage of 6.2 ML. This coverage is very high compared to other samples prepared under similar conditions; usually for a temperature of 1350°C we would achieve ≤ 2 ML of graphene on the surface [34,104].

We interpret the unusually high graphene coverage for the sample of Fig. 4.1, as well the presence of the disordered surface layer itself, in the following manner. First, we recall from our prior studies of NCG on the C-face that it is only certain wafers that produce a lot of NCG on their surfaces, with other wafers producing little [71]. The former types of wafers were found to have on their surfaces, after H-etching, a relatively large number of spiral step structures (density $>1\times10^4$ cm⁻²), indicative of a high dislocation density in these wafers. Thus, we believe that it is the dislocation (and/or micro-pipe) density that is the main variable between the wafers. Perhaps it is the spiral step structures themselves that lead to the NCG, through decomposition of the curved step edges. Alternatively, the dislocation cores could perhaps act as a source of carbon (*e.g.* perhaps related to the discussion in Ref. [101]). In situations where large amounts of this carbon are produced, it apparently forms the NCG on the surface. Furthermore, we also consider it likely that this NCG could itself, at sufficiently high temperature, convert to ordered graphene. That conversion process would account for the exceptionally large graphene coverage on the sample of Fig. 4.1.

4.4 Functionalized graphene on SiC(0001)

For transistors used in digital circuits it is desired that the transistor have a well defined on and off state, or in other words a high I_{on}/I_{off} ratio, where I is the current that flows through the transistor. Graphene is a zero bandgap semi-metal because of which graphene devices show a high minimum conductivity and low Ion/Ioff ratio. While the low I_{on}/I_{off} ratio of graphene transistors is not a problem for analog circuits, if one wants to make digital circuits one would need to modify the bandgap of graphene. One way to modify the bandgap of graphene is by functionalizing it i.e by attaching a functional group such as hydrogen or fluorine to the graphene, which alters the bonding and opens up a bandgap. The reaction of a carbon atom in graphene with a functional group causes the delocalized p_z orbitals to become more localized and change character from $\ensuremath{\mathsf{sp}}^2$ hybridized to sp³. Hydrogenated graphene can have a bandgap of 0-3.5 eV depending on the extent of the functionalization [120]. If graphene is completely hydrogenated then every carbon atom in graphene is bonded to a H atom, and the new compound is called graphane. In graphane every carbon atom is sp³ hybridized and thus forms tetragonal σ bonds with the neighboring atoms as shown in Fig. 4.4(a). Graphane (hydrogenated graphene) should not be confused with graphene on a hydrogen passivated substrate which was discussed in Section 3.1.1 and is shown in Fig. 4.4(b) for comparison.



Fig. 4.4 Comparison of structure of graphane on SiC(0001) with graphene on a hydrogen passivated SiC(0001). (a) In graphane the carbon atoms change hybridization from planar sp² to sp³ type. In this case the graphane rests on a $6\sqrt{3}$ buffer layer. (b) In the case of graphene on a hydrogen passivated substrate the H atoms saturate the dangling bonds of underlying substrate, but do not attach to the graphene.

In this study we perform STS on a graphene sample that is electrochemically functionalized with hydrogen. STS allows us to compare the density of states of the functionalized graphene with pristine graphene, and thus determine the extent of the functionalization.

4.5 Experiment

The sample in this study was prepared by Daniels *et. al.* at University of Southern Carolina [121, 122]. They first form epitaxial graphene on SiC(0001) by annealing the substrate to 1400°C in an RF furnace. To functionalize the graphene they use an electrochemical set up with the exposed graphene sample as a cathode, Pt wire as the anode, and dilute H_2SO_4 as the electrolyte. On applying a voltage across the electrodes the electrolyte dissociates, and the H⁺ ions are attracted to the graphene. The resulting graphene is then tested for functionalization by Raman spectroscopy. In our lab we perform AFM and STS measurements on the sample using the setup described in Section 4.2.

