Electron Transport and Charge Control in Epitaxial Graphene

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know Thyself through Thy Way ...
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Abstract

Graphene monolayers and bilayers have attracted research interest in both the physics and electronic materials communities owing to their unique band structures. In a pristine monolayer, carriers travel at the Fermi velocity $v_f \approx 10^8 \text{cm/s}$ and exhibit linear dispersion. However, the lack of an energy gap in monolayer material makes applications in active devices challenging. In bilayers, carriers behave classically with an effective mass of $m^* \approx 0.035m_e$ and exhibit parabolic dispersion along with adequate transport properties. Graphene bilayers are attractive as a narrow energy gap may be opened in the presence of a symmetry breaking potential. Native and intercalated graphene produced by epitaxy on semi-insulating 4H(6H)-SiC substrates are particularly relevant as highly crystalline material may be prepared on large area substrates.

In this work, the low field and high field transport properties of native and intercalated epitaxial layers are investigated in electron devices. The results are then considered within the contextual framework provided by fundamental principles. The influence of charged impurity, neutral impurity, and acoustic phonon scattering on conductivity and carrier mobility is considered alongside low field transport data. High field measurements are performed in order to estimate a saturated electron velocity of $2 \cdot 10^7 \text{cm/s}$ in epitaxial graphene on SiC. Mobility and saturation velocity influence transconductance and frequency performance in active devices. In both native and intercalated devices, velocity saturation occurs as a consequence of scattering with surface optical modes in the SiC substrate. In this respect, SiC is an ideal substrate for graphene as it demonstrates a high energy surface optical mode (115meV) relative to SiO$_2$ (55meV).

Charge control is also investigated via low temperature capacitance voltage measurements in large area metal oxide graphene (GMOS) capacitors with a low temperature Al$_2$O$_3$ dielectric. Results are then correlated with current voltage characteristics in active devices fabricated in graphene monolayers and bilayers in which bias dependent instabilities and hysteresis are frequently observed. The CV results highlight the influence of surface potential fluctuations (90meV) and interface states ($2 \cdot 10^{12} \text{eV}^{-1}\text{cm}^{-2}$) on the transfer characteristics of active devices. The density of interface states is found to be relatively high in graphene MOS relative to the $5 \cdot 10^{10} \text{eV}^{-1}\text{cm}^{-2}$ achieved in thermally oxidized silicon MOS.

Collecting results, it is possible to gain insight into the physical properties of the material while simultaneously outlining perspectives and challenges for technological applications. The electron transport results motivate further investigations into substrate engineering in graphene MOS in order to improve the saturation velocity and transport characteristics. Meanwhile, the charge control experiments demonstrate a need for improved dielectric films in graphene MOS structures. Together, the electron transport and charge control results provide a thorough description of the electronic properties of MOS devices in epitaxial graphene.
## Symbols and Physical Constants

In order to maintain contextual clarity, symbols always defined when introduced in the text. The following list indicates the general context in which symbols are used. Some symbols occasionally appear in multiple contexts. When this occurs, symbol definitions in the list are indicated with parentheses.

<table>
<thead>
<tr>
<th>Symbol</th>
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<td>Density of interface states</td>
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Chapter 1

Introduction

Graphene, a monatomic sheet of sp$^2$ bonded carbon atoms, has attracted the interest of both the physics and electronics communities. With the development of epitaxial methods, wafer scale technologies based upon graphene field effect transistors and passive devices are now feasible. Graphene grown by sublimation or chemical vapor deposition on semi-insulating (SI) 4H-SiC and 6H-SiC, presents the most promising avenue for technology development as it allows for the integration of graphene with established fabrication routines. Epitaxial graphene on SiC holds further advantage insofar as it may be intercalated with hydrogen to form quasi-free standing layers which exhibit enhanced uniformity and electron transport properties.

In this work, epitaxial graphene is assessed for its potential application in high frequency devices through experiments in electron transport and charge control. Of particular interest are field effect transistors in graphene (GFETs), whereby the current in a graphene sheet is controlled via capacitive gating through a dielectric layer. The aim of the transport experiments is to understand current flow in epitaxial graphene under conditions of low and high electric field. Likewise, the charge control experiments are directed at understanding how a current flow in a graphene sheet may be modulated via gating. In this way, the transport and charge control experiments represent a subdivision of the transistor structure into its two component axes as shown in Fig. 1.1.

The work is motivated by two fundamental problems observed in high frequency graphene devices. Firstly, FETs in epitaxial graphene demonstrate modest frequency performance when compared to devices in other semiconductor materials. At the outset, this is rather surprising given the remarkable transport properties of the material. In principle, it should be possible to make competitive devices in graphene, such that the investigation of transport properties is warranted. In addition to the performance issue, FETs in epitaxial graphene also exhibit a strong hysteresis effect in their DC transfer characteristics. The hysteresis introduces a bias dependent instability into device operation making the development of microwave integrated circuits difficult in the current technology. In addition to providing a context for optimal device operation, the charge control experiments allow for a physical description of the hysteresis effect.
CHAPTER 1. INTRODUCTION

Figure 1.1: A schematic of a graphene field effect device with materials labeled. Current density in the conducting graphene channel between the Ohmic contacts is controlled via applying a bias to the gate electrode. The $x$ and $z$ axes may be considered the electron transport and charge control axes respectively.

A primary objective of the work is to present transport, charge control and device data in conjunction with theoretical considerations. This approach is thought to be valuable as theory provides a solid foundation on which the properties of graphene devices may be appreciated. In chapter 2, the band structure ($\epsilon_k$), density of states $\rho(\epsilon)$, and carrier density $n(\epsilon)$ in graphene monolayers and bilayers are investigated theoretically as they are essential for building usable models of device operation. The first principles results are useful insofar as they highlight some fundamental differences between graphene and other semiconductor materials. Further, they serve as a bootstrap through which electron transport and charge control may be understood. First, a treatment of tight-binding approach to band structure in monolayers and bilayers is presented, and the properties of the low energy dispersion relations are investigated. From the band structure, one finds that carriers in monolayer graphene exhibit a light-like dispersion with a high carrier velocity of $v_f \approx 10^8$ cm/s. In contrast to monolayers, carriers in bilayer graphene exhibit parabolic dispersion with an effective mass of $0.035m_e$ where $m_e$ is the electron mass. For this reason, bilayers, are expected to behave more along the lines of a traditional semiconductor. Under ordinary considerations, both materials exhibit a gapless dispersion, which presents a major challenge in the context of device performance. However, an interesting case occurs in bilayers in which a narrow energy gap ($\epsilon_g$) opens in the presence of a symmetry breaking potential. Such a gap is traditionally induced via the application of a vertical electric field. In the case of hydrogen intercalated bilayers, device results suggest that a narrow gap may be present due to surface charge effects making the material particularly attractive.

In Chapter 3. The low and high field electron transport properties are investigated. From temperature dependent low field measurements, it is possible to determine the low field mobility ($\mu$), and conductivity ($\sigma$) of the graphene layers. In a device context, carrier mobility translates into current density and transconductance such that an understanding of carrier scattering is essential.
The carrier mobility in pristine suspended graphene sheets is exceptionally high, and values exceeding $100000 \text{cm}^2/\text{V} \cdot \text{s}$ have been reported.\textsuperscript{1–3} However, mobility values in native and intercalated epitaxial graphene are typically of order $2000-5000 \text{cm}^2/\text{V} \cdot \text{s}$. In order to understand this discrepancy, considerations from Boltzmann transport theory are introduced in parallel with the measurement results in monolayer graphene. Scattering via charged impurities, neutral impurities, and acoustic phonons is assessed and the resulting impact on carrier mobility is detailed. The second critical parameter to assess is the saturated electron velocity ($v_{\text{sat}}$). In a device context, $v_{\text{sat}}$ may be used to determine the transit frequency ($f_t$) which effectively sets an upper limit on the frequency performance of the device. In epitaxial graphene, $v_{\text{sat}} \leq v_f$ due to carrier scattering with surface optical phonon modes in the SiC substrate. Despite their departure from ideal values, both $\mu$ and $v_{\text{sat}}$ are sufficiently high as to enable the development of competitive high frequency devices in graphene.

In Chapter 4, the analysis of charge control in metal-oxide-graphene (GMOS) structures is presented. Analysis begins with a presentation of fundamental charge control relations in graphene MOS including the dependence of carrier density and Fermi energy ($\epsilon_f$) on an applied gate voltage $\epsilon_g(v_g)$. Results are then considered in the context of measured capacitance-voltage (CV) data, and a functional model of charge control in graphene MOS capacitors is presented. By accurately modeling CV curves, it is possible to assess several properties of the MOS structure such as the density of interface states ($D_{\text{it}}$), the magnitude of surface potential fluctuations ($\delta \epsilon_f$), and the presence of a substrate induced energy gap in bilayer material $\epsilon_g \approx 250 \text{meV}$. The MOS capacitor measurements also describe a temperature dependent hysteresis which is attributed to charge injection and trapping the oxide. This result may be carried over to the transistor context in which a strong gate hysteresis is observed at room temperature. Together, the CV and transport data allows for a thorough analysis of field effect transistors in epitaxial graphene.

In Chapter 5, the characteristics of field effect transistors (FETs) in intercalated monolayers and bilayers are investigated via DC measurements and scaling studies. The transit frequency ($f_t$) and maximum frequency of oscillation ($f_{\text{max}}$) are presented, and results are connected with the limitation on $v_{\text{sat}}$ explored in Chapter 3. A significant difference is observed between monolayer and bilayer FETs with regard to current modulation which supports the notion of the substrate induced gap inferred when modeling CV data. Following the presentation of core transistor data, a description of gate hysteresis in graphene FETs is provided. In addition to traditional MOS structures, charge control in graphene self-switching diodes is presented. Self switching diodes are field effect devices whereby a graphene nanowire is laterally gated to produce a nonlinear IV characteristic. The quality of the nonlinearity is significant insofar as it facilitates high frequency power detection at zero bias. The devices also offer further advantage as they are not passivated, and therefore do not suffer from the frequency dispersion observed in GFETs.

In Chapter 6, a short assessment of material growth and characterization is presented in conjunction with processing techniques. Material uniformity is a critical parameter which must be evaluated prior to the fabrication of devices or integrated circuits. The large area uniformity epitaxial graphene layers is assessed via multiple methods. A surface characterization generally begins with a combination of optical microscopy, scanning electron microscopy, and atomic force microscopy. Further details regarding the number of graphene layers, the mechanism of growth, doping, defect density, and uniaxial strain may be obtained via Raman
spectroscopy and reflectance mapping.

Additionally, developing viable fabrication techniques is central to the development of a graphene-based technology. Several methods of processing epitaxial graphene layers are evaluated including standard photolithography (PL), deep ultraviolet lithography (DUV), and electron beam lithography (EBL). Other important design considerations must also be taken into account such as the dielectric selected for gating, and the method of dielectric deposition, and etching. Thermal management is also important in processing graphene, such that high temperature processing steps are generally avoided. Details outlining several processing techniques and various device engineering considerations are also provided.
Chapter 2

Fundamental Principles

In contrast to conventional semiconductor materials which exhibit parabolic bands, graphene exhibits a linear band structure. For this reason, electrons and holes in graphene behave as massless particles and are characterized by a high velocity \(10^8 \text{ cm/s}\). An investigation of band structure from a theoretical perspective provides insight into the motivation behind contemporary research in the area. As a consequence of the band structure, electrons in graphene are found behave differently than electrons in conventional semiconductors. Specifically, they are found to carry a pseudospin quantum number, which has important implications with regard to electron transport. Further, the theoretical considerations allow for the calculation of carrier densities which is essential for quantitative models of charge control.

In addition to monolayers, graphene bilayers are also of interest as an electronic material as they may be rendered either semi-conducting or semi-metallic depending on the presence of a symmetry breaking potential. This is in contrast to monolayer material, which is always semi-metallic in nature. Using the results from monolayer theory, it is straightforward to generalize to the case of a bilayer. This collection of results serves as a solid foundation on with to analyze electron transport and charge control in graphene devices.

2.1 Epitaxial Graphene

Prior to undertaking a the theoretical treatment, it is worthwhile to introduce epitaxial graphene on SiC in the historical and scientific context of the field. In the early 20th century, Landau and Perils argued that free standing two dimensional crystals were thermodynamically unstable. It was believed that thermal fluctuations would generate atomic displacements which were on the order of the inter-atomic spacing. Nevertheless, graphene was studied as a subsystem of graphite, and theoretical models sought to determine the physical properties of single and few layer graphitic sheets such as conductivity, heat capacity, and band structure.\(^6,7\) It was not until 2004 that experimental evidence argued for the stability of two dimensional materials. With the observation of conductivity modulation and the famous half-integer quantum hall effect in exfoliated graphene flakes, two dimensional materials gained wide acceptance within the scientific community.\(^8-10\)

It is little known fact that the history of graphene predates the work of Novoselov et.
Graphene growth occurs on the (0001) and (000\overline{1}) polar faces of the SiC crystal which are terminated by Si and C atoms respectively.\textsuperscript{15} Epitaxy on the silicon face generally results in few layer graphene, whereas epitaxy on the carbon face results in a more three dimensional growth mode characterized by a greater number of layers. For this reason, epitaxy on the silicon face is of greatest interest for electron devices. When performing graphene epitaxy, a carbon buffer layer (CBL) forms at the graphene/SiC interface which consists of sp\textsuperscript{2} bonded graphitic carbon. The CBL terminates dangling bonds on the SiC interface and can be converted into an additional quasi-free standing graphene layer via intercalation with hydrogen (Fig. 2.2).\textsuperscript{*} The primary motivation behind intercalation is to improve the uniformity and transport properties of the resulting epitaxial layers.

\textsuperscript{*}Intercalation describes the reversible insertion or inclusion of a molecule or ion into a layered structure such as potassium into graphite.
2.1. EPITAXIAL GRAPHENE

Native epitaxy produces graphene demonstrating electron conduction. This n-type doping is due to a transfer of charge from the graphene layer from donor like states at the graphene-SiC interface ($D_{\text{it}}^{\text{sub}}$).\(^{16}\) The carrier density of native material is highly variable from sample to sample and reflects variations in $D_{\text{it}}^{\text{sub}}$. Typical carrier densities in native layers can range from $0.3(1.0) \cdot 10^{13} \text{cm}^{-2}$ and carrier mobilities as high as $2000 \text{cm}^{2}/\text{V} \cdot \text{s}$ have been observed in native layers in context of this work. Upon intercalation, epitaxial graphene converts to hole conduction (p-type) with carrier densities of order $0.7(1.7) \cdot 10^{13} \text{cm}^{-2}$.\(^{17}\) Intercalated layers typically demonstrate a higher mobilities and values of order $6000 \text{cm}^{2}/\text{V} \cdot \text{s}$ have been observed on large area samples.

The conversion from electron density to hole density upon intercalation may be understood by considering the surface chemistry and crystalinity of the SiC substrate. Prior to intercalation, the SiC surface contains many Si-C dangling bonds which give rise to the donor states responsible for electron conduction in native layers. Upon intercalation, these dangling bonds become saturated to form Si-H bonds which are electronically inactive. What remains is the interaction between the epitaxial layer and the silicon terminated SiC surface.

The hexagonal polytypes of SiC used for graphene epitaxy are polar crystals. In general, the 2N(hexagonal)-SiC polytypes can be thought of as 3(cubic)-SiC with a stacking fault introduced at every $N^{th}$ repetition of the 3C-SiC unit cell as shown in Fig. 2.3.\(^*\) The stacking faults introduce a spontaneous polarization ($\Delta P$) the boundary between unit cells. The polarization is strongly localized on stacking fault boundaries and manifests as a positive(negative) charge density on the C(Si) faces respectively.\(^{19}\) The strength of the polarization effect varies linearly with the degree of hexagonality exhibited by the crystal. For this reason 2H-SiC(100% hexagonal) exhibits the strongest spontaneous polarization. Increasing the distance between stacking faults gives a weaker polarization effect until no polarization is seen for the case of 3C-SiC(0% hexagonal).\(^{16,19,20}\) Within the bulk of the crystal the $\Delta P$ of adjoining unit cells cancels out while at the surfaces a residual surface potential is observed. The conversion to p-type upon intercalation reflects the negative surface potential due to

\*In this way, 3C-SiC can be thought of as $\infty$H-SiC. Note that 3C-SiC exhibits diamond cubic structure with silicon and carbon atoms taking alternate positions in the lattice (i.e zincblende).
Figure 2.3: A schematic demonstrating the structure of some important polytypes of SiC. The hexagonal 4H(6H) arrangements are generated by introducing a stacking faults(mirror reversals) into the 3C-SiC structure as indicated by the vertical arrows. The introduction of stacking faults generates a spontaneous polarization ($\Delta P$) which increases linearly with the density of stacking faults(% hexagonality). $\Delta P$ is responsible for the hole conduction observed in intercalated layers prepared on the silicon terminated face of SiC.

The spontaneous polarization of the substrate. Epitaxial graphene is typically prepared on the silicon face of either 4H-SiC(50% hexagonal) or 6H-SiC(33% hexagonal). In this case, the ratio of hole carrier densities on the 4H:6H polytypes is usually of order 3:2.\textsuperscript{16}

The polarization effect is the first indication that the properties of the substrate have a significant effect on the epitaxial graphene layers. Incidentally, the sign and carrier density can be engineered by choosing a substrate of appropriate hexagonality and growing the epitaxial layers on the appropriate face. If intercalated, epitaxial layers on the silicon(carbon) terminated surfaces will exhibit hole(electron) conduction in proportion to $\Delta P$. It is worthwhile to note that the spontaneous polarization effect is not unique to intercalated graphene. An analogous situation exists in the case of AlGaN/GaN heterostructures in which spontaneous polarization is partially responsible for the formation of a two-dimensional electron gas at the heterojunction interface. This is not surprising in light of the graphene result, as GaN exhibits a wurtzite crystal structure (100% hexagonal) in direct analogy to 2H-SiC.\textsuperscript{21}

In literature, the term “doping” commonly appears to describe the electron or hole conductivity in epitaxial graphene. This is somewhat misleading, as it implies the substitution of donor/acceptor atoms for carbon atoms in the graphene lattice. In both native and intercalated material, no such substitution is occurring. The conductivity the native(intercalated) cases is due to $D_{it}^{sub}$ (pseudo-donors) and $\Delta P$(pseudo-acceptors) respectively.