4.6 Results

The graphene sample was tested by our collaborators for functionalization using Raman spectroscopy. In functionalized graphene some of the carbon atoms change from sp² hybridization to sp³ which disrupts the order of the sample, resulting in a higher D peak in the raman spectra while the G peak remains unaffected [123]. For the sample in this study it was found that the functionalization was not uniform but was higher in the center compared to the edge. The Raman spectrum of the center displayed a higher D peak, and also a small C-H peak which got lost in the noise as one moved towards the edge of the sample (not shown here). Fig. 4.5 shows AFM images acquired from the edge of the sample and the center of the sample. There is no significant difference between the two images except that the image from the center shows white specks that could be due to contamination. The STM/S data in this study was acquired on relatively flat parts of the sample, contaminants such as in Fig. 4.5(b) are too large in size to be imaged and are necessarily avoided.(The AFM results from USC were also rougher on the functionalized graphene).



Fig. 4.5 AFM images of functionalized graphene. (a) Image acquired at the edge of the sample corresponding to pristine graphene, gray scale of 3.7 nm. (b) Image acquired at the center of the sample corresponding to functionalized graphene, gray scale of 5.1 nm.



Fig. 4.6 Scanning tunneling spectroscopy results measured at the center and at the edge of the sample. The sample voltage corresponds to the energy of a state relative to the Fermi-level (0 V). The normalized dI/dV plotted is $(dI/dV)/(\overline{I/V})$ and is computed as described in the text. $(dI/dV)/(\overline{I/V})$ is proportional to the density of states of the sample, and we can see in this figure, it does not go to zero in either of the spectra, implying no energy gap. The second spectrum is shifted upward for ease of display, the zero normalized conductance level for this spectrum is shown with a dotted line.

Spectroscopy measurements were performed at the edge of the sample (corresponding to pristine graphene) and at the center of the sample (corresponding to functionalized graphene) as shown in Fig. 4.6. For both spectra, there is no energy gap and the measured conductance at 0 V is nonzero, but relatively small, indicative of weakly metallic (semi-metallic) behavior. The lack of an energy gap implies that all the carbon atoms in the graphene are not functionalized. The main differences between the spectrum from the pristine graphene and the spectrum from the functionalized graphene is that the latter shows a spectral peak at -0.4 V as well as a weak feature near +0.5 V. These differences are similar to those seen between graphene and the $6\sqrt{3} \times 6\sqrt{3}$ "buffer layer" on SiC [39]. Thus it can be argued that, similar to the buffer layer, the functionalized graphene has some covalent bonds involving sp³ hybrid states. It should be mentioned that the spectra from the edge and center of the sample were obtained with different probe tips; nevertheless, multiple tips were employed for measurements

at both positions and the differences shown in Fig. 4.6 were reproducible over the measurement set.

4.7 Discussion and Summary

The STS results in Section 4.3 show that some regions with NCG can have additional states present in their normalized conductance spectra. The additional states can correspond to dangling bonds or defects, which is consistent with the Raman results where a high D peak was observed for the NCG on the C-face. On the functionalized graphene sample discussed in Section 4.6 we also observe additional states in the normalized conductance spectra. We attribute the additional states to some change in the bonding nature from sp^2 to sp^3 hybridization. The localized regions of sp^3 hybridization act as defects that break the symmetry of the graphene lattice and can open up additional states near the Fermi energy [124]. The presence of localized regions of sp³ hybridization is consistent with the enhanced D peak observed in the functionalized region of the graphene. As mentioned in Section 4.6 the central region of the sample is functionalized while the outer region is not. On the functionalized regions the additional states are distinct and reproducible consistent with adsorbed hydrogen (chemisorption), but even on the areas expected to be non-functionalized we occasionally see additional states in the spectrum near the Fermi energy (not shown here). We attribute this to an occasional H atom being adsorbed on the surface (but not to the same extent as in the functionalized regions). Some groups [124,125] report the opening up of an energy gap of around 0.4 V in graphene functionalized by hydrogen. We believe the lack of an energy gap in our spectra is due to the graphene sample not being completely functionalized, rather, the H-atoms adsorb to the carbon atoms non uniformly.

Chapter 5

Graphene on Copper Substrates

5.1 Introduction

As discussed in Section 1.3 a popular technique to produce graphene is to heat a metal to a temperature just below its melting point in the presence of a hydrocarbon. The high temperature decomposes the hydrocarbon, and the carbon dissolves into the metal. Due to its limited solubility the carbon segregates onto the surface, and it is thus capable of forming large areas of monolayer graphene.

Growing graphene on Cu is a viable way to grow large area graphene cheaply [52, 126]. Sizes as large as 30 inches have been reached and successfully transferred to other substrates [127]. A problem with graphene grown on Cu is that the graphene does not have a fixed orientation with the substrate but rather has a distribution of orientations. The presence of grain boundaries between different orientations adversely affects the graphene mobility and other electronic properties [128].