### 2.2 Electronic Band Structure in Graphene

The real space lattice of carbon atoms in graphene is shown in Fig. 2.4. The lattice exhibits hexagonal symmetry such that each unit cell of contains two carbon atoms. In this way, the lattice consists of two interleaved sub-lattices denoted $a$ and $b$ respectively. The electronic band structure ($\epsilon_k$) describes the energy momentum relationship of electrons living the lattice, and derivations of the electronic band structure naturally inherit this lattice symmetry.
2.2. ELECTRONIC BAND STRUCTURE IN GRAPHENE

Figure 2.4: A diagram showing the sp$_2$ bonded structure of graphene in real space. The $a$ and $b$ sublattices are shown in grey and black respectively. The interatomic spacing ($a_0 = 1.42\ \text{Å}$) is shown in blue and the primitive cell is shown in red.

A common approach for determining band the structure is to apply the tight binding model in which the wavefunctions closely resemble those of ordinary atomic orbitals. In graphene, conduction states may be represented as a linear combination of p$_2$ atomic orbitals, and motion through the lattice is interpreted as quantum tunneling from atom to atom.\footnote{The valence structure of carbon is 2s$_1$2s$_2$2p$_2$. During bonding, the 2s$_2$2p$_2$ arrangement is hybridized to become 3sp$_2$2p$_2$. The 3sp$_2$ electrons undergo bonding to form the hexagonal lattice of Fig. 2.4, while the remaining p$_2$ state is a loosely bound conduction state.}

The Hamiltonian ($H$) in the tight binding approach is constructed by considering the interaction of a single electron at a lattice site with all other atoms in the lattice.

$$H = \sum_i \epsilon_i c_i^\dagger c_i - \sum_{\langle ij \rangle} \gamma_{ij} c_i^\dagger c_j$$ \hspace{1cm} (2.1)

In this formulation $c_i^\dagger$ and $c_i$ create and annihilate an electron at a lattice site $R_i$. The first term represents the self-energy of the electron at $R_i$, and the second term represents the hopping of an electron from $R_i$ to $R_j$. The sums are then taken over all atoms in the lattice. In graphene, a nearest neighbor model may be applied whereby an electron on the $a$($b$) sublattice couples only to its nearest neighbors on the $b$($a$) sublattice. Working the basis of sublattices, the tight binding Hamiltonian in graphene becomes.\footnote{The valence structure of carbon is 2s$_1$2s$_2$2p$_2$. During bonding, the 2s$_2$2p$_2$ arrangement is hybridized to become 3sp$_2$2p$_2$. The 3sp$_2$ electrons undergo bonding to form the hexagonal lattice of Fig. 2.4, while the remaining p$_2$ state is a loosely bound conduction state.}

$$H = \sum_i \epsilon_{p_2} a_i^\dagger a_i + \sum_i \epsilon_{p_2} b_i^\dagger b_i - \gamma \sum_{\langle ij \rangle} b_j^\dagger a_i + a_j^\dagger b_i$$ \hspace{1cm} (2.2)

The quantity $\epsilon_{p_2}$ represents the self energy of the p$_2$ atomic orbital, and $\gamma$ represents the hopping amplitude between sublattices. In order to determine the band structure ($\epsilon_k$), one must solve the Schrödinger equation.

$$|H - \epsilon_k S| = 0$$ \hspace{1cm} (2.3)

The matrix $S$ accounts for the overlap of the wavefunction of an electron on an $a$($b$) lattice site with the wavefunctions of its nearest neighbors in the $b$($a$) sublattice. If one assumes
Figure 2.5: [left] The conduction band in graphene as calculated from the nearest neighbor tight binding Hamiltonian in the first BZ for $\gamma = 3.013$ eV and $s_0 = 0$. The irreducible path between high symmetry points is also labeled ($\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$). [right] The conduction (blue) and valence (red) bands shown plotted along the irreducible path joining high symmetry points for the case of $s_0 = 0$. The symmetry breaking effect of $s_0 = 0.065$ eV and $s_0 = 0.129$ eV on the valence and conduction band energies is also shown (black). In both simulations the self energy term is assumed to be zero $\epsilon_{p2} = 0$.

that there is no overlap of the atomic orbitals between adjacent lattice sites, $S$ becomes the identity matrix. Since $H$ and $S$ are initially expressed in position space, it is necessary to transform them into momentum space to determine $\epsilon_k$. Taking the Fourier transform of the real space Hamiltonian and allowing the sum to only extend over nearest neighbors ($\delta_i$), one arrives at the following for $H$.

$$H = -\gamma \sum_k f(k) b_k^\dagger a_k + f^*(k) a_k^\dagger b_k$$

(2.4)

In momentum space, the operator $a_k^\dagger$ is interpreted as creating an electron of momentum $k$ on the $a$ sublattice. The quantity $f(k)$ denotes a sum over the nearest neighbor vectors which appears as a consequence of the Fourier transform.

$$f(k) = \sum_n e^{i\delta_n \cdot k}$$

(2.5)

It is convenient to express $H$ and $S$ as 2x2 matrices. In $H$, diagonal terms represent contributions from self energy and hopping within a given sublattice. Anti-diagonal terms represent hopping between sublattices ($a \rightarrow b$ and $b \rightarrow a$).$^{23,24}$

$$H = \begin{bmatrix} \epsilon_{p2} & -\gamma f(k) \\ -\gamma f^*(k) & \epsilon_{p2} \end{bmatrix} \quad S = \begin{bmatrix} 1 & s_0 f(k) \\ s_0 f^*(k) & 1 \end{bmatrix}$$

(2.6)
In Eq. 2.6 the quantity $s_0$ represents the value of the overlap integral between the atomic wavefunctions. Substituting Eq. 2.6 into Eq. 2.3 and solving for $\epsilon_k$ yields the following for the electronic band structure:

$$\epsilon_k = \frac{\epsilon_{p^2} \mp \gamma|f(k)|}{1 \pm s_0|f(k)|}$$

(2.7)

Together, the three quantities $\epsilon_{p^2} \approx 0$, $\gamma = -3.013\text{eV}$, and $s_0 \leq 0.2\text{eV}$ parameterize the nearest neighbor tight binding model. In the case of $s_0 = 0$, the conduction and valence bands obtained are symmetric about $\epsilon_{p^2}$. Taking $s_0 = 0$ yields the following familiar result for the band structure.

$$\epsilon_k = \pm \gamma|f(k)| = \pm \gamma \sqrt{3 + 2 \cos(\sqrt{3}a_0 k_y) + 4 \cos\left(\frac{3a_0}{2} k_x\right) \cos\left(\frac{\sqrt{3}a_0}{2} k_y\right)}$$

(2.8)

Fig. 2.5 shows the energy band structure plotted in the first Brillouin zone. Electrons near the zone center have the highest energy, and low energy electrons exist primarily in the $K$ and $K'$ valleys. Conduction electrons tend to aggregate in these low energy valleys where the energy momentum dispersion becomes linear. Additionally, the energy band structure in graphene is always symmetric at low energy such that conduction states and valence states are equally spaced about $\epsilon_k = 0$. Note that the effect of a nonzero $s_0$ is to introduce an asymmetry into the band structure in graphene at high energy.

### 2.3 Low Energy Electrons in Graphene

As electrons are introduced into the lattice, they fill electronic states starting from $\epsilon_k = 0$ according to the Pauli exclusion principle. Upon examination, this corresponds to the points $K$ and $K'$ within the first Brillouin zone. In graphene, the low energy band structure is conical (linear) and makes pointwise contact at $K$ and $K'$. For this reason, $K$ and $K'$ are known as Dirac points as they lead to a relativistic Hamiltonian. Further, due to the lack of an energy gap, graphene is described as a *zero-bandgap semiconductor* or alternatively as a *semi-metal*. Expanding Eq. 2.6 about $K$ or $K'$, one arrives at the low energy Hamiltonian:

$$H_\xi = v_f|\delta p| \begin{bmatrix} 0 & e^{-i\xi \theta(\delta k)} \\ e^{i\xi \theta(\delta k)} & 0 \end{bmatrix} = v_f|\delta p|\sigma \cdot \delta \hat{p}$$

(2.9)

The notation $\delta k$ indicates that momenta are being measured relative to the $K$ point in the band structure, and the phase angle $\theta(\delta k)$ describes the angle of $\delta k$ relative to the x-axis. The valley isospin $\xi$ selects the $K(K')$ by taking values of $+1(-1)$ respectively such that $H_\xi$ describes two independent Hamiltonians for the degenerate $K(K')$ valleys. By the de-Broglie relation, the quantity $|\delta p| = \hbar|\delta k|$ defines the momentum of an electron near $K(K')$. The energy eigenvalues $\epsilon_{\delta k}$ in the Dirac cone are given by the following

$$\epsilon_{\delta k} = \pm v_f|\delta p| = \frac{\pm 3\gamma a_0}{2} |\delta k|$$

(2.10)
The quantity $v_f \approx 10^8 \text{cm/s}$ describes the velocity of electrons near the Dirac point. The low energy dispersion ($\epsilon_\delta k$) describes electrons behaving as massless particles. Additional insight may be gained by examining the relativistic energy momentum relation.

$$\epsilon^2 = (|p|c)^2 + (mc^2)^2$$  \hfill (2.11)

In the limit of a massless particle such as a photon, the above relation reduces to $\epsilon = |p|c$. By analogy, the low energy dispersion relation indicates that electrons in graphene behave analogously to photons in which $c$ is replaced by $v_f$. For $\xi = 1$, the eigenstates of the Hamiltonian are given by the following

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}} \left( \frac{1}{\pm e^{i\theta(\delta k)}} \right)$$  \hfill (2.12)

where $+(-)$ represent conduction(valence) states respectively. The Hamiltonian in monolayer graphene may also be written in terms of the Pauli matrices $\sigma = [\sigma_x, \sigma_y]$ as shown in Eq. 2.9. This form of the Hamiltonian is identical to that of the quantum mechanical helicity operator such that eigenstates of the Hamiltonian are simultaneously eigenstates of helicity.

$$h = \frac{1}{2} \sigma \cdot \delta \hat{p} \quad h |\psi_\pm\rangle = \pm \frac{1}{2} |\psi_\pm\rangle$$  \hfill (2.13)

The quantum mechanical helicity, which defines the projection of an electron’s spin onto its momentum, is a conserved quantity in graphene. This supposes a pseudospin quantum number, analogous to spin, describing the relative amplitude of $|\psi_\pm\rangle$ on the $a$ and $b$ sublattices. In graphene, the helicity appears as a consequence of the symmetry of the $a$ and $b$ sublattices. Eq. 2.13 indicates that conduction and valence states are of opposite helicity, such that pseudospin of a conduction(valence) state is parallel(anti-parallel) to its direction of motion.

The appearance of pseudospin indicates that electrons in graphene have a chiral property. Furthermore, Eq. 2.13 implies that the pseudospin operator $\sigma$ itself has two eigenstates corresponding to pseudospin up $|\uparrow\rangle$ and pseudospin down $|\downarrow\rangle$. The $|\uparrow\rangle$ state describes an electron density which is located entirely on the $a$ sublattice, and the $|\downarrow\rangle$ state describes an electron density located entirely on the $b$ sublattice. Writing Eq. 2.12 in terms of $|\uparrow\rangle$ and $|\downarrow\rangle$, one finds the following

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\rangle \pm e^{i\theta(\delta k)} |\downarrow\rangle \right)$$  \hfill (2.14)

Geometrically, the $|\uparrow\rangle$ and $|\downarrow\rangle$ states describe a pseudospin which is normal and anti-normal to the graphene sheet respectively. Since the total pseudospin is always parallel or anti-parallel to the direction of motion, $|\psi_\pm\rangle$ is necessarily a linear combination of the $|\uparrow\rangle$ and $|\downarrow\rangle$ states. The fact that $|\psi_\pm\rangle$ consists of a linear superposition of the $|\uparrow\rangle$ and $|\downarrow\rangle$ pseudospin states indicates that the electron density in graphene is shared equally between the $a$ and $b$ sublattices.26

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*Electrons and holes in graphene are not unique with respect to their helicity property. An analogous case
2.4 Bilayer Graphene

Figure 2.6: A schematic showing the bilayer graphene in which the $b$ sublattice of layer $B$ stacks upon the $a$ sublattice of layer $A$. This layer orientation tends to be the most energetically favorable and is known as $AB$ or Bernal stacking.

Using the monolayer Hamiltonian, it is possible to generalize to the case of other graphene-like systems such as nanoribbons, nanotubes, and few layer graphene.\(^{29,30}\) One system which has generated a significant amount of interest is a graphene bilayer. A graphene bilayer is formed by stacking two monolayer lattices (denoted $A$ and $B$) as shown in Fig. 2.6. The bilayer Hamiltonian is composed of a block diagonal matrix representing two non-interacting monolayers. Interactions between the monolayers are introduced by adding terms off of the block diagonal. A rudimentary model is constructed by adding an interlayer hopping amplitude $\gamma_\perp$ which describes coupling between the $a(b)$ sublattice of layer $A$ and the $b(a)$ sublattice of layer $B$. The valley index has been selected such that $\xi = 1$.

\[
\mathcal{H} = \begin{bmatrix}
-\Delta & v_f|\delta p|e^{i\theta(\delta p)} & 0 & 0 \\
v_f|\delta p|e^{-i\theta(\delta p)} & -\Delta & 0 & 0 \\
0 & 0 & \gamma_\perp & 0 \\
0 & \gamma_\perp & \Delta & v_f|\delta p|e^{i\theta(\delta p)} \\
\end{bmatrix}
\]

The introduction of the term $\pm \Delta$ along the diagonal is a divergence from the case of a monolayer as diagonal terms indicate the self-energy of the $a$ and $b$ sublattices within layers $A$ and $B$. In the case of a monolayer it is non-physical to consider the $a$ and $b$ sublattices to be at different potentials such that the diagonal terms of the monolayer Hamiltonian must always be equal. However, in the case of a bilayer, one may consider the two layers as possibly existing at different potential energies. Solving for the energy eigenvalues yields the following for the dispersion.\(^{31,32}\)

occurs regarding neutrinos(anti-neutrinos) which exhibit anti-parallel(parallel) helicity respectively. Neutrinos are the only chiral particles which are currently found in the Standard Model of quantum field theory. However, observations of flavor oscillation in neutrino beams suggest they may have a small mass. Thus their helicity property may be subject to revision.\(^{27,28}\)
CHAPTER 2. FUNDAMENTAL PRINCIPLES

Figure 2.7: Several low energy dispersion relations in graphene. [left] Monolayer graphene [center] Bilayer graphene with $\Delta = 0$ [right] Bilayer graphene with $\Delta = 0.2\text{eV}$. In bilayer graphene, a bandgap of $\Delta$ opens for non-zero $\Delta$ at finite momentum. In the bilayer simulations the interlayer coupling amplitude is $\gamma_{\perp} = 0.4\text{eV}$.

\[
\epsilon_{\delta p}^2 = \Delta^2 + (v_f |\delta p|)^2 + \frac{\gamma_{\perp}^2}{2} \pm \sqrt{[4\Delta^2 + \gamma_{\perp}^2](v_f |\delta p|)^2 + \gamma_{\perp}^4/4} \quad (2.16)
\]

Eq. 2.16 describes four energy bands symmetrically placed about $\epsilon = 0$. Two bands are designated for conduction states, and two for valence states. The low energy band structures for monolayers and bilayers are summarized in Fig. 2.7. When $\gamma_{\perp} = 0$ and $\Delta = 0$ the layers are effectively decoupled, and the linear dispersion relation of a monolayer is recovered. For bilayer graphene ($\gamma_{\perp} = 0.4\text{eV}$), the monolayer conduction(valence) bands bifurcate into high and low energy bands and inherit a parabolic low energy behavior. If there is no potential difference between layers $\Delta = 0$, the low and high energy bands are separated by $\gamma_{\perp}$.

In order to further investigate the properties of low energy electrons in a bilayer it is possible to partition the Hamiltonian in a manner which decouples the low energy and high energy states. This allows one to isolate the effective Hamiltonian for low energy electrons in graphene. In the case of $\Delta = 0$ the effective low energy Hamiltonian is as follows.\footnote{33}

\[
\mathcal{H}_{\text{eff}} = -\frac{|\delta p|^2}{2m^*} \begin{bmatrix} 0 & e^{2i\theta(\delta k)} \\ e^{-2i\theta(\delta k)} & 0 \end{bmatrix} = \frac{|\delta p|^2}{2m^*} \sigma \cdot \delta \hat{p} \quad (2.17)
\]

Solving for the energy eigenvalues of Eq. 2.17, one finds the parabolic bands.

\[
\epsilon_{|\delta p|} = \frac{|\delta p|^2}{2m^*} = \frac{v_f^2 |\delta p|^2}{\gamma_{\perp}} \quad (2.18)
\]

The prefactor has been written in terms of the effective mass $m^* = \gamma_{\perp}/2v_f^2 \approx 0.035m_e$ and is analogous to the classical kinetic energy $T = p^2/2m^*$. Electrons in a bilayer near
2.5. CHIRALITY, PSEUDOSPIN, AND TRANSPORT

The points $K$ and $K'$ thus behave have as classical free electrons with an effective mass given by $m^*$. This is a fundamental difference with respect to the monolayer case in which massless Dirac fermions are expected (Eq. 2.9). As the wavenumber increases outside of the parabolic regime, the band structure becomes linear.

The case of a finite interlayer potential $\Delta > 0$ is relevant as an energy gap opens within the bilayer band structure. At $|\delta k| = 0$, the gap is maximally open and takes a value of $2\Delta$. Due to the Mexican hat structure of the opening, the true value of the gap $\bar{\Delta}$ occurs at finite a momentum away from the $K$ point.\(^{34-36}\)

\[ \bar{\Delta} = \frac{2\Delta \gamma_\perp}{\sqrt{\gamma_\perp^2 + 4\Delta^2}} \]
\[ |\delta p|_{\bar{\Delta}} = \frac{2\Delta}{v_f} \sqrt{\frac{2\gamma_\perp^2 + 4\Delta^2}{\gamma_\perp^2 + 4\Delta^2}} \] (2.19)

As was the case with a monolayer, a pseudospin degree of freedom also manifests in bilayers. In the case of a monolayer, one finds massless chiral fermions whereas in the case of a bilayer one finds massive chiral fermions. Though analogous, the chiral property in a bilayer is somewhat different than in monolayers. Rather than describing electron densities existing on the sublattices $a$ and $b$ respectively, the pseudospin eigenstates in a bilayer describe electron densities existing exclusively on layer $A$ or $B$. Energy eigenstates in a bilayer then describe electron wavefunctions which are a linear superposition of the $A$ and $B$ pseudospin states such that electron density is shared between the layers.

\[ |\psi_\pm \rangle = \frac{1}{\sqrt{2}} \left( \frac{1}{\pm e^{2i\theta(\delta k)}} \right) = \frac{1}{\sqrt{2}} \left( |\uparrow \rangle + e^{2i\theta(\delta k)} |\downarrow \rangle \right) \] (2.20)

It is important to note the general similarities between a monolayer and a bilayer. A monolayer is described in the basis of the $a$ and $b$ sublattices, whereas a bilayer is described in the basis of the $A$ and $B$ layers. Both systems give rise to chiral particles, and are described by a $\sigma \cdot \delta \hat{p}$ Hamiltonian. In general, the monolayer and bilayer are related by transforming $\theta \rightarrow 2\theta$ and $v_f |\delta p| \rightarrow |\delta p|^2/2m^*$.

2.5 Chirality, Pseudospin, and Transport

The chiral property of electrons in graphene gives rise to anisotropic scattering. When an electron undergoes scattering, its momentum incurs a change magnitude and direction. In graphene, electrons carry a pseudospin degree of freedom which is parallel or anti-parallel to its momentum (Eq. 2.14). As helicity commutes with the Hamiltonian, it is a conserved quantity such that scattering events must conserve pseudospin. This has the effect of limiting the possible scattering events which may occur in graphene. The scattering amplitude between states of differing momentum in a monolayer includes the chiral term.

\[ \Gamma_k^k (\theta) \sim |\langle \psi_k | \psi_k \rangle|^2 = \cos^2 (\theta/2) \] (2.21)

Eq. 2.21 shows that a scattering events which rotate $\delta p$ by $\pi$ have zero amplitude of 0. Pure back-scattering is suppressed in monolayer graphene as a consequence of chirality. The case is manifestly different in a bilayer, in which pseudospin rotates by $2\theta$ upon rotation of the
momentum by $\theta$ (Eq. 2.20). In a bilayer, $\Gamma_{k'}(\phi) \sim \cos^2(\theta)$ such that scattering by $\pm \pi/2$ is suppressed as a consequence of chirality. These considerations are of importance when describing carrier transport via the Boltzmann Transport Equation and Fermi’s Golden Rule (see Appendix A).

2.6 Electrons and Holes in Graphene

In order to calculate the electron and hole densities, one begins with the density of states (DOS). The DOS describes the number of available electronic states which exist for a given energy ($\epsilon$). The two-dimensional density of states is given by the following.

$$\rho(\epsilon) = \frac{g_s}{A_{BZ}} \sum_{k \in BZ} \delta(\epsilon - \epsilon_k)$$

The sum extends over an area of momentum space ($A_{BZ}$) which is equivalent to the first BZ. The quantity $\delta$ is the Kronecker delta (i.e. $\delta = 1$ if the state with momentum $k$ has an energy $\epsilon_k$ and $\delta = 0$ otherwise). The above formulation discretely counts the number of states with energy $\epsilon_k$ within the first BZ and divides the sum by $A_{BZ}$. The spin degeneracy ($g_s = 2$) indicates that each state can be populated by two electrons of opposite spin. Generally, it is only necessary to consider a reduced area ($A$) which includes low energy electrons such that the low energy dispersion relations may be used. Since the first BZ contains two low energy valleys ($K$ and $K'$) which are degenerate in energy, it is necessary to include a valley degeneracy ($g_v = 2$) in the sum.$^{37}$

$$\rho(\epsilon) = \frac{g_sg_v}{A} \sum_{\delta k} \delta(\epsilon - \epsilon_{\delta k})$$

The carrier density may be evaluated in a similar manner. Instead of simply counting states, one counts the probabilities that a given state is occupied.

$$n(\epsilon) = \frac{g_sg_v}{A} \sum_{\delta k} f(\epsilon_{\delta k} : \epsilon_f, \beta)$$

For fermions, the probability that a given state is occupied is given by the Fermi-Dirac distribution $f(\epsilon : \epsilon_f, \beta)$ with $\beta = (k_B T)^{-1}$. The sums can be evaluated by converting to integrals and integrating radially away from the Dirac point.

$$\rho(\epsilon) = \frac{g_sg_v}{A} \frac{A}{(2\pi)^2} \int \delta(\epsilon - \epsilon_{\delta k})d\Omega$$

$$n(\epsilon) = \frac{g_sg_v}{A} \frac{A}{(2\pi)^2} \int f(\epsilon_{\delta k} : \epsilon_f, \beta)d\Omega$$

Here $d\Omega = |\delta k| d|\delta k| d\theta$ is the total differential in momentum space. The integral over $\theta$ contributes a factor of $2\pi$ to the result. The differential over $|\delta k|$ is then evaluated via

$$f(\epsilon : \epsilon_f, \beta) = \left[1 + e^{\beta(\epsilon - \epsilon_f)}\right]^{-1}$$
2.6. ELECTRONS AND HOLES IN GRAPHENE

Figure 2.8: The electron (black) and hole (red) densities as calculated by Eq. 2.26 for a monolayer [left] and a bilayer [center] at $T \in [100, 200, 300 \text{K}]$. [right] The intrinsic carrier density calculated by Eq. 2.32 for a monolayer(black) and a bilayer(red).

Eqs. 2.10 and 2.16. Finally, the integration is carried out in energy space. Note that in Eq. 2.25 that $\delta(\epsilon - \epsilon_{\delta k})$ represents a Dirac delta function. Evaluating integrals leads to the following identity for the electron density.

$$n(\epsilon_f) = \int_0^\infty \rho(\epsilon) f(\epsilon : \epsilon_f, \beta) d\epsilon \quad (2.26)$$

The hole density is similarly calculated via the transformation $[\epsilon, \epsilon_f] \rightarrow [-\epsilon, -\epsilon_f]$ and integrating on the interval $\epsilon \in [0, -\infty)$. In the case of a monolayer evaluation of the density of states leads to the following.

$$\rho_m(\epsilon) = \frac{g_s g_v}{2\pi} \frac{|\epsilon|}{(\hbar v_f)^2} \quad (2.27)$$

The case of a bilayer is treated by approximating the dispersion as the sum of a parabolic and linear bands. In the event $\Delta = 0$, Eq. 2.16 for the low energy bands becomes.

$$\epsilon_{\pm} = \pm \frac{\gamma_{\perp}}{2} \left[ \sqrt{\left(2v_f |\delta p| / \gamma_{\perp}\right)^2 + 1 - 1} \right] \quad (2.28)$$

At low energy $v_f |\delta p| \ll \gamma_{\perp}$ such that the bands are parabolic $\epsilon_{\pm} \approx \pm v_f^2 |\delta p|^2 / \gamma_{\perp}$ while at high energy it $v_f |\delta p| \gg \gamma_{\perp}$ the bands are linear $\epsilon_{\pm} \approx \pm v_f |\delta p|$. In the parabolic region, the density of states is constant, while in the linear region the density of states increases linearly with energy. Thus, it is reasonable to approximate the total density of states in a bilayer to be the sum of the contributions from the low and high energy limits.

$$\rho_b(\epsilon) = \frac{g_s g_v}{2\pi} \frac{|\epsilon| + \gamma_{\perp}/2}{(h v_f)^2} \quad (2.29)$$

Low energy electrons in a bilayer behave analogously to a two dimensional electron gas (2DEG) with an effective mass of $m^*$, and high energy electrons behave quite similarly to
the case of a monolayer. Fig. 2.8 shows the carrier densities as calculated using the DOS
expressions for monolayers (Eq. 2.27) and a bilayers (Eq. 2.29) for several temperatures.
An analytic expression to Eq. 2.26 may be obtained by considering the zero temperature
approximation in which the Fermi-Dirac distribution becomes a step function.

\[ n(\epsilon_f) = \int_0^\infty \rho(\epsilon) [1 - \Theta(\epsilon_f)] d\epsilon \]  

(2.30)

Here \( \Theta(\epsilon_f) \) represents the Heavyside function centered on \( \epsilon_f \). Carrying out the integral
yields the following useful approximations for the carrier densities in a monolayer and a
bilayer respectively.

\[ n_m(\epsilon_f) = \frac{g_s g_v}{4\pi} \frac{\epsilon_f^2}{(h\nu_f)^2} \]
\[ n_b(\epsilon_f) = \frac{g_s g_v}{4\pi} \frac{\epsilon_f^2 + \gamma_{\perp}|\epsilon_f|}{(h\nu_f)^2} \]  

(2.31)

From Eq. 2.31, one has that \( n_m < n_b \) for a given \( \epsilon_f \) as a consequence of the parabolic dispersion in bilayers. Evaluating the temperature dependence of the intrinsic electron densities
(\( \epsilon_f = 0 \)) in monolayer and bilayer material yields the following.\(^{16,38*}\)

\[ n_m(0) = \frac{\pi}{6} \frac{(k_BT)^2}{(h\nu_f)^2} \]
\[ n_b(0) = n_m(0) + \frac{\log(2) \gamma_{\perp} k_BT}{\pi} \frac{1}{(h\nu_f)^2} \]  

(2.32)

At \( \epsilon_f = 0 \), the carrier density in both monolayer and bilayer graphene is ambipolar and
consists of \( n_{m,b}(0) \) electrons and \( n_{m,b}(0) \) holes.

\(^*\)Here the identity \( \int_0^\infty u[1+e^u]^{-1}du = \text{Li}_2(0) - \text{Li}_2(-1) = \pi^2/12 \) has been applied. For more information
on the intriguing dilogarithm function \( \text{Li}_2(z) \) see [39].
The unique band structures of monolayer and bilayer graphene motivate their use as electronic materials. In monolayers, electrons behave as massless chiral particles and move Fermi velocity \( v_f \approx 1 \cdot 10^8 \text{ cm/s} \), while in bilayers, electrons behave as massive chiral particles and move classically with an effective mass \( m^* = 0.035m_e \). While the band structure outlines the quantum mechanical picture electrons living in these lattices, it does not facilitate a description of how macroscopic sheets of graphene will behave. In order to describe what happens in the context of an electron device, it is necessary to forge a link between the quantum and classical worlds. This may be achieved via Boltzmann’s transport theory.

The macroscopic picture provides an intuitive basis from which to approach the problem. When an electric field \( E \) is applied across a sheet of material, electrons will acquire a drift velocity \( \langle v \rangle \) which represents the ensemble average of all the microscopic motion that occurs within the lattice. This ensemble motion of electrons moving in the lattice can be measured as a current density flowing through the material \( J \). Here, \( J \) is the product of number of charges in the sheet \( en(\epsilon_f) \) and the velocity at which they are moving.

\[
J = en(\epsilon_f)\langle v \rangle
\]  

At low electric field, the current density and drift velocity are related to the applied electric field via the conductivity \( \sigma(\epsilon_f) \) and mobility \( \mu(\epsilon_f) \).

\[
J = \sigma(\epsilon_f)E \\
\langle v \rangle = \mu(\epsilon_f)E
\]

Combining Eqs. 3.1 and 3.2 one obtains a relationship between the low field transport parameters of the material.

\[
\sigma(\epsilon_f) = en(\epsilon_f)\mu(\epsilon_f)
\]

The conductivity \( \sigma \), carrier density \( n \), and mobility \( \mu \), encode the microscopic dynamics of the material as single quantities and are thus the bridge between the quantum and classical weltanschauungs. As has been shown previously, \( n \) is readily obtained via the band structure via integration of the density of states (Eq. 2.26). Thus, in order to gain a describe transport, it is necessary to pursue a description of the conductivity \( \sigma \).*

*Mobility and conductivity may be thought of as conjugate variables such that only a description of one is needed (Eq. 3.3).
A description conductivity is necessarily quite different than the description of carrier density as it requires a treatment of non-equilibrium dynamics of the system. In other words, one must account for dynamic effects such as the scattering of carriers, and temperature gradients which will generate diffusion. By investigating the properties of the macroscopic transport parameters, it is possible to ascertain the dominant scattering mechanisms which affect current flows in a device at low and high electric field. Additionally, transport considerations allow one develop fundamental limitations on device performance which in turn allow for a comparative evaluation of epitaxial graphene against other technologies.

3.1 Semi-Classical Transport

As current flow in a conducting channel requires a potential difference or temperature gradient, the channel itself is not in thermodynamic equilibrium. One technique to explore non-equilibrium dynamics is to examine the properties of the system near equilibrium (the perturbative method). At equilibrium, carriers fill electronic states according to Fermi-Dirac statistics $f_0(\epsilon : \epsilon_f, \beta)$. When an electric field is applied, the Fermi energy (chemical potential) will vary with position in the conducting channel $\epsilon_f = \epsilon_f(x)$. This implies that the occupation statistics will vary with position in the channel $f_0 \rightarrow f_0 + \delta f$. The perturbation to $f$ due the applied field is obtained by solving the Boltzmann Transport Equation.*

\[
\delta f = \tau e \left( -\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v} \cdot \mathbf{E} \tag{3.4}
\]

Here, Eq 3.4 assumes that the perturbation term $\delta f$ decays exponentially to zero when the field is removed. The time constant ($\tau$) which describes this relaxation to equilibrium is known as the momentum relaxation time and is a result of various scattering processes occurring the material. The electron velocity is then obtained via differentiation of the band structure with respect to wavenumber $\mathbf{v} = \hbar^{-1} \nabla \delta k$, which leads to the following for monolayers and bilayers.

\[
\mathbf{v}_m = v_f \delta \mathbf{p} \quad \mathbf{v}_b = \frac{\left| \delta \mathbf{p} \right|}{m^*} \delta \mathbf{p} \tag{3.5}
\]

Substituting into Eq. 3.4 yields the following for $\delta f$ in the monolayer case.

\[
\delta f = \{ \tau e |E| v_f \} \left( -\frac{\partial f_0}{\partial \epsilon} \right) \delta \mathbf{p} \cdot \mathbf{E} \tag{3.6}
\]

The result for a bilayer is obtained by transforming $v_f \rightarrow |\delta \mathbf{p}|/m^*$. Eq. 3.6 has useful physical interpretation. The probability that a momentum state is occupied is given by $f = f_0 + \delta f$. The quantity $\delta \mathbf{p} \cdot \mathbf{E} = \cos(\phi)$ indicates that $\delta f$ varies with the projection of the electron’s velocity onto the applied electric field. The effect of $\cos(\phi)$ is to increase the probability that an electronic state with a momentum anti-parallel to the electric field is occupied, and to decrease the probability that a state with momentum parallel to the electric field is occupied. Due to the skewed occupation statistics, the ensemble acquires a drift velocity ($v_d \equiv \langle \mathbf{v} \rangle$) which is anti-parallel to the electric field.† As $\delta f$ is proportional to

*The BTE: $(\partial_t f)_{coll} = (\partial_t + \mathbf{v} \cdot \nabla_r + \hbar^{-1} \mathbf{f} \cdot \nabla_k) f$. Note that $f = f(r,k)$

†This reflects the convention that electrons move against the electric field.
3.1. SEMI-CLASSICAL TRANSPORT

Figure 3.1: The occupation statistics for \((\delta \hat{p} \cdot \hat{E} = \pm 1)\) for \(\epsilon_\Delta = 25\text{meV}\) and \(f_0 = f(\epsilon; 150\text{meV}, 300\text{K})\). \(f_0, \delta f, \text{and } f_0 \pm \delta f\) are shown. The effect of \(\epsilon_\Delta\) is to shift the \(\epsilon_f\) to \(\approx \epsilon_f \pm \epsilon_\Delta\).

\(\partial_\epsilon f_0\), the momentum states near \(\epsilon_f\) are most affected. Furthermore, \(\delta f\) increases with \(|E|\) and \(\tau\) such that larger fields and longer relaxation times generate larger perturbations to \(f_0\) leading to a larger current. Additionally, the term in braces has units of energy such that Eq. 3.6 may be expressed as follows

\[
\delta f = \epsilon_\Delta \left(-\frac{\partial f_0}{\partial \epsilon}\right) \delta \hat{p} \cdot \hat{E} \tag{3.7}
\]

For a small perturbation, it is possible to approximate the non-equilibrium population statistics in terms of equilibrium population statistics.

\[
f_0 + \delta f \approx f(\epsilon, \epsilon_f - \epsilon_\Delta \cos(\phi), \beta) \tag{3.8}
\]

Electrons moving anti-parallel(parallel) to \(E\) are likely to populate momentum states corresponding to higher(lower) energy. The Fermi sphere shifting effect is summarized in Fig. 3.1 for the case of \(\cos(\phi) = \pm 1\). The current density is calculated by evaluating a velocity weighted sum over the population statistics.

\[
\mathbf{J} = \frac{e g_s g_v}{A} \sum_{\delta k} \mathbf{v}(f_0 + \delta f) \tag{3.9}
\]

In Eq 3.9 the contribution from \(f_0\) is zero since there is no current at thermodynamic equilibrium. Note the similar form of Eq. 3.9 to Eqs. 2.23 and 2.24. For conductivity, one is interested in the component of the current in the direction of the electric field \(\mathbf{J} \cdot \hat{E}\). Substituting for \(\delta f\) and taking the ensemble average, the sum becomes.

\[
\langle \mathbf{J} \cdot \hat{E} \rangle = \frac{e^2 g_s g_v}{A} \sum_{\delta k} \tau |\mathbf{v}|^2 |E| \left(-\frac{\partial f_0}{\partial \epsilon}\right) \langle (\delta \hat{p} \cdot \hat{E})^2 \rangle \tag{3.10}
\]
The ensemble average on the right hand side may be approximated via \( \langle (\delta \hat{p} \cdot \hat{E})^2 \rangle = \frac{1}{2} \).

Converting the sum to an integral yields the following expressions for the current density in a monolayer and bilayer:

\[
\langle J_m \cdot \hat{E} \rangle = \left\{ \frac{e^2 v_f^2}{2} \int \tau(\epsilon) \rho_m(\epsilon) \left( -\frac{\partial f_0}{\partial \epsilon} \right) d\epsilon \right\} |\hat{E}| \tag{3.11}
\]

\[
\langle J_b \cdot \hat{E} \rangle = \left\{ \frac{e^2}{m^*} \int \tau(\epsilon) \rho_b(\epsilon) \left( -\frac{\partial f_0}{\partial \epsilon} \right) \epsilon d\epsilon \right\} |\hat{E}| \tag{3.11}
\]

The term in braces may now be recognized as the conductivity as the conductivity \( (\mathbf{J} = \sigma \mathbf{E}) \).