By varying the growth conditions it is possible to optimize the size of single crystal monolayer domains on the Cu substrate. The samples studied in this study were prepared by the standard technique [52] of heating Cu in a CVD chamber below its melting point under a flow of methane and hydrogen [54]. By varying the flow rate of methane, graphene domains of differing shapes, sizes and thicknesses are obtained. These are then investigated in LEEM to determine the domain thicknesses and size of single crystal domains.

5.2 Preparation

The samples are prepared by Vlassouik *et al.* at Oak Ridge National Laboratory [54]. The three samples described here are called Sample # 1, 2, and 3. Single crystal Cu is difficult to obtain, so the substrate used in this case is a polycrystalline Cu foil 0.5 mm thick and 99.999% pure (Alfa Aesar # 10950). The grain size in such foils is around 200 μ m. For cleaning, the Cu is annealed at 1000°C for 30 minutes under 500 sccm (standard cubic centimeters per minute) of 2.5% H₂ in Ar. After this, the graphene growth is performed in which CH₄ in Ar is flowed over the sample while it is continued to be heated at 1000°C. For Sample#1, 10 sccm of 0.1% CH₄ in Ar is used while the sample is heated for 90 minutes. For Sample#2 the growth conditions are identical to those of Sample#1 but the graphene nucleation density is lower, probably due to a

different CVD tube being used. For Sample#3 20 sccm of 0.1% CH₄ in Ar is used while the sample is heated for 30 min.

The samples were studied in the Elmitec LEEM III described in Section 2.4. The samples were briefly outgassed at 250°C in the LEEM before acquiring data.

5.3 Results



Fig. 5.1 PEEM images for Sample#1, 2, and 3 respectively, made under different preparation conditions.



Fig. 5.2 LEEM images on the top and corresponding reflectivity curves at the bottom. (a), (b), and (c) are LEEM images of Sample#1, 2, and 3 respectively at 4.0 eV. (d), (e), and (f) are reflectivity curves from points marked in (a), (b), and (c) respectively. Brown, blue, red, and

green reflectivity curves correspond to bare Cu, 1 ML, 2 ML, and 3 ML of graphene respectively.

Large area images of these samples can be obtained by doing PEEM (Fig. 5.1). The graphene domains appear as bright hexagonal domains against a dark background of copper, consistent with other works [129, 130]. Sample# 1 and 3 (Fig. 5.1 (a) and (c) respectively) show domains that start to coalesce to form a continuous graphene film while Sample #2 (Fig. 5.1(b)) shows large isolated hexagonal domains. The linear boundaries apparent in Fig. 5.1(c) (and images from the other samples not shown here) could arise from grain boundaries of the Cu foils, or from inadvertent folding while loading the sample. In some of the graphene domains of Sample#2 and 3, the center shows a dark contrast compared to the periphery. LEEM reflectivity measurements discussed later reveal that this darker contrast arises from thicker graphene in the center.

We will now analyze the reflectivity curves obtained from these samples, to determine the graphene thickness. Figure 5.2 shows the LEEM images of Sample #1, 2 and 3 in the top panel, with the corresponding reflectivity curves in the bottom panel. For all of this data, several months passed between the sample production and the LEEM studies, with the samples exposed to air during that time. For Sample #1 [Figs. 5.2 (a) and (d)], regions A and B are from bare Cu, while C, D, and E are from graphene. Most of the surface is like regions marked C and D. Selected area diffraction from such regions showed a graphene diffraction pattern and the corresponding reflectivity curve was featureless from 2-10 eV. We associate this featureless reflectivity curve with monolayer graphene. The reflectivity curve from E shows a minimum at 3.5 eV which we associate with bilayer graphene. Analyzing the reflectivity curves of Samples #2 and 3 reveals a higher fraction of multilayer graphene compared to Sample #1. The reflectivity curves with two minima correspond to 3 ML of graphene. For the area shown in Fig. 5.2(b) the hexagonal domains have centers that are 2 ML thick compared to the periphery which is 1 ML. Sample #3 shows some regions with has small regions of 2 ML and 3 ML. For all the samples, the reflectivity curve of Cu is featureless between 3-10 eV.