Given the conductivity, it is straightforward to determine the carrier mobility by Eq. 3.3. It is useful to evaluate these expressions in the case of the zero temperature approximation in order to obtain the \( \epsilon_f \) dependence of \( \sigma \). In this case the derivative becomes a delta function \( \partial f_0 = \delta(\epsilon - \epsilon_f) \). For constant \( \tau \), one finds that the conductivity in both materials exhibits a linear dependence on \( \epsilon_f \).

\[
\sigma_m(\epsilon_f) = \frac{e^2 v_f^2}{|\epsilon_f|} \tau(\epsilon_f) n_m(\epsilon_f) \quad \sigma_b(\epsilon_f) = \frac{e^2}{m^*} \tau(\epsilon_f) n_b(\epsilon_f) \tag{3.12}
\]

Using this result, one has for the mobilities in a monolayer and bilayer

\[
\mu_m(\epsilon_f) = \frac{e v_f^2}{|\epsilon_f|} \tau(\epsilon_f) \quad \mu_b(\epsilon_f) = \frac{e}{m^*} \tau(\epsilon_f) \tag{3.13}
\]

Mobility in a monolayer carries an intrinsic \( \mu \propto \epsilon_f^{-1} \) dependence as a consequence of linear dispersion. Meanwhile, mobility in a bilayer behaves identically to the case of a traditional semiconductor \( (\mu = e\tau/m^*) \). Here, the entire analysis has been classical and all of the quantum theory has been hidden away in \( \tau \).

Physically, \( \tau \) is related to the mean free path \( (\lambda) \) of a charge carrier in the system (i.e. the distance a charge carrier travels in the channel before a scattering event occurs). When \( \lambda \) is much larger than the channel length, carrier transport becomes ballistic and conductivity varies with channel length. When \( \lambda \) is much shorter than the channel length, transport is considered to be diffusive and conductivity does not vary with channel length. In epitaxial graphene, the carrier density is high, and transport is generally in the diffusive regime. A detailed description of the calculation of \( \tau \) for some relevant scattering channels may be found in Appendix A.

### 3.1.1 Mobility and Conductivity Modeling

The behavior of mobility and conductivity in graphene is determined by scattering via three channels: neutral impurities, charged impurities, and acoustic phonons. In order to model mobility and conductivity curves, it is useful to summarize the results presented in Appendix A regarding the associated momentum relaxation times. In the following relations, monolayer

\[
\text{Here we assume a hemi-Maxwellian distribution of electron velocities such that } (\delta \hat{p} \cdot \hat{E} > 0) \text{ for all carriers contributing to the current. In this case one has: } \langle (\delta \hat{p} \cdot \hat{E})^2 \rangle = \pi^{-1} \int_{-\pi/2}^{\pi/2} \cos^2(\phi) d\phi = \frac{1}{2}.
\]
results are shown along with the monolayer → bilayer transformation relations. For neutral impurities one has the following

\[
\frac{1}{\tau_n(\epsilon_f)} = \left( \frac{|\epsilon_f|}{4\hbar^3v_f^2} \right) n_i V_0^2 \quad [\epsilon_f \to \gamma] \quad (3.14)
\]

Here, \(n_i\) represents the impurity density, and \(V_0\) represents the strength of the scattering potential. For acoustic phonons one obtains a similar result

\[
\frac{1}{\tau_{ph}(\epsilon_f)} = \left( \frac{|\epsilon_f|}{4\hbar^3v_f^2} \right) \left( \frac{D^2}{\rho_m v_{ph}^2} \right) k_b T \quad [\epsilon_f \to \gamma] \quad (3.15)
\]

Here, \(\rho_m\) is the density of the material, \(v_{ph}\) is the phonon velocity, and \(D\) is the strength of the deformation potential. Both acoustic phonon scattering and neutral impurity scattering have \(\tau \propto \epsilon_f (\tau = \text{const})\) in the monolayer (bilayer) cases respectively. For charged impurities, one has the following

\[
\frac{1}{\tau_c(\epsilon_f)} = \frac{n_c}{\hbar} \left( \frac{\pi e^2}{\kappa} \right)^2 \frac{1}{|\epsilon_f|} \quad [n_c \to n_c/2] \quad (3.16)
\]

Where \(n_c\) is the density of impurities and \(\kappa\) is the dielectric constant of the material. Note that neutral impurity scattering may be considered a special case of charged impurity scattering in which the Coulomb potential is exchanged for a delta function. This is known as the short range approximation. In the case of charged impurities, one that \(\tau \propto \epsilon_f\) in both monolayer and bilayer material. By Matthiessen’s rule, the effective momentum relaxation time from several scattering channels \(\tau_i\) may be approximated in the following way.

\[
\frac{1}{\tau_{eff}} \approx \sum_i \frac{1}{\tau_i} \quad (3.17)
\]

Collecting the results for the three scattering channels of interest and isolating the dependence on \(\epsilon_f\) and \(\epsilon_{th} = k_b T\), the total momentum relaxation times in monolayers and bilayers are given by.

\[
\begin{align*}
\tau_m^{-1} &= \alpha_c \epsilon_f^{-1} + \epsilon_f (\alpha_n + \alpha_{ph} \epsilon_{th}) \\
\tau_b^{-1} &= \frac{1}{2} \alpha_c \epsilon_f^{-1} + \gamma (\alpha_n + \alpha_{ph} \epsilon_{th})
\end{align*} \quad (3.18)
\]

Here the constants \(\alpha_n, \alpha_{ph},\) and \(\alpha_c\) consolidate the remaining constants in Eqs. 3.14, 3.14 and Eq. 3.16 respectively. By Eq. 3.13 one has that the effective mobility is proportional to \(\tau_{eff}\). Collecting terms in Eq. 3.18, the mobility in a monolayer may be expressed in the following way.

\[
\mu_{eff}(\epsilon_f, \epsilon_{th}) = \frac{e v_f^2}{\alpha_c + \frac{\epsilon_f^2}{\epsilon_f} (\alpha_n + \alpha_{ph} \epsilon_{th})} \quad (3.19)
\]

From Eq. 3.19 it is straightforward to calculate the dependence of conductivity on \(\epsilon_f\) and \(k_b T\) via the familiar relation \(\sigma = e \mu n(\epsilon_f)\). The temperature dependent behavior of mobility (Eq. 3.19) and conductivity are summarized in Fig. 3.2. At low carrier density, charged impurity scattering dominates, and conductivity increases linearly with carrier density.
Figure 3.2: Monolayer $\sigma$ and $\mu$ as a function of temperature and carrier density for $\alpha_n/\alpha_c = 1.0$ and $\epsilon_{th}\alpha_{ph}/\alpha_c = 1.3$ at 300K. The corresponding momentum relaxation times are $\tau_c = 0.10\text{ps}$, $\tau_n = 1.16\text{ps}$, $\tau_{ph} = 0.89\text{ps}$ respectively for $\epsilon_f = 300\text{meV}$. This represents approximate values for an intercalated monolayer. For $\epsilon_f \approx 0$, charged impurity scattering dominates. As carrier density increases, conductivity decreases due to neutral impurity scattering and phonon scattering. Note that the conductance quantum $\sigma_0 = 4e^2/\hbar$ is not included.

carrier density increases, a rolloff in conductivity is observed at low temperature due to neutral impurity scattering. The rolloff becomes more severe at high temperature due to acoustic phonon scattering.\(^{40-42}\)

It is useful to compare conductivity and mobility in monolayers and bilayers near $\epsilon_f = 0$. If only charged impurities are considered one has that $\tau \propto |\epsilon_f|$ in both materials. In this case, the conductivity relations show the following dependence on carrier density.

\begin{equation}
\sigma_m(\epsilon_f) = \sigma_0^m n_m(\epsilon_f) \quad \sigma_b(\epsilon_f) = \sigma_0^b n_b^2(\epsilon_f)
\end{equation}

With regard to charged impurity scattering, the conductivity in monolayers(bilayers) should demonstrate a $n(n^2)$ dependence respectively.\(^{43}\) In monolayers, the linear dependence on carrier density describes conductivity behavior well. However, experimental observations in the bilayers suggest that $\sigma \propto n$ implying that $\mu = \text{const.}$.\(^{3,44}\)

In monolayers(bilayers), there is a qualitative difference insofar as charged impurity (neutral impurity) screening determine the dependence of conductivity on carrier density. In the case of neutral impurity(short range) scattering in a bilayer, $\tau$ and mobility are constant in a bilayer such that $\sigma \propto n$.

### 3.1.2 High Field Transport

The case of transport at high field is difficult to analyze and near-equilibrium dynamics is not sufficient to capture all of the relevant transport dynamics. At high electric field, carriers gain access to a wider array of scattering events which are forbidden at low electric field due
3.1. SEMI-CLASSICAL TRANSPORT

to energy conservation. In the context of the BTE, this has the effect of reducing $\tau$ with increasing $E$ which generates a field dependent mobility.

A classic example of this is intervalley scattering in GaAs. At high electric field, hot electrons in GaAs scatter inelastically from the $\Gamma$ valley into the $L$ valley. As the effective mass in the $L$ valley is higher than that of the $\Gamma$ valley, intervalley scattering generates velocity overshoot in $v_d(|E|)$.\(^{45}\) While a theoretical treatment of inelastic scattering processes via the BTE is possible,\(^{46, 47}\) statistical methods such as Monte Carlo simulation are often used to gain physical insight into high field transport.\(^{48}\) In graphene, inelastic scattering events with optical phonons play a crucial role at high field. Hot electrons may scatter inelastically with the optical phonon field in graphene or via surface optical phonon modes in the substrate.

Graphene monolayers and bilayers have two degenerate low energy valleys ($K$ and $K'$) of equivalent dispersion. As there are no inequivalent valleys in the band structure, one does not expect a velocity overshoot effect as in the case of GaAs. A crude model of high field transport is to consider that an applied electric field can only induce a certain maximal shift in the Fermi sphere (see Fig. 3.1)

$$\epsilon_f \rightarrow \epsilon_f \pm \epsilon^\text{max}_\Delta$$

(3.21)

As soon as $\epsilon_f$ approaches $\epsilon_f \pm \epsilon^\text{max}_\Delta$ inelastic scattering will occur such that states above $\epsilon^\text{max}_\Delta$ cannot be occupied above zero temperature. It is then straightforward to calculate the current density in this approximation by Eq. 3.7. This results in the following integral.

$$\langle \mathbf{J} \cdot \hat{E} \rangle = \frac{g_sg_v}{(2\pi)^2} \int \frac{\epsilon^\text{max}_\Delta}{\epsilon_f} |\mathbf{v}| \left( -\frac{\partial f_0}{\partial \epsilon} \right) \langle (\delta \mathbf{p} \cdot \hat{E})^2 \rangle d\Omega$$

(3.22)

Carrying out the integration, one has the following for current density

$$\langle \mathbf{J} \cdot \hat{E} \rangle = e \left( \frac{g_sg_v}{4\pi} \frac{\epsilon_f^2}{(\hbar v_f)^2} \right) \left( \frac{\epsilon^\text{max}_\Delta}{\epsilon_f} v_f \right) = en(\epsilon_f)v_{\text{sat}}$$

(3.23)

The first term in braces evaluates to the carrier density in the zero temperature approximation, while the second term defines the drift velocity in the event of a maximal shift of the Fermi sphere by $\epsilon^\text{max}_\Delta$. Defining this as the saturated electron velocity one finds.\(^{49, 50}\)

$$v_{\text{sat}} = \epsilon^\text{max}_\Delta \left( \frac{v_f}{\epsilon_f} \right) = \frac{\epsilon^\text{max}_\Delta}{\hbar \sqrt{\pi n}}$$

(3.24)

In monolayer graphene, one finds that $v_{\text{sat}} \propto n^{-1/2}$ such that higher carrier densities lead to lower saturated velocities. Analysis of a bilayer leads to an identical result. Additionally, $v_{\text{sat}}$ increases linearly with $\epsilon^\text{max}_\Delta$. This is somehow expected, as larger shifts in the population statistics implies higher drift velocities and thus higher currents. In practice, Eq. 3.24 tends to overestimate $v_{\text{sat}}$ due to the approximation $\langle (\delta \mathbf{p} \cdot \hat{E})^2 \rangle \approx \frac{2}{3}$. This approximation assumes that there are no carriers moving against the electric field. In practice some backscattering will occur at high field. A more careful treatment of leads to the following approximation for $v_{\text{sat}}$.\(^{51}\)

$$v_{\text{sat}} = \frac{2}{\pi} \frac{\epsilon^\text{max}_\Delta}{\hbar \sqrt{\pi n}}$$

(3.25)
The $2/\pi$ is a correction factor which accounts for the proportion of carriers moving against the field consequent to optical phonon emission.\textsuperscript{52} Incidentally, inelastic scattering via optical phonons will not occur at thermal equilibrium as such scattering events are prevented by Pauli exclusion (i.e., the available states for electrons to scatter into are occupied). By displacing the Fermi sphere by $\epsilon_{\Delta}^{\text{max}}$, electrons occupy higher energy states anti-parallel to the electric field leaving lower energy states parallel to the electric field unoccupied. Upon inelastic scattering, electrons can back-scatter into these states by emission of an optical phonon.

Generally, $\epsilon_{\Delta}^{\text{max}}$ may be taken to be equivalent to the optical phonon mode of lowest energy. In the case of graphene on SiC, the polar optical mode in the SiC substrate $\epsilon_{SO} \approx 115\text{meV}$ is the lowest energy phonon. Thus velocity saturation in graphene is due to scattering with polar optical phonons \textit{in the substrate}. Remote polar phonon scattering was first analyzed in the context of determining the saturation velocity in inversion layers in silicon MOS. In the case of silicon, electrons in an inversion layer can couple to remote polar phonon modes in the field oxide generating velocity saturation.\textsuperscript{53–55} In graphene, a similar situation is tractable regarding to carriers coupling to phonons in the substrate.\textsuperscript{56}\textsuperscript{*}

### 3.2 Measuring Electron Transport

#### 3.2.1 The Velocity Field Characteristic

By investigating low field transport properties in graphene, it is possible to gain insight into the dominant scattering mechanisms within the material by examining field and temperature dependence. As both $\mu$ and $\sigma$ are related to the momentum relaxation time $\tau$, they may be used to probe scattering mechanisms. Similarly, the high field transport properties allow one to probe scattering mechanisms which are energetically forbidden at low field.

The velocity field characteristic relevant insofar as it lends insight into both low field and high field transport properties simultaneously. At low field, the carrier velocity varies linearly with electric field. As the electric field increases carriers acquire more kinetic energy such that scattering with optical phonons becomes energetically allowed. These additional scattering events generate a saturating tendency in the drift velocity which manifests as current compression in a device context. To introduce saturation in the context of Eq.3.2, one introduces a field-dependent mobility $\mu(\epsilon_f, \epsilon_{th}, |E|)$ which is be expressed in terms of the low-field mobility $\mu(\epsilon_f, \epsilon_{th})$.\textsuperscript{58,59} The empirical model is constructed such that as $|E| \rightarrow \infty$ that $\langle v \rangle \rightarrow v_{\text{sat}}$.

$$
\mu(\epsilon_f, \epsilon_{th}, |E|) = \frac{\mu(\epsilon_f, \epsilon_{th})}{\left[1 + \left(\frac{\mu(\epsilon_f, \epsilon_{th})|E|}{v_{\text{sat}}}\right)^{\frac{1}{\alpha}}\right]^{\frac{1}{\alpha}}}
$$

(3.26)

A measurement of the velocity field characteristic is not always straightforward and many approaches appear in the literature. A common approach is to first measure the current

\textsuperscript{*}In graphene MOS systems, the surface optical mode in the dielectric must also be considered. In [57], the following values are tabulated for $\epsilon_{SO}$: SiO$_2$(55meV), Al$_2$O$_3$(48.1meV), AlN(81.4meV), HfO$_2$(12.4meV).
3.2. MEASURING ELECTRON TRANSPORT

Figure 3.3: [left] Current waveforms obtained from pulsed IV measurements on graphene micro-bridges for increasing voltage pulses. The current compression which occurs with increasing voltage amplitude indicates the onset of velocity saturation. (inset) The corresponding IV characteristic extracted from the pulsed waveforms via the convolution integral. Fitting to Eq. 3.28 is also shown. [right] A schematic of the geometry of the bridge structures under consideration with important dimensions annotated.

voltage (IV) characteristic using short pulses. With prudent analysis, the currents(voltages) obtained from the pulsed IV measurements may be transformed into velocities(fields) respectively.

The advantage of the pulsed IV technique is that it minimizes the Joule heating in the material such that electrothermal effects can be neglected in the analysis. In the case of epitaxial graphene, pulsed measurements also preclude hysteresis effects which otherwise make a velocity field extraction from DC measurements intractable. If electrothermal properties must be accounted for, an analysis of large signal RF waveforms may be used to infer the field dependence of the current.60 Such an analysis is warranted when devices are designed to operate at high field/high current conditions (e.g. AlGaN/GaN HEMTs).

In order to measure the velocity field characteristic, electrically isolated 5x10μm micro-bridge structures are fabricated on native and intercalated monolayers.61 A measurement of the velocity field characteristic begins with a measurement of the pulsed IV curve of the bridge. In order to transform the IV measurement into a velocity field characteristic, three additional measurements are required. First, the geometry of each microbridge must be characterized such that the electric field in the bridge may be accurately estimated. Second, the contact resistance must be measured in order to account for the voltage drop across the contacts. Finally, statistics on the low field transport properties are needed such that one can estimate the carrier density on a basis of the measured low-field conductivity.

Voltage pulses of order 1μs are applied to the bridge, and the resulting current waveforms are monitored on an oscilloscope. This results in a pulse ladder as shown in Fig. 3.3. For a given voltage/current pulse pair in the time domain, a point of the IV curve is then extracted
**Figure 3.4:** Measured and modeled velocity field curves for native [left] and intercalated [right] monolayers plotted as function of temperature. Both materials exhibit a monotonic weakly saturating behavior at high field. The native material demonstrates a stronger temperature dependence in both mobility and saturated electron velocity. Both materials exhibit $v_{\text{sat}} < v_f$ as expected due to scattering via substrate optical modes by examining the derivatives of the convolution integrals inside the pulses.

\[
\frac{\partial}{\partial t} \int i(t)v(t-\tau)d\tau = 0 \\
\frac{\partial}{\partial t} \int v(t)v(t-\tau)d\tau = 0
\]  

(3.27)

The IV characteristic can then be fitted to the following empirical relationship which is borrowed from MESFET modeling.\(^{64}\) Note that the hyperbolic tangent function introduces a weakly saturating behavior into the IV characteristic.

\[
i = i_0 [1 + \lambda v] \tanh (\beta v)
\]  

(3.28)

Each step of the pulse ladder shown in Fig. 3.3 represents the device response to a voltage pulse of increasing amplitude. The amplitude of the voltage pulse is increased from $0V$ to $28V$ in steps of $1V$. As the amplitude of the voltage pulses are increased, current compression is observed indicating the onset of velocity saturation within the bridge via Eq. 3.26.