In the above analysis we associated m-1 minima in the reflectivity curves between 2-10 eV, with *m* layers layers of graphene. The LEEM results for graphene on Cu from

Ref. [130] also show m-1 minima for m layers of graphene, with similar results also reported for graphene on Pt(111) [131]. Reflectivity curves from systems like graphene on SiC however, show m minima for m layers of graphene [67]. Reflectivity curves and the number of minima thus depend on what type of substrate the graphene is grown on, as further discussed in Section 5.4.

Figure 5.3 shows additional LEEM results obtained from Sample#1 which, in contrast to Fig. 5.2, had been exposed to air for only a few days (i.e. this data was acquired *prior* to that of Fig. 5.2). The image of the surface in Fig. 5.3 (a) looks similar to that from 5.2 (a), but the reflectivity curves from monolayer regions in Fig. 5.3 (b) look somewhat different from those in Fig. 5.2 (d). Whereas the monolayer reflectivity curves from Fig. 5.2 (d) are featureless over 2-10 eV, those from Fig. 5. 3 (b) show a shallow minimum near 5.5 eV. The monolayer reflectivity curves from Ref. [130], for graphene on Cu also show a shallow minimum near 5.0 eV. We believe that this feature near 5.0 V in monolayer graphene is only seen in samples that have not undergone prolonged air exposure. When the sample is exposed to air for a prolonged time, oxygen starts intercalating the graphene-Cu interface and weakens the interaction between the graphene and the Cu. The change in the graphene-Cu interface can modify the reflectivity curves, causing the the minima to disappear. Thus the difference in monolayer reflectivity curves between Fig. 5.2 (d) and 5.3 (b) is because in the former the graphene-Cu interface is intercalated by oxygen.



Fig. 5.3 LEEM results for Sample#1, taken after a few days of air exposure. This is to be compared with Fig. 5.2 (a) and (d) which were acquired from Sample#1 after a few months of air exposure. (a) LEEM image at 4.0 eV. (b) Reflectivity curves from points marked in (a).



Fig. 5.4 Typical LEED pattern at 44 V with no illumination aperture. The arrows mark a 60° sector and point to graphene (1,0) spots. K is the length of the reciprocal lattice vector of graphene.



Fig. 5.5 LEEM image from Sample #1 and micro LEED patterns from areas marked A-E. The circles are proportional to the size of the area from which the LEED pattern is acquired. The LEEM image is at 4.0 V, and the LEED patterns are at 44 V. Dashed arrows indicate additional

spots that are simply graphene spots that got shifted due to the tilt of the sample. The length of the solid and dashed arrows is K, which is the wave vector of graphene.

We will now analyze the LEED patterns to understand how the different grains are oriented. As discussed in Section 2.4.1 to obtain the LEED pattern from only a selected area on the surface (also known as selected area diffraction or micro-diffraction) we use an illumination aperture. The illumination aperture blocks out part of the incident electron beam, thereby illuminating only a particular area on the sample. The three illumination apertures in our LEEM system can select an area 2 μ m, 5 μ m, or 10 μ m in diameter. Without an illumination aperture, the area on the sample that is illuminated is ~50 μ m. Figure 5.4 above shows a typical LEED pattern acquired without any illumination aperture. This pattern shows multiple occurrences of the graphene six-fold LEED spot arrangements, with different rotational orientations of each six-fold arrangement. Also, the pattern varies with position, further revealing rotational disorder of the different graphene grains across the sample. The grain size of graphene is seen to increase in samples with larger hexagonal domains.

Figure 5.5 shows selected area diffraction (SAD) patterns acquired by employing a 5 μ m illumination aperture at different positions on Sample #1. The graphene grains have different orientations with respect to each other. Regions A and C are single crystal as they just show one set of diffraction spots arranged on a hexagon. Regions B, D, and E show multiple diffraction spots and are hence not single crystal. The grain size is ~ 5 μ m, which is less than the size of the original hexagonal domains due to the overlap with neighboring domains. The LEED patterns also show additional spots, pairs of which are marked by dashed arrows. For example in Fig. 5.5 the diffraction pattern from A shows four additional spots that lie within radius vector K. Dashed arrows are drawn to three of these spots, using the fourth spot (encircled in blue) as the origin. The spots marked by dashed arrows are shifted from the closest (1,0) graphene diffraction spot by the same amount the encircled spot is shifted from the (0,0) spot. We conclude that the encircled spot is a shifted (0,0) spot, and the additional spots marked dashed arrows are simply graphene (1,0) spots that got shifted, most likely due to an uneven tilt of the copper sample (the sample consist of thin copper foils, which invariably become somewhat wrinkled during the sample handling and mounting process). The length of the dashed arrows are equal to length of graphene lattice vector, which is another way of understanding that additional spots are just graphene.