Self heating effects are generally characterized by a decaying transient inside the pulse. In Fig. 3.3, the current pulses obtained are flat, which indicates that there is minimal resistive self heating during the applied voltage pulse. Graphene exhibits an exceptionally high thermal conductivity, and values of order ($\kappa_{th} \approx 25.0\text{Wcm}^{-1}\text{K}^{-1}$) have been reported for suspended layers.\(^{65}\) This is somewhat reduced in the case of supported layers, whereby phonon scattering across the graphene substrate interface has a limiting effect on thermal conductivity ($\kappa_{th} \approx 6.0\text{Wcm}^{-1}\text{K}^{-1}$).\(^{66}\)
Table 3.1: A comparison of the parameters of the above fits to those of other well characterized materials at 300K. The data for silicon(GaN) corresponds to n-type doping $10^{15} (10^{17}) \text{cm}^{-3}$. $v_{\text{sat}}$ values reported for GaAs represent the peak velocity. Figures for GaN include measurements on AlGaN/GaN heterostructures and bulk GaN substrates.

<table>
<thead>
<tr>
<th>Material</th>
<th>$v_{\text{sat}}$ (10$^7$ cm/s)</th>
<th>$\mu$ (cm$^2$/V·s)</th>
<th>$E_{\text{sat}}$ (kV/cm)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>2.3</td>
<td>630</td>
<td>37.0</td>
<td>1.80</td>
</tr>
<tr>
<td>Intercalated</td>
<td>1.4</td>
<td>700</td>
<td>19.4</td>
<td>1.85</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>1.6</td>
<td>130</td>
<td>123.7</td>
<td>-</td>
</tr>
<tr>
<td>AlGaN/GaN</td>
<td>3.1</td>
<td>430</td>
<td>72.0</td>
<td>-</td>
</tr>
<tr>
<td>GaN</td>
<td>2.5</td>
<td>250</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>1.0</td>
<td>1400</td>
<td>7.1</td>
<td>2.0</td>
</tr>
<tr>
<td>GaAs</td>
<td>2.1</td>
<td>7500</td>
<td>2.8</td>
<td>-</td>
</tr>
</tbody>
</table>

In the case of epitaxial graphene, the 4H(6H)-SiC substrate provides excellent thermal conductivity ($\kappa_{\text{th}} \approx 3.7(4.9)\text{Wcm}^{-1}\text{K}^{-1}$) such that the lack of self heating effects in the measurement is not surprising. Similar measurements on SiO$_2$ ($\kappa_{\text{th}} \approx 0.013\text{Wcm}^{-1}\text{K}^{-1}$) reveal a decaying transient in the pulsed IV characteristic demonstrating a self heating effect due to the low thermal conductivity of the substrate. For short pulses ($<10\mu\text{s}$), the pulsed IV characteristic is repeatable, and no hysteresis is observed when cycling the voltage amplitude.

Given the pulsed IV characteristic, the calculation of fields begins by considering an integral form of Ohms law. One has the following for the differential resistance

$$\frac{\partial v}{\partial i} = \{\lambda i_0 \left[ \tanh (\beta v) + v \beta \text{sech}^2(\beta v) \right] \}^{-1}$$ (3.29)

The differential resistance has a contribution from the contacts $r_c$ and the bridge $r_b$. Here $r_c = \rho_c/w_c$ is the total resistance of the contact. If the sheet resistance $\rho_{sh}$ is assumed constant for the entire microbridge structure, then one can express $r_b$ as an integral over the geometry of the sheet.

$$\frac{\partial v}{\partial i} = \left[ 2r_c + \rho_{sh} \int_{0}^{l_0} \frac{dl}{w(l)} \right]$$ (3.30)

The integral is over the length of the bridge $l_0$, and $w(l)$ is the varying width of the sheet. The integral on the right hand side behaves as a form factor and is a generalization of the aspect ratio of the sheet. Integrating over the geometry shown in Fig. 3.3, one has for the sheet resistance:

$$\rho_{sh} = r_b \left[ \frac{2 \log(w_{\text{end}}/w_{\text{ch}})}{\tan(\theta)} + \frac{l_{\text{ch}}}{w_{\text{ch}}} \right]^{-1}$$ (3.31)

Here $\theta$ is the current spreading angle which is given by the following:

$$\tan(\theta) = \frac{2l_{\text{end}}}{w_{\text{end}} - w_{\text{ch}}}$$ (3.32)

*For comparison, isotopically pure $^{12}\text{C}$ diamond offers the highest thermal conductivity any known bulk material ($\kappa_{\text{th}} \approx 33.7\text{Wcm}^{-1}\text{K}^{-1}$). The 4H(6H)-SiC polytypes have a thermal conductivity which is similar to that of copper ($\kappa_{\text{th}} \approx 3.8\text{Wcm}^{-1}\text{K}^{-1}$). All values of $\kappa_{\text{th}}$ are reported at 300K.
CHAPTER 3. ELECTRON TRANSPORT IN GRAPHENE

Figure 3.5: Extracted low-field [left] and high-field [right] transport parameters for the velocity field curves shown in Fig. 3.4. The temperature dependence in the low field mobility for native material indicates phonon scattering in the high temperature regime. This is in contrast to the H-intercalated case in which the low field mobility is constant, indicating charged and neutral impurity scattering limited transport. In both materials, the high field transport demonstrates only a weak temperature dependence. Curves represent fitting to Eq. 3.19 and Eq. 3.25 for mobility and saturation velocity respectively.

It is useful to consider the straight channel case in which \( w_{\text{end}} = w_{\text{ch}} \) and \( l_{\text{end}} = 0 \). In this case the sheet resistance simplifies to the familiar form \( r_b = \rho_{\text{sh}} l_{\text{ch}} / w_{\text{ch}} \). The electric field may then be calculated in the following way.

\[
|E| = \frac{v_0 - 2i_0 [r_{\text{end}} + r_c]}{l_{\text{ch}}} \tag{3.33}
\]

Currents can be translated into drift velocities by considering the drift velocity of carriers in a current carrying sheet.

\[
\langle v \rangle = \frac{i_0}{\varepsilon w_{\text{sh}} n(\epsilon_f)} \tag{3.34}
\]

Note that \( \langle v \rangle \) depends on the carrier density \( n(\epsilon_f) \). However, in the consideration of transforming voltages into electric fields, the sheet resistance was obtained from the IV characteristic. From low field statistics, it is possible to obtain the relationship between sheet resistance and carrier density \( n(\epsilon_f) = [\varepsilon \rho_{\text{sh}} \mu]^{-1} \).

The average mobility can be obtained either by fitting Hall data, or via microwave reflectivity (Leheighton) measurements taken prior to fabrication. The transformed data is then optimized against Eq. 3.26 in order to extract a low-field carrier mobility \( \mu(\epsilon_f, \epsilon_{\text{th}}) \) and saturated velocity \( v_{\text{sat}} \) for the bridge. Fig. 3.4 shows the velocity field curves for both native and intercalated material as a function of temperature, and Table 3.1 compares the
### 3.2. MEASURING ELECTRON TRANSPORT

#### Table 3.2:

The Fermi energy as calculated via velocity data presented in [62] compared with fitting of low field data in Fig. 3.4 to Eq. 3.19. The fitting of low field data allows for the estimation of momentum relaxation times of the three scattering channels in both materials: neutral impurities ($\tau_n$), charged impurities ($\tau_c$), and acoustic phonons ($\tau_{ph}$). The mean free path $\lambda_{tot}$ is shown for $T = 300$K. Results may be compared with the simulation data shown in Fig. 3.2.

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon_f$(meV)</th>
<th>$\epsilon_f$(meV)</th>
<th>$\epsilon_{\Delta}^{\text{max}}$(meV)</th>
<th>$\lambda_{tot}$(nm)</th>
<th>$\tau_c$(ps)</th>
<th>$\tau_n$(ps)</th>
<th>$\tau_{ph}$(ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>250</td>
<td>248</td>
<td>115.9</td>
<td>14.67</td>
<td>0.025</td>
<td>0.415</td>
<td>0.037</td>
</tr>
<tr>
<td>Intercalated</td>
<td>520</td>
<td>523</td>
<td>115.0</td>
<td>15.91</td>
<td>0.020</td>
<td>0.082</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

#### 3.2.2 Extracting $\tau$, $\epsilon_f$, and $\epsilon_{\Delta}^{\text{max}}$

By fitting the velocity field data shown in Fig. 3.4 to Eq. 3.26 the mobility and saturation velocity may be plotted as a function of temperature as shown in 3.5. Mobility and saturation velocity can then in turn be fitted to the low field and high field relations of Eq. 3.19 and Eq. 3.25 respectively.

In [62], the estimation of $\epsilon_{\Delta}^{\text{max}}$ was performed by fitting of the velocity vs. temperature data. However, the mobility data may be used to equal effect with the added advantage of being able to estimate the momentum relaxation lifetimes associated with the charged impurities $\tau_c$, neutral impurities $\tau_n$, and acoustic phonons $\tau_{ph}$. The results are summarized in Table 3.2. In the case of native monolayers, the dependence of mobility on temperature manifests direct as finite relaxation time associated with acoustic phonon scattering $\tau_{ph}$. This is contrasted to the case of intercalated monolayers where no temperature dependence is seen. In both cases, charged impurity scattering yields the lowest $\tau$ and is thus dominant scattering channel. With a knowledge of the momentum relaxation times, it is possible to estimate the mean free path in the material $\lambda_{tot}$.

$$\lambda_{tot} = v_f \left( \sum_i \tau_i^{-1} \right)^{-1}$$  \quad (3.35)

From mobility modeling, a mean free path of about 15nm is found in the native and intercalated samples. As the channel length is of order $\mu$m, one concludes that transport is in the diffusive regime. Generally, mobility values in epitaxial graphene are $< 10000$cm$^2$/V·s which equates to maximal mean free paths of order 100nm. Thus, transport in epitaxial graphene will be in the diffusive regime for all but the smallest devices.

As the resulting values for $\epsilon_f$ are large, the zero temperature approximation may be invoked for a direct calculation of $v_{sat}$. In both materials, a value of $\epsilon_{\Delta}^{\text{max}} \approx 115$meV is
CHAPTER 3. ELECTRON TRANSPORT IN GRAPHENE

Figure 3.6: [top] Low field transport measurements on symmetric 25 μm² and 100 μm² van der Pauw structures fabricated on a 1 cm² monolayer sample. Fitting to Eq. 3.3 is also shown (dashed). The data is plotted to indicate the number of terraces \( n_T \) which transect the structure. Higher mobility values are consistently observed in structures with less transections, with the highest values being observed in structures that are located entirely on a single terrace [bottom left]). Relatively low mobility values are observed in structures with multiple transections with the lowest being observed in structures falling on threading screw dislocations [bottom right].

obtained suggesting that the mechanism of velocity saturation in both materials is identical. The close correspondence between \( \epsilon_{\Delta}^{\text{max}} \) and the energy of the surface optical modes \( \epsilon_{SO} \) in 4H-SiC and 6H-SiC demonstrates that velocity saturation in epitaxial graphene occurs when carriers in the graphene have sufficient energy couple to optical modes in the substrate.\(^{68}\)

3.2.3 Transport Anisotropy in Epitaxial Graphene

The need for low field statistics in the velocity field extraction originates from observations of material non-uniformity and transport anisotropy in epitaxial monolayers and bilayers. Mobility, carrier density, and conductivity may be estimated by measuring the Hall voltage of the sample. When a current flows \((i_x\hat{x})\) in a conducting sheet in the presence of a magnetic field normal to the sheet \((B_z\hat{z})\), an electric field will be generated \((E_y\hat{y})\) as consequence of
the Lorentz force law. Integrating the electric field across the width of the sheet yields the Hall voltage.

\[ v_H = \frac{iB \cdot \hat{z}}{en(\epsilon_f)} \quad \mu = \frac{\sigma v_H}{iB \cdot \hat{z}} \] (3.36)

The Hall voltage is inversely proportional to the sheet carrier density. With a separate measurement of the conductivity, it is possible to calculate the low field mobility. The low field transport parameters are readily acquired by measuring \( v_H \) and \( \sigma \) on symmetric van der Pauw structures or Hall bars.

The measurements shown in Fig. 3.6 show the measured \( \mu \), \( \sigma \), and \( n \) on several symmetric \( 25 \mu m^2 \) and \( 100 \mu m^2 \) van der Pauw structures fabricated in monolayer graphene on 6H-SIC. The measurements shown in Fig. 3.6 are typical for epitaxial graphene and reveal the relationship between sheet conductivity and mobility shown in Eq. 3.3. By fitting to Eq. 3.3, an average carrier density (Fermi energy) of \( 8.939 \times 10^{12} \text{cm}^{-2} \) (\( -345 \text{meV} \)) is extracted for the sample. Deviations from the fit line shown in the sheet resistance vs. mobility (right) indicate fluctuations in carrier density (Fermi energy) over the sample.

In addition to the low field measurements, each structure is also investigated by scanning electron microscopy in order to determine sources of non-uniformity. Of primary interest is the number of substrate terraces that transect the active area of the structure \( n_t \). Here \( n_t \) is defined as the maximum number of terraces between two adjacent contacts within a given structure. Terrace edges introduce inclusions of bilayer or multilayer graphene in monolayer samples as a result of growth. These multilayer inclusions in turn affect the results obtained in low field transport measurements. Structures with a low \( n_t \) tend to be found at the high end of the mobility curve, while structures with a high \( n_t \) are found near the lower end of the mobility curve. An extreme case of mobility degradation occurs when Hall structures are fabricated on regions of the substrate exhibiting an exceptionally high density of terraces as seen on threading screw dislocations. Additionally, included structures also tend to exhibit transport anisotropy whereby current paths parallel to terraces demonstrate higher conductance than current paths normal to terraces resulting in higher asymmetry factors in low field transport measurements.

---

*The Lorentz force law relates the force of a charged particle \( \mathbf{f} \) to its velocity \( \mathbf{v} \) and the applied electric \( \mathbf{E} \) and magnetic fields \( \mathbf{B} \). \( \mathbf{f} = e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \)
Chapter 4

Charge Control in Graphene MOS Devices

Metal oxide semiconductor (MOS) capacitors in graphene are of primary importance from both a physical and technological perspective, and careful analysis of graphene MOS structures provides a promenade into the underlying physics of device operation. The MOS capacitors analyzed consist of an aluminium electrode, a 15nm aluminium oxide dielectric layer, the graphene layer itself, and the semi insulating SI 4H(6H)-SiC substrate. A metalization step is also performed in order to facilitate Ohmic contact to the graphene layer.

MOS systems in intercalated monolayers and bilayers are considered, and several important differences are outlined in the context of theoretical considerations. From the capacitance voltage measurements (CV) it is possible to assess several important quantities including the density of interface states ($D_{it}$), the mean emission time of interface states ($\tau_e$), and the magnitude of surface potential fluctuations ($\delta\epsilon_f$). CV measurements also serve as an indirect method to probe the band structure of the graphene. In the case of a bilayer, measurement data and modeling support the notion of a substrate induced energy gap ($\epsilon_g$) which is of interest from both a physical and technological point of view. Although the analysis is carried out in the context of intercalated layers, the results and methods are extensible to the case of native layers without loss of generality. Further, the results are also applicable in the transistor context as they provide a valuable commentary on the expectations of device performance.

4.1 MOS Capacitors in Graphene

Charge control in graphene MOS can be visualized with the aid of the band diagram shown in Fig. 4.1. In Fig. 4.1 the $z$ axis represents the vertical axis through the transistor structure shown in Fig. 1.1. To construct the band diagram, one first considers the band alignment between the SI 4H(6H)-SiC substrate and the graphene. Since there are no free carriers in the SI SiC bulk, there should be minimal band bending such that $\epsilon_f$ passes through the midgap of the SiC. In this case, the band offset between the valence band maximum (VBM)

*Details on fabrication routines for graphene MOS structures are available in Chapter 6. A characterization of various low temperature aluminium oxides is also included.
in the SiC and the $\epsilon_f$ in the graphene is $\epsilon_{SiC}^g/2$. Note that the energy gaps in the 4H(6H)-SiC are $\epsilon_{SiC}^g \approx 3.2(3.0)$eV resulting in a band offset of $1.6(1.5)$eV.