The SAD patterns for a hexagonal domain from sample #2 are shown in Fig. 5.6. The LEED pattern from the outer monolayer B and D is a 1×1 pattern identical to that from the inner bilayer region A. This implies the bilayer is single crystal and the stacking is of the type that has a 6 fold symmetry i.e AA, AB or AC (Fig. 2.6 shows the AA and AB stacking arrangements of graphite) , assuming we can also see the diffraction pattern coming from the lower layer. Further studies will be required to confirm which of the three possible stacking arrangements exists for the bilayer graphene in this case. Bernal stacking was found for multilayer hexagonal graphene domains in Ref [56] using TEM. As seen in the LEEM image a large fraction of D and E is bare Cu, which shows up in the corresponding diffraction pattern as linear streaks. Region E also encompasses the graphene grain to the right of the grain studied in A-D. The graphene grain in E has a different orientation from A-D, consistent with Sample#1 in which different grains have different orientations with respect to each other. Sample#2 has a grain size of ~15 µm, the largest in our study.



Fig. 5.6 LEEM image from Sample #1 and micro LEED patterns from areas marked A-E. The circles are proportional to the size of the area from which the LEED pattern is acquired. The LEEM image is at 1.5 V, and the LEED patterns are at 44 V. The LEED patterns from the smaller areas have a low signal to noise ratio.



Fig. 5.7 Selected area diffraction patterns from Sample#3. The LEEM images are at 4.0 eV, and the LEED patterns are at 44 eV. The radius vector of graphene is marked by the arrow labeled K. C and D show blurred additional spots due to folds running through the grains.

The SAD results from Sample#3 are shown in Fig. 5.7. The LEEM image in the top panel is the same area displayed in Fig. 5.2 (c). Regions A, B and the graphene strip they lie on appear to be formed from many domains that coalesced together. The graphene pattern from A and B show multiple orientations, as expected for coalesced domains. The grain size of this sample is less than 5 μ m. In the lower panel of Fig. 5.7 is another area on the sample where we could find domains that had not coalesced. Regions C and D both show a distinct 1×1 graphene pattern with additional blurred spots. The blurred spots are the 1×1 spots that got shifted due to the linear boundaries that run through these domains (these boundaries can be seen in the lower voltage

LEEM images not shown here). The part of region D that shows a dark contrast in LEEM is bilayer graphene. As argued for the bilayer in Fig. 5.6 this bilayer must be AA, AB or AC stacked as the diffraction pattern only shows a 1×1 LEED pattern.

5.4 Discussion and Summary

Graphene samples grown on Cu foil were studied in LEEM. Selected-area diffraction performed in the LEEM allowed us to determine the graphene orientation and whether it was single-crystal or not. The number of minima in the LEEM reflectivity curves allowed us to determine the graphene thickness. We found that for *m* layers of graphene on Cu the number of minima between 0-10 eV was m-1. In the literature and in our own group we find that the relation between the number of minima in the reflectivity curves at low energies and the number of graphene layers is highly substrate dependent. As discussed in Section 2.4 Hibino et al., provided a model that could explain the reflectivity curves of graphene on SiC but no model can yet fully explain the number of minima in the reflectivity curves (for a given graphene thickness) for different types of substrates. The nature of the interface between graphene and the substrate plays a significant role in determining the reflectivity curves so any model that attempts to explain the reflectivity curves will have to take that into consideration. Future work on this project is to develop a theoretical model that satisfactorily explains the substrate dependence of reflectivity curves from a graphene sample. The following table summarizes the reflectivity curves observed for different graphene-substrate systems. Entries 1-4 were observed in our work, the remainder are from different research groups.