The energy gap in Al$_2$O$_3$ oxide $\epsilon_{ox}^g$ has been shown vary on the phase of the material and its quality. Values for high quality crystalline films range from 8.8eV in $\alpha$-Al$_2$O$_3$ to 7.1-8.0eV in $\gamma$-Al$_2$O$_3$.\cite{72,73} In the case of lower quality amorphous films, values of 5.1-7.1eV are reported. Measurements for the conduction band offset between in the amorphous Al$_2$O$_3$/SiC system yield values of 2.06eV.\cite{74,75,76} Thus, the charge neutrality point in the graphene lies near the midgap making Al$_2$O$_3$ an ideal field oxide. The work function of the aluminium metal $\phi_m = 4.02$eV is smaller than that of graphene $\phi_g \approx 5.0$eV such that the equilibrium case does not represent a flatband condition.\cite{77,78,79,80}

An analysis of charge control in MOS devices begins by considering the modulation of the current density in a conducting channel ($J$). The current density may be calculated with knowledge of the signed electron(hole) densities and their respective mobilities $\mu_n$($\mu_p$). For a given applied electric field $E$ one has the following.

$$J = e \left[ \mu_n n_n(\epsilon_f) + \mu_p n_p(\epsilon_f) \right] E$$

(4.1)

In 4.1, the current density exhibits a linear dependence on the electron and hole densities. When a bias is applied via the aluminium electrode ($v$), it modulates the current density by controlling the carrier density(Fermi energy) in the current carrying layer. In order to investigate charge control in graphene MOS structures, it is necessary to develop a relation between $v$ and $\epsilon_f$. With such a relation, it is possible to transform Eq.4.1 such that it reflects the applied gate and drain biases in the transistor context.
4.1. MOS CAPACITORS IN GRAPHENE

The graphene MOS structure may modeled as a capacitive divider as shown in Fig. 4.2. Here, $C_{ox}$ represents the capacitance of the oxide, $C_q$ represents the capacitance associated with modulating the carrier density in the graphene, and $C_{it}$ represents the capacitance associated with charge trapping and charge injection at the graphene/oxide interface. Typically, $C_{ox} = \kappa \varepsilon_0 / t_{ox}$ is treated as an ideal parallel plate capacitor where $\kappa$ is the dielectric constant, and $t_{ox}$ is the thickness of the oxide. All variations in total capacitance are thus presumed to originate in $C_q$ and $C_{it}$. The capacitance associated with the graphene $C_q$ may be calculated as follows:

$$C_q \equiv \partial_v Q_n = e \partial_v (e n(\varepsilon))$$  (4.2)

Here $Q_n = e n(\varepsilon_f)$ represents the total charge in the graphene layer ($n_n + n_p$). Taking the derivative yields $C_q = e^2 \partial_v n \approx e^2 \rho(\varepsilon_f)$ where $\rho(\varepsilon_f)$ represents the density of states in graphene. For this reason, $C_q$ is known as the density of states capacitance or alternatively as the quantum capacitance. In both monolayer and bilayer material one finds that $C_q$ varies linearly with $\varepsilon_f$. A similar argument applies for $C_{it}$

$$C_{it} = \partial_v Q_{it} = e^2 D_{it}(\varepsilon_f)$$  (4.3)

Here, $Q_{it}$ represents the total interface charge, and $D_{it}(\varepsilon_f)$ represents the density of interface states. Note that $D_{it}(\varepsilon_f)$ and $\rho(\varepsilon_f)$ represent distributions in energy space and have units of eV$^{-1}$cm$^{-2}$. The total capacitance is then given by the following relation.

$$C_{tot}(v) = \left[ \frac{1}{C_{ox}} + \frac{1}{e^2 \rho(\varepsilon_f) + e^2 D_{it}(\varepsilon_f)} \right]^{-1}$$  (4.4)

Eq. 4.4 represents the capacitance voltage (CV) characteristic of the graphene MOS system.
CHAPTER 4. CHARGE CONTROL IN GRAPHENE MOS DEVICES

4.1.1 The $\epsilon_f(v)$ Relation

The CV characteristic is it may be used to obtain the desired relation $v(\epsilon_f)$, which is important insofar as it allows the right hand side of Eq. 4.4 to be expressed in terms of the applied bias voltage. This is achieved by considering capacitive division in the MOS structure shown in Fig. 4.2. Let $v_\epsilon = \epsilon/e$ represent the chemical potential at graphene/oxide interface. By capacitive division, the following holds

$$\frac{\partial v_\epsilon}{\partial v} = \frac{1}{e} \frac{\partial \epsilon}{\partial v} = \frac{C_{ox}}{C_{ox} + C_q + C_{it}}$$  (4.5)

Expressing this in terms of the total capacitance yields the following relation.

$$\frac{1}{e} \frac{\partial \epsilon}{\partial v} = \frac{C_{tot}(v)}{C_q(\epsilon) + C_{it}(\epsilon)}$$  (4.6)

When $C_{it}(\epsilon) = 0$, one obtains the fundamental charge control relation of an ideal MOS capacitor. Rearranging terms and integrating Eq. 4.5 over $\epsilon \in [0, \epsilon_f]$ and $v \in [v_D, v_g]$ yields the following relation.

$$n(\epsilon_f) = \frac{1}{e} \int_{v_D}^v C_{tot}(v) dv$$  (4.7)

Note that the carrier density is introduced via the integral over $C_q(\epsilon) = e^2 \rho(\epsilon)$. The explicit relationship between $\epsilon_f$ and $v_g$ may also be obtained via similar integration of Eq. 4.5.\textsuperscript{85}

$$\Delta v = \frac{\epsilon_f}{e} + \frac{e}{C_{ox}} \left[ n(\epsilon_f) + \int_0^{\epsilon_f} D_{it}(\epsilon) d\epsilon \right]$$  (4.8)

Here $\Delta v = v - v_D$ represents the difference between the applied gate voltage and the Dirac voltage (i.e. the electrode voltage at which $\epsilon_f = 0$). Additionally, the effect of a general $D_{it}$ has been included. Eq. 4.8 is the equivalent of the Berglund integral in graphene MOS.\textsuperscript{85} Upon examination of Eq. 4.8 one finds that gate voltage varies linearly with respect to carrier density.

4.1.2 Extracting $D_{it}$

As shown in Eq. 4.4, a measurement of the total capacitance of a MOS structure contains information about the capacitances $C_q$ and $C_{it}$. In a CV measurement the bias is quasistatically swept and the capacitive(conductive) responses of the device are measured at several frequencies. Both monolayer and bilayer material exhibit significant dispersion when measuring capacitance and conductance as a function of frequency reflecting the presence of interface states. A common approach to estimate $D_{it}$ is to compare the capacitive response of the system to low and high frequency test signals.\textsuperscript{86}

$$eD_{it}^*(v) = \left( \frac{C_{ox}C_{0tot}}{C_{ox} - C_{0tot}} - \frac{C_{ox}C_{\infty}}{C_{ox} - C_{\infty}} \right)$$  (4.9)

Here the superscripted $D_{it}^*$ indicates that the value extracted from measurement data. At low frequency, the total capacitance $C_{0tot}$ will contain contributions from $C_{ox}$, $C_q$, and $C_{it}$.\textsuperscript{86}
However, as the frequency of the test signal $\omega$ is increased, interface states will contribute less to the total capacitance observed. At very high frequencies, only $C_q$ and $C_{ox}$ will contribute to the observed capacitance $C_{\infty}^{\text{tot}}$. Thus, Eq. 4.9 represents a kind of capacitive difference relation by which $D^*_{\text{it}}$ may be obtained. The dispersive effect in the total capacitance is due to the fact that interface states have a finite capture and emission lifetimes $\tau_{c,e}$. In the majority of dielectric/semiconductor systems, $\tau_e \gg \tau_c$ such that the dominant contribution to frequency dependence in $C_{\text{tot}}$ is $\tau_e$. The following holds for the total capacitance measured at high frequency $C_{\infty}^{\text{tot}}$

$$C_{\infty}^{\text{tot}} = \left( \frac{C_{ox}C_q}{C_{ox} + C_q} \right)$$  \hspace{1cm} (4.10)

Eq. 4.9 tends to underestimate the total $D_{\text{it}}$ especially when the $C_q \gg C_{\text{it}}$. In order to account for this, the effective $D_{\text{it}}$ may be estimated by multiplying Eq. 4.9 by a scaling factor $D_0$. Often, the dispersion well described by a simple exponential. Note that $\omega = 2\pi f$ where $f$ is the measurement frequency.

$$D_{\text{it}}(v, \omega) = D_0 D^*_{\text{it}}(v)e^{-\omega\tau_e}$$  \hspace{1cm} (4.11)

The movement of charge in and out of interface states also gives rise to a small signal conductance $G_{\text{it}}$. In the absence of DC leakage, the density of interface states can be estimated by examining the dependence of the conductance on frequency.

$$\left( \frac{G_{\text{it}}}{\omega} \right) = \frac{e\omega\tau_e D_{\text{it}}}{1 + (\omega\tau_e)^2}$$  \hspace{1cm} (4.12)

Eq. 4.12 exhibits a maximum in conductance when interface states are in resonance with the test signal.

### 4.2 CV/GV Measurements in Graphene MOS

The measured and modeled low frequency CV/GV characteristics for the monolayer and bilayer material are shown in Fig. 4.3 for frequencies $\omega \in [1, 10, 100, 200, 500, 1000\text{kHz}]$ as measured on an Agilent E4980A LCR meter. The measurement data presented in Fig. 4.3 were taken at a temperature of 77K in vacuum as a part of a temperature sweep. The measurements in Fig. 4.3 were performed on 10000$\mu$m$^2$ planar MOS capacitors as shown in Fig. 4.2. The planar design offers an advantage it allows for the contact pads to be extended to arbitrary size and precludes the need to probe directly over the active area. However, this comes at the cost of introducing an additional parasitic capacitance/inductance into the measurement data which should be accounted for.

When performing CV measurements, it is essential the devices do not demonstrate a DC leakage which would otherwise obscure the effect of $C_q$ and $C_{\text{it}}$. In the case of a significant DC leakage, a non-saturating capacitance will be observed in conjunction with appreciable low frequency conductance ($> 1\mu\text{S}$) making an estimation of $D_{\text{it}}$ impossible by either the CV or GV method. In all CV curves presented in the following sections, the mean low frequency conductance was observed to be $< 1\mu\text{S}$.
Upon examination, several effects are visible. Both materials exhibit a local minimum in capacitance which corresponds to \( v_D \). As both materials are intercalated, \( v_D > 0 \) indicating hole density at zero bias. The CV curves are approximately symmetric around \( v_D \), which is a direct consequence of the fact that the density of states relations \( \rho_{m,b}(\epsilon_f) \) are symmetric about \( \epsilon_f = 0 \) in both materials. Moving away from \( v_D \) in either direction, the capacitance increases and subsequently saturates indicating accumulation of carriers at the graphene/oxide interface. In saturation, \( C_q \gg C_{ox} \) such that the oxide capacitance may be estimated. From the measured CV curves, one finds an oxide capacitance of 34(32)\( \text{pF} \) and corresponding static dielectric constant \( \kappa = 5.76(5.42) \) of for the monolayer and bilayer devices respectively. This estimation of \( \kappa \) is somewhat lower than the 8.9-11.1 seen in \( \alpha-\text{Al}_2\text{O}_3 \) and reflects the amorphous nature of the material.\(^{87}\) Generally, these features will reincarnate in the transistor context such that the CV curves should serve as a template for interpreting \( i_d(v_g) \) curves.

Both the monolayer and bilayer graphene exhibit dispersion in their CV characteristics indicating a nonzero density of interface states in both materials. The extraction of \( D_{it} \) via the CV and GV methods is shown in 4.4. For the data shown, the CV(GV) methods yield a peak \( D_{it} \) of 3.75(1.75)\( \cdot 10^{12}\text{eV}^{-1}\text{cm}^{-2} \) for the monolayer material and 1.51(1.50)\( \cdot 10^{12}\text{eV}^{-1}\text{cm}^{-2} \) for the bilayer material respectively. This should be compared with 5 \( \cdot 10^{10}\text{eV}^{-1}\text{cm}^{-2} \) and \( 10^{11}\text{eV}^{-1}\text{cm}^{-2} \) achieved in silicon and SiC MOS devices respectively.\(^{88,89}\)

Fitting to Eqs. 4.11(4.12) for the emission lifetime \( \tau_e \) yields 0.82(0.55)\( \mu\text{s} \) for the monolayer material and 0.34(0.38)\( \mu\text{s} \) for the bilayer material respectively. It should be noted that the peaks observed in \( D_{it} \) and \( G \) curves are likely artificial. This can be seen by noting that \( \epsilon_f \in [-0.32, 0.28\text{eV}] \) for the monolayer material and \( \epsilon_f \in [-0.23, 0.20\text{eV}] \) for the bilayer material over the applied bias range \( v \in [-2, 2\text{V}] \). In other words, the measurement only probes a 0.60eV energy interval near the middle of the dielectric bandgap. The \( D_{it} \) for such a limited energy range are in most cases rather flat (e.g for SiO\(_2\) and Al\(_2\)O\(_3\) on SiC and Si) such that the peak near the \( v_D \) is artifact of the extraction.
4.2. CV/GV MEASUREMENTS IN GRAPHENE MOS

Figure 4.4: [left] Extraction of the emission lifetime $\tau_e$ via Eq. 4.11. (inset) $D_{it}$ as calculated from Eq. 4.9 including the scaling factor $D_0$. [right] Extraction of $\tau_e$ via the conductance method Eq. 4.12. (inset) Measured conductance curves for monolayer (black) and bilayer (red) material. The 1kHz and 1MHz, while intermediate frequencies are shown dashed.

4.2.1 Modeling GMOS Capacitors

Fig. 4.3 also contains modeled CV curves. In order to accurately model the curves, it is necessary to account for surface potential fluctuations, material anisotropy, and an induced energy gap in bilayer material. Surface potential fluctuations are generated by charge inhomogeneities at the substrate and oxide interfaces.\textsuperscript{90–92} These charge inhomogeneities generate a spatial variation in the potential at the graphene layer and can arise due to a variety of effects such as fixed oxide charge, interface roughness, material anisotropy (i.e. terraces and inclusions), the presence of charged impurities, and a non-uniform graphene substrate interaction. Local variations in the surface potential imply local fluctuations in Fermi energy $\delta\epsilon_f$.

In graphene, surface potential fluctuations are most significant near $\epsilon_f = 0$. A nonzero $\delta\epsilon_f$ implies that the graphene will exhibit localized islands of electron and hole conduction (i.e. electron/hole puddles).\textsuperscript{90} In a CV measurement, the effect of surface potential fluctuations is most readily observed near $\nu_D$ where statistical variations in the Fermi energy have a large effect on the quantum capacitance $C_q$. In absence of surface potential fluctuations, one has that $\rho_{ph}(0) = 0$ such that the total high frequency capacitance should sharply approach zero for $\nu_D \approx 0$ (Eq. 2.27). The effect of fluctuations near $\epsilon_f = 0$ is to create a finite number of carriers near the Dirac point such that a distributed capacitance minimum is observed.\textsuperscript{83,93}

In order to determine the statistical distribution of surface potential fluctuations, frequency modulated Kelvin Probe Force Microscopy (KPFM) is performed on small 25\textmu m$^2$ van der Pauw (vdP) structures. KPFM is a scanning probe (SPM) technique which allows for the investigation of the local variations in the surface potential and work function in materials by measuring the potential difference between the probe tip and a grounded sample.\textsuperscript{94} As graphene is sensitive to atmospheric conditions, it is necessary to perform work function investigations in a controlled atmosphere.\textsuperscript{77,95,96} From the KPFM measurements, it is possible to motivate a model for surface potential fluctuations. One can assume that
for any given bias, the local Fermi energy will be normally distributed (see. Fig. 4.5).

\[ \tilde{\epsilon}_f = \mathcal{N}(\epsilon_f, \sigma) \]  \hspace{1cm} (4.13)

Here the term \( \mathcal{N} \) denotes a normally distributed random variable of mean \( \epsilon_f \) and standard deviation \( \sigma \). Here \( \sigma \) describes the behavior of potential fluctuations.

\[ \sigma(\epsilon_f) = \delta \epsilon_f \cdot \exp \left( \frac{-\epsilon_f^2}{2\delta \sigma_f^2} \right) \]  \hspace{1cm} (4.14)

In Eq. 4.14, the term \( \delta \epsilon_f \) represents the standard deviation in surface potential fluctuations at \( \epsilon_f = 0 \). The additional exponential term appearing in Eq. 4.14 describes a case where the magnitude of the surface potential fluctuations decays with standard deviation \( \delta \sigma_f \) as one moves further from the Dirac point.

In Si MOS and SiC MOS capacitors the estimate of the surface potential fluctuations is typically independent of bias, and values of 25-40meV and 30-100meV respectively are reported.\(^97, 98\) In the graphene MOS capacitors, values of 80-90 meV are extracted from the CV curves. This is in good agreement with the 100meV which is estimated in exfoliated monolayer FETs on SiO\(_2\).\(^93\) These values are similar to the 80meV obtained from KPFM measurements on clean intercalated monolayers suggesting that monolayer(bilayer) inclusions strongly contribute to surface potential fluctuations. Other contributing factors might include fixed charges and interface states in the oxide.

When modeling CV curves, the term \( \delta \sigma_f \) should be large such that the statistics of surface potential fluctuations are described by a pure normal distribution with mean \( \epsilon_f \) and standard deviation \( \delta \epsilon_f \). Generally the term \( \delta \sigma_f \) is found to be of order 150meV such that near the Dirac point \( \sigma = \delta \epsilon_f \). The left and center plots in Fig. 4.6 illustrate the effect of surface fluctuations on the CV curve.
4.2 CV/GV Measurements in Graphene MOS

Figure 4.6: [left(center)] A demonstration of the sensitivity of modeled CV curves on surface potential fluctuations for monolayer(bilayer) material. $\delta\epsilon_f$ is scaled linearly from 0meV to the values arrived at by modeling 118(80)meV. [right] A similar demonstration regarding the $\epsilon_g$ in the case of bilayer material. In all plots the measured CV curve is shown in red while modeled curves are shown in black.

Potential fluctuations on simulated CV curves for the case of monolayer and bilayer material respectively. Measured CV traces are also shown for both materials. A sharp capacitance minimum occurs when surface potential fluctuations are not present. Increasing $\delta\epsilon_f$ leads the development of the distributed capacitance minimum observed in both materials.

The presence of a narrow energy gap $\epsilon_g$ in the case of bilayers arises due to a symmetry breaking of the bilayer Hamiltonian as described in Chapter 2. The symmetry breaking occurs when a potential difference exists between the layers. An analogous case does not exist in the case of a monolayer as an energy gap would only open in the case of a broken symmetry with regard to the $a$ and $b$ sublattices (see Fig. 2.4). A potential difference in the bilayer may be induced either via application of a strong electric field, or due to the presence of surface charges at the graphene/substrate ($D_{it}\Delta P$) and graphene/oxide ($D_{it}$) interfaces.

The effect of an energy gap ($\epsilon_g$) may be included by considering the dispersion of Eq. 2.16 for $\Delta \neq 0$ and calculating the corresponding density of states via Eq. 2.23. However, in the case of an induced gap in a large area MOS capacitor, $\Delta$ is likely to vary due to spatial fluctuations in sources of surface charge density ($D_{it}, D_{it}^{st}$, $\Delta P$). In this case, an empirical model of the energy gap is viable. Physically, an energy gap describes a region in energy where the density of states becomes zero as a consequence of the band structure $\rho(\epsilon) = 0$. This can be enforced by considering the bilayer density of states to take the following form.

$$\rho_b(\epsilon) = \rho^0_b(\epsilon)\rho_g(\epsilon : \epsilon_g, \sigma_g)$$

(4.15)

In Eq. 4.15, $\rho^0_b(\epsilon)$ represents the density of states in the case of $\Delta = 0$ as given by Eq. 2.29. The term $\rho_g(\epsilon : \epsilon_g, \sigma_g)$ enforces the gap by cutting a smoothed notch out of $\rho^0_b(\epsilon)$.

$$\rho_g(\epsilon : \epsilon_g, \sigma_g) = 1 - \frac{1}{2}\text{erfc}\left(\frac{\epsilon + \epsilon_g/2}{\sqrt{2}\sigma_g}\right) + \frac{1}{2}\text{erfc}\left(\frac{\epsilon - \epsilon_g/2}{\sqrt{2}\sigma_g}\right)$$

(4.16)
Though heuristic, this approach is justified by noting that the $\rho_0^0(\epsilon)$ in the $\Delta \neq 0$ approaches that of $\Delta = 0$ when $|\epsilon_f|$ is large.

The presence of an induced gap can be appreciated by examining the CV curves shown in Fig. 4.3. In a bilayer, $C_q \neq 0$ when $\epsilon_f = 0$. Evaluating the quantum capacitance $C_q = e^2\rho_0^0(\epsilon)$ in the case of a bilayer one finds a value of $4.170\mu F/cm^2$. Multiplying by the total area of the MOS capacitors in question, one finds a total capacitance of $471pF$. By contrast, the observed oxide capacitance is $C_{ox}A \approx 33pF$. Thus, the minimum expected capacitance in a high frequency CV measurement on bilayer material is $30.8pF$. In other words, a gapless bilayer would produce a nearly flat CV characteristic in contrast to what is observed in the measurement data. From CV modeling, an induced gap of $\epsilon_g \approx 250meV$ is found for the bilayer case. The effect of the nonzero energy gap is shown in the modeled CV curves shown in Fig. 4.6. For $\epsilon_g = 0$ a nearly flat CV characteristic is obtained. As $\epsilon_g$ increases, the CV characteristic deepens around $\epsilon_f = 0$ and approaches what is observed in measured data.