	Substrate	Observed reflectivity curves in LEEM	Reference
		between 0-10 eV	
1	SiC(0001)	m minima for m layers of graphene on the	67,104
		$6\sqrt{3}$ buffer layer	
2	SiC $(000\overline{1})$ with	m minima for m layers of graphene	46,132
	no buffer layer		
3	SiC $(000\overline{1})$ with	Decoupled buffer layer does not show simple	114

	decoupled	oscillation between $0-6.5$ eV but shows an	
	buffer layer	unusual minimum near 6.5 eV . The <i>m</i> th	
		graphene layer on the decoupled buffer layer	
		shows <i>m</i> minima between $0-6.5$ eV, and an	
		additional minimum near 6.5 eV	
4	Cu	m-1 minima for <i>m</i> layers of graphene	130,133
5	SiC(0001) with	Depends on which element is used to	81, 84, 86,
	decoupled	intercalate the buffer layer but in general m	
	buffer layer	minima for <i>m</i> layers of graphene. The	
		minima however occur at different energies	
		than for graphene on SiC(0001) with regular	
		buffer layer	
6	Pt	m-1 minima for <i>m</i> layers of graphene	131
7	Ni	m-1 minima for <i>m</i> layers of graphene	134
8	Suspended and	<i>m</i> minima for <i>m</i> layers of graphene, but no	135
	supported	minima seen for 1 layer of graphene!	
	graphene on		
	SiO ₂		

Chapter 6

Summary

Summary

In this thesis we studied epitaxial graphene produced by thermal decomposition of SiC. Earlier studies on graphitization of SiC focused on UHV annealing of SiC [71,103]. It was found by researchers that the use of a background gas such as disilane or argon during graphitization improved the quality of graphene formed [43,44,45] compared to vacuum formation. We found that the interface of graphene and SiC depends on which polar face of SiC is used for graphitization, and also on the preparation conditions. The three environments in which we compared graphene formation were UHV, an atmosphere or argon and 10^{-4} Torr of disilane. The two polar faces we studied were the Si-face and the C-face.

6.1 Graphene formation on the Si-face for different preparation conditions

On the Si-face we find that for all three environments the interface structure is a $6\sqrt{3}$ 'buffer layer' that is covalently bonded to the substrate and acts a template for graphene growth. This result is summarized in Fig. 6.1 below.



Fig. 6.1 Whether the Si-face is graphitized in UHV, in an atmosphere or argon or in a background of disilane, in all three cases the interface structure is the $6\sqrt{3}$ graphenen'buffer layer'. This buffer layer has a structure similar to graphene but is bonded to the underlying substrate, It is also referred to as the zeroth graphene layer or 'G₀'.

Graphitizing the Si-face in a disilane environment results in an improved morphology and fewer pits than vacuum formed samples as expected. The improvement in the morphology for disilane prepared samples is not as significant as that seen for samples prepared in argon. In our prior work argon samples showed single layer graphene domains that extended across the sample with occasional bilayers that occupied only a small fraction of the entire surface [75,104].



6.2 Graphene formation on the C-face for different preparation conditions

Fig. 6.2 For vacuum prepared samples the graphene layers lie on a 3×3 (or in some cases a 2×2) interface structure that does not acts as a template for graphene formation. For argon prepared sample the surface gets covered by a silicate layer that inhibits graphene growth. For disilane prepared samples the interface layer is a graphene like $\sqrt{43}$ layer bonded to the substrate (the exact bonding with the substrate is not yet known).

On the C-face we find that the interface structure between graphene and the substrate depends on the environment used for graphitization. For UHV prepared samples we find a 3×3 interface structure whose atomic arrangement is not yet known (some groups also report a 2×2 interface [41,90)]. Samples that are graphitized in argon get unintentionally oxidized during the argon flow, and the oxidized surface (which is a

silicate) is resistant to graphitization. Disilane prepared C-face samples show a $\sqrt{43}$ layer at the interface, we believe this layer acts as a buffer layer similar to that seen on the Si-face. The interface structure on the C-face for different environments is summarized in Fig. 6.2.

For vacuum prepared samples the thickness of the graphene formed is hard to control compared to the Si-face, presumably due to the lack of a buffer layer. For argon prepared samples the substrate gets covered by a silicate layer which inhibits graphene formation. Regions that are not covered by a silicate layer develop thick islands of graphene. In a disilane environment the oxidation that occurs in argon is avoided by superior cleanliness conditions. We are able to able to form thin uniform films of graphene and we believe the $\sqrt{43}$ buffer-like layer acts as a template for graphene growth.

An understanding of the relation between growth conditions and the interface structure between graphene and SiC is crucial to reproducibly forming high quality graphene, and understanding the electronic properties of the graphene thus formed.

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