In the case of exfoliated bilayers a tunable gap has been demonstrated via the application of a vertical electric field.\textsuperscript{31} Energy gaps of up to $250meV$ have been reported in the literature on exfoliated bilayers on SiO\textsubscript{2};\textsuperscript{99} and theory predicts a maximum opening of $300meV$.\textsuperscript{99–101}

An interesting case occurs in the case of epitaxial bilayers on SiC in which substrate interface charges $D_{int}$ and spontaneous polarization $\Delta P$ can provide the charge densities needed for a symmetry breaking material. Such a substrate induced gap of $140meV$ has been shown in the case of native bilayers layers on 4H-SiC.\textsuperscript{102} For the intercalated bilayers on 6H-SiC shown in Fig. 4.3, the induced gap is generated via $D_{it}$ and $\Delta P$, with $\Delta P$ being providing the dominant contribution to symmetry breaking.

As may be seen in Figs. 4.2, and 3.6 the graphene layer is far from uniform. This property is inherited from the growth process where monolayer(bilayer) material forms on terraces and bilayer(multilayer) material forms on terrace edges.\textsuperscript{103,104} Additionally, on monolayer(bilayer) terrace regions may have inclusions of bilayer(monolayer/multilayer) material as may be seen in Figs. 4.5, 6.1, 6.2, and 6.3. It is straightforward to account for this in CV measurements by considering the density of states to be a linear combination of the monolayer and bilayer results.

$$\rho_{eff}(\epsilon) = p\rho_m(\epsilon) + (1-p)\rho_b(\epsilon) \quad (4.17)$$

Here, the quantity $p$ represents the mixing ratio of monolayer area to the total area of the device. In order to gain a feeling for $p$, a combination of SEM and AFM imaging may be performed. Terraces and terrace edges are clearly visible on the surface of the substrate. In the case of the measured devices, a value of $0.8(0.1)$ is obtained for $p$. The above relation allows for a realistic estimation of the density of states when computing $\epsilon_f(v_g)$.

### 4.2.2 Hysteresis and Charge Injection

When measuring the CV characteristic as a function of temperature, several effects are observed (Fig 4.7). Most notably, a hysteresis of anti-clockwise orientation gradually opens in both monolayer and bilayer material for temperatures(thermal energies) greater than $160K(13.7meV)$. Hysteresis is a common problem in the context of graphene field effect transistors and has been attributed to a variety of trapping mechanisms.\textsuperscript{105–110} The orientation of the hysteresis is significant and suggests a charge injection effect.\textsuperscript{111,112}
Figure 4.7: Measured CV curves as a function of temperature and frequency for monolayer (black) and bilayer (red) MOS capacitors. A hysteresis in the CV characteristic opens in both materials around 160K suggesting a thermally activated trap related effect. Arrows indicate the clockwise orientation of the hysteresis.

The hysteresis observed in graphene MOS may be understood by considering different charging conditions on the forward \((v_1 \rightarrow v_2)\) and return sweeps independently \((v_2 \rightarrow v_1)\). In the case of no charge injection, the Dirac voltage on the forward sweep \((v_D^f)\) will be equivalent to the Dirac voltage observed on the return sweep \((v_D^r)\). Now consider a situation in which some quantity of negative charge is injected into the oxide. In this case more positive bias will be required to raise \(\epsilon_f\) to zero as it would have to compensate for the negative charge stored in the oxide. Thus, if charge injection occurs during the forward sweep, the Dirac voltage on the return sweep will appear to the right of the Dirac voltage on the forward sweep \((v_D^r > v_D^f)\) generating hysteresis.

The charge injection effects observed in the graphene MOS case can be understood by examining the behavior of the Dirac voltage on the forward \((v_D^f)\) and reverse \((v_D^r)\) sweeps (Fig. 4.8 inset). In both the monolayer and bilayer devices, \(v_D^f\) is nearly constant with temperature suggesting that \(v_D^f \approx v_D\). However, as temperature increases \(v_D^r\) drifts towards positive bias indicating charge injection. For \(v < v_D\), the devices exhibit hole conduction, and no charge injection occurs. However, for \(v > v_D\) the devices exhibit electron conduction and charge injection begins to occur. This causes \(\epsilon_f\) to lag behind as negative charge becomes trapped in the oxide. On the return sweep, the accumulation of negative charge results in a CV curve which is shifted towards positive bias on the return sweep.

The hysteresis effect becomes more severe with increasing temperature. In monolayer (bilayer) material a maximum opening of 430(520)mV is seen at 280K indicating similar levels of charge injection in both materials. The hysteresis is clearly an oxide related effect, as the CV characteristics are otherwise somewhat different in monolayer and bilayer devices.
Figure 4.8: [left] The zero bias capacitance measured in monolayer graphene as a function of temperature for several frequencies. [right] Measured CV curves at 300K consisting of repeated hysteresis sweeps of increasing amplitude for monolayer material. A consistent drift of the capacitance minimum towards positive bias is observed indicating permanent charge injection into the oxide. (inset) Extracted $v_f^D$ (dashed) and $v_r^D$ (solid) for the temperature dependent CV curves shown in Fig. 4.7.

The effect of oxide charging tends to be deleterious to with regard to charge control as the lagging of $\epsilon_f$ behind $v$ generates a more shallow slope accompanied with additional broadening in the CV characteristic on either side of $v_D$. The charge injection hysteresis is observed at all frequencies owing to the fact that it is essentially DC effect. The frequency relevant to charge injection is the sweep rate of the applied bias rather than that of the applied test signal.

In order to further investigate the charge injection hysteresis, the zero bias capacitance is measured as a function of temperature for several frequencies. A monotonic decrease in capacitance is observed as shown in the left plot of Fig. 4.8. As temperature decreases, carriers in the graphene no longer have access to the trap state responsible for hysteresis such that the decrease in capacitance is expected. A similar decrease in capacitance along with hysteresis has also been observed in MOS capacitors fabricated in transferred graphene layers in SiO$_2$ with an Al$_2$O$_3$ gate dielectric grown by atomic layer deposition. Upon further increasing the temperature to 300K, charge injection becomes severe as shown in repeat sweep experiments summarized in the right plot of Fig. 4.8. Upon repeated CV sweeps of increasing amplitude, a strong hysteresis is observed. A drift of the capacitance minima towards positive bias is also seen indicating permanent injection of negative charge into the oxide layer.
Electron Devices in Epitaxial Graphene

High frequency electron devices are an attractive yet challenging avenue for graphene from an application perspective, and significant research interest has been directed towards the development of competitive devices in transferred, exfoliated and epitaxial layers. Such devices may find use in a variety of applications including microwave integrated circuits, high frequency electromagnetic detectors, and optoelectronic devices. Proof of concept high-frequency mixers,\textsuperscript{113} amplifiers,\textsuperscript{114–116} oscillators,\textsuperscript{117} and power detectors\textsuperscript{118–121} have been presented demonstrating the versatility of the material. In conjunction with theoretical considerations, the electron transport and charge control experiments presented thus far represent a bridge to understanding fundamental aspects of device operation. Further, they provide a context in which to outline performance limits and develop effective design strategies. Epitaxial layers grown on semi insulating SiC hold the most promise from the application perspective as large area samples can be prepared. The epitaxial technique also offers adequate design flexibility as samples can be prepared with a controlled number of layers and may be optionally intercalated with hydrogen to produce quasi free standing layers which offer enhanced transport properties.

5.1 Graphene Field Effect Transistors

Fig. 5.1 shows a scanning electron micrograph of a graphene field effect transistor (FET) along with two associated schematics describing the design and intrinsic small signal model of the device. In a graphene FET, the transport and charge control properties determine the behavior of the current density ($J$) and transconductance ($g_m$) in the device as a function of the applied gate voltage ($v_g$) and drain voltage ($v_d$). As the CV characteristic in graphene MOS is symmetric about $v_D$, a similar behavior is expected in the $g_m$ observed in the GFET case. In GFETs, a minimum(zero) is expected in the current density and transconductance is expected when $v_g$ crosses $v_D$. In contrast to the CV case, $J$ and $g_m$ are usually not symmetric about $v_D$ due to electron/hole conduction asymmetry ($\mu_n \neq \mu_p$).\textsuperscript{122,123}

Example DC characteristics for monolayer and bilayer graphene FETs are shown in Fig. 5.2 for several gate lengths ($l_g$). In both materials, a very high current density of order 2A/mm is observed. In bilayer devices shown, a maximum transconductance of about
Figure 5.1: [left] A scanning electron micrograph of a coplanar 2x50 μm dual gated GFET. The top(bottom) contacts are the gate(drain) respectively. The left and right contacts are the coplanar source. The gate length is 1 μm. [right] A device schematic and two-port small signal intrinsic device model with some important parameters labeled. The transconductance $g_m$ and output conductance $g_d$ constellate results from charge control and electron transport considerations respectively.

700 mS/mm, and values of up to 1200 mS/mm have been observed on similar devices. By contrast, monolayers typically exhibit a lower transconductance on the order of 100-200 mS/mm reflecting reduced current modulation. In the bilayer GFETs, the maximum transconductance ($g_m^{\max}$) occurs for a $v_g(v_d)$ of $-0.1 (-1.2)$ V. In the devices, the gate is positioned symmetrically between the source and drain such that the potential under the gate may be approximated $-0.6$ V. Thus at low drain bias, one expects $g_m^{\max}$ to occur near $v_g = 0.5$ V. In a transistor measurement, $v_D$ will always shift in the same direction as the applied drain bias $v_d$. As hydrogen intercalated layers are p-type ($v_D > 0$), a negative drain bias is desirable as it tends to shift $v_D$ towards lower bias.

The non-idealities described in the graphene MOS capacitors lend further insight into the GFET transfer characteristics. The low(high) current modulation in the monolayer(bilayer) devices correspond to the low(high) capacitance modulation observed in the 1kHz CV curves shown in Fig. 4.3. Transport considerations suggest that the dominant scattering mechanism in intercalated monolayers(bilayers) is charged impurity(short range) scattering. This implies that the $\mu$ is independent of carrier density in both materials. In this case, the on/off ratio may be estimated by the ratio of maximum/minimum carrier densities that can be reached during device operation.

$$i_{on}/i_{off} \approx n(\epsilon_f^{acc})/n(0) \quad (5.1)$$

Here, $n(\epsilon_f^{acc})$ represents the carrier density in accumulation, and $n(0)$ represents the intrinsic carrier density (Eq. 2.32). At 300K, the intrinsic carrier densities $n(0)$ in monolayer(bilayer) material are $0.16(1.20) \cdot 10^{12}$ cm$^{-2}$. If the carrier density in accumulation is of order $10^{13}$ cm$^{-2}$, then one expects a maximal on/off ratio of 62.5(8.3) for the monolayer(bilayer). As previously described, surface potential fluctuations reduce the amount of modulation that can be achieved in the graphene layers (Fig. 4.6). In this case $n(0)$ in Eq. 5.1 must be replaced
5.1. GRAPHENE FIELD EFFECT TRANSISTORS

Figure 5.2: Typical DC characteristics for hydrogen intercalated monolayer(left) and bilayer(right) transistors on 4H-SiC. The main plot shows the output characteristics $i_d(v_d)$, and the inset shows the transfer characteristics $g_m(v)$. Results are shown for several gate lengths $l_g \in [1.0, 0.5, 0.25 \mu m]$ in order to illustrate the scaling properties. The gate widths $w_g$ for the mono-layer(bilayer) devices are $2x24(1x12) \mu m$ respectively.

with $n(\delta \epsilon_f)$ where $\delta \epsilon_f$ represents the magnitude of surface potential fluctuations. From CV measurements, one has $(\delta \epsilon_f \approx 90$meV) such that $n(\delta \epsilon_f)$ becomes $2.0(7.0) \cdot 10^{12}$cm$^{-2}$. The corresponding on/off ratio is then $5.0(1.4)$ for the monolayer(bilayer) respectively.

Current modulation in both materials is further aggravated by the relatively high density of interface states ($D_{it}$) in the MOS structure. In the case of monolayer material, the $D_{it}$ destroys the remaining current modulation as may be inferred from the respective 1 kHz CV curve (Fig. 4.3). The filling of interface states tends to screen out the already compromised modulation of the carrier density in the channel. Incidentally, this effect explains the lack of a well defined peak in the transconductance curves shown in Fig. 5.2. In bilayer devices, appreciable current modulation still observed despite a similar $D_{it}$ and $\delta \epsilon_f$. This is in agreement with CV data, and further supports the notion of a narrow substrate induced energy gap in bilayers $\epsilon_g \approx 250$meV.

Another feature common to devices in monolayer and bilayer graphene is the lack of current saturation at high drain bias. This gives rise to a nonzero output conductance ($g_d$) which compromises device performance. In the conventional MOS case (i.e. silicon), saturation occurs due to the influence of the drain voltage on the carrier density near the drain contact. At high drain bias the gate can no longer support the inversion layer near the drain such that a depletion condition manifests which precipitates current saturation. In the case of monolayer and bilayer graphene no such depletion condition exists precluding saturation. However, in a bilayer, the narrow energy gap may manifest as a stronger saturation in the current density and a reduced output conductance. In the monolayer(bilayer) devices shown in Fig. 4.3, a minimum output conductance of $210(150)$mS/mm is observed in line with these arguments.

In summary, the DC characteristics indicate immediate challenges toward a competitive high frequency device in graphene. In the case of monolayers, the role of surface potential fluctuations and interface states undermines current modulation ($g_m$), while in bilayer mate-
Table 5.1: A table comparing hydrogen intercalated epitaxial monolayer (h-MLG) and bilayer (h-BLG) graphene to other device technologies. t-MLG indicates transferred monolayer graphene grown by CVD on Cu. For the graphene devices, the substrate material is also indicated. In the case of bilayers on SiC, the estimated induced energy gap is listed. $v_{\text{sat}}$ for the monolayer and bilayer devices is calculated via Eq. 3.25 via Hall measurements of the carrier density.

For GaAs and InP PHEMTs the peak(saturation) velocities are reported as these materials demonstrate velocity overshoot due to intervalley scattering. In the HEMT devices, the energy gap, mobility, and saturation velocity are reported for the transport layer. For the bipolar devices (InP/SiGe) transport properties are listed for the base material, and the mean $\epsilon_g$ is estimated for the emitter(base) materials respectively. In the InP(SiGe) technologies, the value of $x$ is typically graded from 0.53-0.68(0.15-0.25) across the base.

In addition, both devices suffer from an appreciable $g_d$ which is deleterious from the high frequency perspective. In the following sections, the frequency behavior of GFETs and the problem of hysteresis are investigated in the context of measured GFET data.

### 5.1.1 Frequency Performance and Scaling Effects

In light of the device results presented in the previous section, it is important to describe some performance limitations in epitaxial GFETs. From transport and charge control considerations, two fundamental limitations on device performance emerge. With regard to transport, scattering via surface optical phonons modes in the substrate implies a limitation on $v_{\text{sat}}$ (Eq. 3.25). This can be seen via the definition of the transport limited transit frequency ($f_t$).

$$f_t^{\text{max}} = \frac{v_{\text{sat}}}{2\pi l_g} = \frac{\epsilon_g^{\text{max}}}{l_g\pi^2\sqrt{\pi n}}$$  \hspace{1cm} (5.2)

In Eq. 5.2, $l_g$ represents the gate length of the device and $n$ represents the carrier density. Eq. 5.2 immediately implies a limitation on transit frequency as carrier densities in inter-
5.1. GRAPHENE FIELD EFFECT TRANSISTORS

### Table 5.2
The scaling properties of the hydrogen intercalated monolayer and bilayer FETs shown in Fig. 5.2. The transit frequency $f_t$ and maximum frequency of oscillation $f_{\text{max}}$ are reported in GHz, and the maximum transconductance $g_{\text{max}}$ is reported in mS/mm. The superscript in each column indicates the gate length in $\mu$m.

<table>
<thead>
<tr>
<th>Technology</th>
<th>$f_t^{1.0}$</th>
<th>$f_t^{0.5}$</th>
<th>$f_t^{0.25}$</th>
<th>$f_{\text{max}}^{1.0}$</th>
<th>$f_{\text{max}}^{0.5}$</th>
<th>$f_{\text{max}}^{0.25}$</th>
<th>$g_{\text{m}}^{1.0}$</th>
<th>$g_{\text{m}}^{0.5}$</th>
<th>$g_{\text{m}}^{0.25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-MLG(Si-SiC)</td>
<td>9.0</td>
<td>14</td>
<td>17</td>
<td>8.5</td>
<td>11</td>
<td>17</td>
<td>120</td>
<td>95</td>
<td>87</td>
</tr>
<tr>
<td>h-BLG(Si-SiC)</td>
<td>12</td>
<td>28</td>
<td>38</td>
<td>11</td>
<td>25</td>
<td>26</td>
<td>470</td>
<td>650</td>
<td>510</td>
</tr>
</tbody>
</table>

Calculated layers are typically about $10^{13}$ cm$^2$. Substituting for the surface optical mode in hexagonal SiC ($\epsilon_{\text{max}}^\Delta \approx 115$ meV) yields $f_{\text{max}}^{\text{int}} \cdot l_g \approx 31.5$ GHz $\cdot \mu$m for the transport limited intrinsic transit frequency at zero gate bias. It should be noted that this figure does not consider scattering with surface optical modes in the dielectric and is therefore optimistic. In a real device, the measured transit frequency will be less than this optimal value and will depend on the degree to which the gate can control the current density in the channel. Expressing the transit frequency in terms of transconductance yields the following expression.

$$f_{\text{int}}^{\text{int}} = \frac{g_{\text{m}}}{2\pi \sqrt{C_{\text{gs}}^2 + 2C_{\text{gs}}C_{\text{gd}}}}$$  \hspace{1cm} (5.3)$$

In Eq. 5.3, $g_{\text{m}}$ represents the transconductance, $C_{\text{gs}}$ the gate source capacitance, and $C_{\text{gd}}$ the gate drain capacitance as shown in Fig. 5.1. Note that Eq. 5.3 represents the intrinsic transit frequency (i.e. excluding parasitic effects). Electron transport enters into Eq. 5.3 via $g_{\text{m}}$ which is generally proportional to $\mu$. The effect of a high output conductance is important when considering the maximum frequency of oscillation ($f_{\text{max}}$).

$$f_{\text{max}} = \frac{f_t}{2\sqrt{g_d(r_g + r_s) + 2\pi f_t r_g C_{\text{gd}}}}$$  \hspace{1cm} (5.4)$$

In Eq. 5.4, $r_s$ and $r_g$ represent the parasitic source and gate resistances respectively. The effect of a large $g_d$ is to decrease the maximum frequency of oscillation. In graphene FETs, the large $g_d$ typically manifests as $f_{\text{max}} \leq f_t$.

S-parameter measurements of $f_{\text{ext}}^{\text{int}}(f_{\text{max}})$ on epitaxial monolayer and bilayer FETs yield values of 17(17)GHz and 38(26)GHz respectively for devices with $l_g = 0.25 \mu$m. Generally, intercalated layers tend to perform better than native layers, and an increase of $f_{\text{ext}}^{\text{int}}$ from 2.3GHz to 7.3GHz was demonstrated for monolayer GFETs with intercalation ($l_g = 1 \mu$m). Further improvement of $f_{\text{ext}}^{\text{int}}$ to 23GHz was achieved via scaling of the gate length to 0.25$\mu$m in the intercalated monolayers.\textsuperscript{147} The value $f_{\text{max}}^{\text{int}}$ represents the maximum that would be expected upon de-embedding parasitic effects. In the case of 0.2$\mu$m intercalated bilayer GFETs, de-embedding yielded an $f_{\text{int}}^{\text{int}}(f_{\text{max}})$ of 135(120)GHz yielding an $f_t \cdot l_g$ product of 26.5GHz which adheres well to the theoretical maximum ($f_{\text{int}}^{\text{int}} \leq f_{\text{max}}^{\text{int}}$).\textsuperscript{148}

It is interesting to compare the case of the intercalated layers on SiC with that of transferred graphene layers on diamond.\textsuperscript{126} Diamond is an ideal substrate for graphene as it has a high energy surface optical mode $\epsilon_{\text{max}}^\Delta \approx 150$ meV.\textsuperscript{124} Graphene on diamond should thus demonstrate superior frequency performance when compared to identical devices on SiC.
CHAPTER 5. ELECTRON DEVICES IN EPITAXIAL GRAPHENE

Monolayer GFETs on diamond demonstrate an $f_t(f_{max})$ of 70(13)GHz. This is considerably higher than the values observed in epitaxial layers on SiC despite the significantly lower transconductance. In this case, the low transconductance is likely due to the fact that the mobility in transferred layers is typically lower ($<1500\text{cm}^2/\text{V} \cdot \text{s}$) than that of epitaxial layers as a consequence of the transfer process.

Table 5.1 compares graphene to several other device technologies with regard to mobility, velocity saturation, transconductance, and frequency performance. Of the devices shown, only the second intercalated bilayer device demonstrates a competitive $f_t \cdot l_g$ product suggesting that high frequency performance can be achieved with scaling. The scaling properties for the GFETs shown in Fig. 5.2 are reported in Table 5.2. In both materials, the scaling properties are sublinear such that $f_t \cdot l_g$ drops with decreasing gate length as a consequence of increased output conductance in conjunction with the onset of short channel effects.

5.1.2 Hysteresis and Instability

As with graphene MOS capacitors, electron trapping at the graphene-dielectric and graphene-substrate interfaces are found to command significant influence over the transfer characteristics observed in graphene MOS transistors. In the case of the measurements shown in Fig. 5.3, a strong hysteresis of clockwise orientation is observed. The hysteresis loops are similar to those seen in temperature dependent CV measurements (see Fig. 4.7). The hysteresis effect introduces a severe bias dependent instability into device operation which represents a major technological challenge. The GFET hysteresis is not unique to hydrogen intercalated graphene and both clockwise and anti-clockwise varieties have been observed in a range of materials including exfoliated flakes, transferred large area layers on SiO$_2$ and SiO$_2$/Si$_3$N$_4$, and native layers on SiC grown by CVD and sublimation.

Hysteresis in MOS structures is usually attributed to charge trapping at the semiconductor dielectric interface, ion drift within the insulator, or space charge effects related to dielectric polarization. Electron trapping in the dielectric always introduces a hysteresis of anti-clockwise orientation, whereas polarization and space charge effects generate a hysteresis with clockwise orientation. The field effect hysteresis is not unique to graphene. Gate hysteresis has been observed in a variety of semiconductor materials such as AlGaAs/GaAs heterostructures, AlGaN/GaN heterostructures, and SiC MOS structures. Technology development often aims at the elimination of hysteretic phenomena for the purpose of reducing bias dependent instabilities.

The current density versus gate voltage curves ($i_d(v_g)$) shown in Fig. 5.3 are typical for what is observed in hydrogen intercalated graphene MOS devices. The measurements were performed on $l_g = 1\mu\text{m}$ bilayer FETs at low drain bias (50mV) to preclude short channel effects and to keep the channel in the low field transport regime.

A conductance minimum is observed at positive bias in all measurements indicating hole conduction at zero gate bias. The orientation of the hysteresis shown in Fig. 5.3 contrasts to the case of the hysteresis observed in CV measurements where a anti-clockwise orientation is observed reflecting different properties of the field oxides deposited in the respective devices. In the MOS capacitor case, oxide was deposited via cyclic evaporation of aluminium metal, while in the transistor case, deposition was performed via seeded atomic layer deposition (ALD).
5.1. GRAPHENE FIELD EFFECT TRANSISTORS

Figure 5.3: DC hysteresis measurements of $i_d(v_g)$ in hydrogen intercalated bilayer graphene FETs on 4H-SiC. Black curves represent measured data, red curves represent modeled data, and blue curves represent hysteresis free simulations obtained from hysteresis modeling. In each successive measurement, the sweep range of the bias is increased. In all measurements, the drain bias is held at a constant 50mV.

The anti-clockwise hysteresis in the CV measurements was determined to be temperature dependent indicating a thermally generated trap mechanism. This is different than what is observed in the ALD case where the clockwise orientation suggests a polarization effect. Although crystalline Al$_2$O$_3$ is not ferroelectric, CV measurements on evaporated Al$_2$O$_3$ films embedded with Ag nanoparticles reveal a strong hysteresis of clockwise orientation, while complementary measurements on evaporated Al$_2$O$_3$ films grown without metal nanoparticles reveal no hysteresis.\textsuperscript{159} Analogous results have been observed in SiO$_2$ films with embedded Si nanoparticles.\textsuperscript{160} A similar process may be responsible for the ferroelectric-like hysteresis observed in the GFETs. In this case, oxygen vacancies may be introduced unintentionally into the dielectric interface via incomplete oxidation of the aluminium nucleation layer thus generating a space charge hysteresis similar to what is observed in [159] and [160].

5.1.3 Modeling Hysteresis

In addition to providing insight into the origin of the hysteresis effect, an accurate hysteresis model provides a deeper understanding into the electron transport and charge control properties of graphene MOS transistors. In order to model hysteresis, one first considers the current expression density given by Eq. 4.1. Note that the current density is expressed as a function of Fermi energy and electric field $J = J(\epsilon_f, E)$. To arrive at a complete model one must transform $\epsilon_f \rightarrow v_g$ and $E \rightarrow v_d$. The first of these transformations is achieved via Eq. 4.8, while the second is achieved by considering the voltage drop across the contacts, as well as the sheet resistance of the graphene sheet in a manner analogous to the case of...
velocity field modeling (see Eq. 3.33).

Two approaches may be taken to generate a hysteresis in current density \( J \). First, one may consider a delay equation in which the current density at time \( t \) is a function of the Fermi energy at time \( t - \tau \). Although such a model is straightforward in practice, it is only applicable in the case of systems governed by a single time constant. A more sophisticated approach involving Preisach kernels \( (P[\epsilon_f]) \) may be also employed when systems exhibit a more complex time dependence. Given \( P[\epsilon_f] \) it is straightforward to calculate the hysteretic current density via the operator transform \( \epsilon_f \rightarrow P[\epsilon_f] \).

\[
J = e [\mu_n n_n(P[\epsilon_f]) + \mu_p n_p(P[\epsilon_f])] E
\]  

(5.5)

A Preisach kernel describes a weighted sum of an infinite number of relay elements \( (R_{\epsilon_0-\epsilon_\delta,\epsilon_0+\epsilon_\delta}) \). Such an operator was first introduced by Preisach in 1935 to describe the hysteresis in magnetic materials.\(^{161}\)

\[
P[\epsilon_f] = \int_{0}^{\infty} \int_{-\infty}^{\infty} \omega(\epsilon_0, \epsilon_\delta) R_{\epsilon_0-\epsilon_\delta,\epsilon_0+\epsilon_\delta}[\epsilon_f : \alpha] d\epsilon_0 d\epsilon_\delta
\]  

(5.6)

The behaviour of a single relay element behaves as shown in the left panel of Fig. 5.4 and may be described mathematically in the following way.

\[
R_{\epsilon_f-\epsilon_\delta,\epsilon_0+\epsilon_\delta}[\epsilon_f : \alpha] = A \begin{cases} 
\alpha \epsilon_f - 1, & \text{if } \epsilon < \epsilon_0 - \epsilon_\delta \\
\alpha \epsilon_f + 1, & \text{if } \epsilon > \epsilon_0 + \epsilon_\delta \\
\alpha \epsilon_f + \kappa, & \text{otherwise}
\end{cases}
\]  

(5.7)

In Eq. 5.7, the parameter \( A \) is a normalization factor and \( \epsilon_0 \) and \( \epsilon_\delta \) represent the location (energy) and half width of the relay.\(^{162}\) The term \( \kappa \) determines the orientation of the hysteresis. For an anti-clockwise relay, \( \kappa = -1 \) if \( \epsilon_f \) crosses the threshold \( \epsilon_0 - \epsilon_\delta \), and \( \kappa = 1 \) if \( \epsilon_f \) crosses the threshold \( \epsilon_0 + \epsilon_\delta \). A clockwise relay is obtained by transforming \( \kappa \rightarrow -\kappa \).

The introduction of the term \( \alpha \epsilon_f \) is a divergence from the traditional Preisach model for \( \alpha > 0 \). The effect of \( \alpha \) is to build the character of the input \( \epsilon_f(v_g) \) waveform into the relay operator. As \( \alpha \rightarrow \infty \) and \( A \rightarrow \alpha^{-1} \) then \( R_{\epsilon_f-\epsilon_\delta,\epsilon_0+\epsilon_\delta}[\epsilon_f : \alpha] \rightarrow \epsilon_f \).

The purpose of the weighting function \( \omega(\epsilon_0, \epsilon_\delta) \) is to assign a normalized weight to the functional relay \( R \) parameterized by \( \epsilon_0 \) and \( \epsilon_\delta \). In most hysteretic models, the density function is an analytic function in the \( [\epsilon_0, \epsilon_\delta] \) plane. Common choices include the elliptic Gaussian,\(^{163}\) the Lorentz distribution,\(^{164}\) and the Derivative Arc Tangent (DAT) function.\(^{165}\) Discrete density functions have also been successfully used to describe hysteretic systems.\(^{166}\)

When modeling DC characteristics in GFETs, the weighting function is assumed to obey the separation ansatz.

\[
\omega(\epsilon_0, \epsilon_\delta) = \omega_0(\epsilon_0) \omega_\delta(\epsilon_\delta)
\]  

(5.8)

The terms \( \omega_0 \) and \( \omega_\delta \) describe how the functional relays are distributed in terms of energy and half-width. The \( \omega_0 \) term describes how the dominant contribution to the hysteresis is in energy, while \( \omega_\delta \) along with the functional parameter \( \alpha \) describes the degree of hysteresis opening. For GFET hysteresis modeling, the difference of two Gaussian cumulative distribution functions is chosen for \( \omega_0 \) and \( \omega_\delta \).

\[
\omega_{0,\delta} = \frac{1}{2} \left[ \text{erf} \left( \frac{\epsilon_{0,\delta} - \epsilon_{0,0,\delta}}{\sqrt{2} \sigma_{0,\delta}} \right) - \text{erf} \left( \frac{\epsilon_{0,\delta} - \epsilon_{1,0,\delta}}{\sqrt{2} \sigma_{1,\delta}} \right) \right]
\]  

(5.9)
5.2. GRAPHENE NANOWIRE DIODE DETECTORS

Figure 5.4: [left] A single functional relay evaluated on a realistic $\epsilon_f(v_g)$ waveform as calculated via Eq. 4.4. (inset) The behavior of a functional relay (solid) vs. a simple relay (dashed) in the $\epsilon_f/\epsilon_f$ plane. [right] A Preisach kernel evaluated with an increasing density of equally weighted ($\omega(\epsilon_0, \epsilon_\delta) = 1$) simple ($\alpha = 0$) relays against sinusoidal load line. The kernel demonstrates asymptotic convergence to a continuous function as the number of relays tends toward infinity.

It is important that $\epsilon_{0,\delta}$ and $\sigma_{0,\delta}^i$ are selected such that $0 < \omega(\epsilon_0, \epsilon_\delta) < 1$ for all $\epsilon_0$ and $\epsilon_\delta$. This ensures that all relays in the Preisach kernel have the same orientation. The primary advantage of accurate hysteresis models is that they allow for the hysteresis to be removed from the $i_d(v_g)$ characteristic as shown in Fig. 5.3. This opens the possibility of developing accurate nonlinear models of GFET operation via the application of electron transport and charge control results.

5.2 Graphene Nanowire Diode Detectors

Graphene has also attracted interest in the area of high frequency photodetectors as a potential alternative to other technologies owing to its outstanding transport properties. Electromagnetic detection in the mm-wave and THz regions of the spectrum is difficult for two reasons. In the case of THz radiation, the frequencies involved (0.3-3THz) are sufficiently high such that carriers in a solid state device will not be able to follow the electric field of an incident photon (transport limitation). Simultaneously the energy scale (1-10meV) is smaller than a typical $\epsilon_g$ such that photovoltaic detection mechanisms are not possible (energy limitation). These two limitations are describe what is known as the “THz gap” in technology.

Detection of mm-waves (30-300GHz) is generally possible in a solid state context and can be achieved via a variety of methods. Common solutions include metal-semiconductor junctions (i.e. Schottky diodes), field effect transistors, and thermo-electric bolometers. The operating principles in the diode and FET solutions are identical; the nonlinear current voltage characteristic in the device generates a DC voltage ($v_{DC}$) on the input signal via rectification. For a given input power $P_{in}$, the responsivity of the detector is given by $\beta = v_{DC}/P_{in}$. Generally, a stronger non-linearity tends to generate a higher responsivity.
CHAPTER 5. ELECTRON DEVICES IN EPITAXIAL GRAPHENE

Figure 5.5: [left] A schematic of a single channel graphene nanowire diode and associated band structures under different biasing conditions. [right] DC characteristics demonstrating the scaling properties of intercalated bilayer GNDs with nanowire width $w \in [100, 70, 50, 30\text{nm}]$. Note the development of the conductance minimum near zero bias for decreasing nanowire width indicating effective lateral gating.

Electronic noise is the primary limitation on detector efficiency. A common figure of merit of detector efficiency is the noise equivalent power (NEP), which is defined via the ratio of RMS noise voltage and responsivity $\sqrt{\langle v_n^2 \rangle}/\beta$. In the case of biased detectors, $1/f$ noise,\textsuperscript{177, 178} shot noise,\textsuperscript{179} and thermal noise\textsuperscript{180, 181} need to be considered. However, Schottky diodes have been developed in III/V materials enabling zero-bias detection thereby offering reduced $1/f$ noise while practically eliminating shot noise.\textsuperscript{169} This, in conjunction with a high mobility transport layer enables highly efficient diode detectors.

Self switched devices (SSDs) offer a unique alternative to detection as the nonlinear IV characteristic is achieved via lateral gating (see Fig. 5.5).\textsuperscript{182, 183} Several studies have been presented in which laterally gated nanowires patterned in semiconducting heterostructures demonstrate asymmetric current/voltage (IV) characteristics facilitating detection at zero bias.\textsuperscript{184–187} This suggests that efficient high frequency detection in graphene nanowire diodes (GNDs) is feasible to similar effect.\textsuperscript{119, 188, 189} As monolayer and bilayer graphene exhibit ambipolar transport, the nonlinearity which facilitates detection is of a different character than that seen in semiconducting nanowire diodes.

Responsivity in GND detectors may be interpreted as a consequence of two interacting nonlinearities: the Dirac point nonlinearity near zero bias, and the velocity saturation nonlinearity at high bias. The responsivity in GNDs is strongly controlled by the nanowire width ($w$), nanowire length ($l$), and the width of the isolating trenches ($w_0$). In this work, the scaling behavior width scaling in nanowire diodes is investigated.

The DC characteristics of the intercalated bilayer GNDs are shown in Fig. 5.5. In order to understand the zero bias nonlinearity, it is useful to recall considerations on band structure. The effect of lateral gating is to generate a region of low carrier density in the conducting channel resulting in reduced conductivity near $v_D$. Both monolayer and bilayer graphene...
5.2. GRAPHENE NANOWIRE DIODE DETECTORS

Figure 5.6: [left] Responsivity scaling for the measured graphene nanowire diodes presented as a function of frequency. (inset) exponential scaling law of responsivity with nanowire width at 1GHz. [right] Noise equivalent power for the nanowire diodes shown on the left.

nanowires transition to a semiconducting state with decreasing width due to the lateral confinement of carriers and edge disorder induced Anderson localization. The energy gap is shown to scale inversely with nanowire width \( \epsilon_g(w) = a(w-w^*)^{-1} \) where \( a = 200 \text{meV} \cdot \text{nm} \) and \( w^* = 16 \text{nm} \) are empirical constants. For the width scales considered in this study, the energy gap is expected to range from 2meV for the 100nm devices to 14meV for the 30nm devices. With regards to the IV characteristic, one would only expect to see a gap induced conductance minimum for \( \epsilon_g > k_B T \). For the bilayer GNDs shown in Fig. 5.5, an induced energy gap may contribute to the conductance minimum observed in the DC conductance.

Generally, \( \epsilon_f \) is not constant across the width of the nanowire. With lateral gating, charge carriers move towards the edges of the nanowire, and screen the electric field induced by lateral gating. The distance which the field penetrates into the nanowire is characterized by the Thomas-Fermi screening length (see Eq. A.25). Near zero bias, the carrier density in intercalated graphene is \( n \approx 10^{13} \text{cm}^{-2} \) such that \( l_F \approx 20 \text{nm} \). It is important to note that this analysis describes the case of a monolayer, and does not account for nonlinear polarization effects. A similar argument for bilayer material yields a value \( l_F \approx 26 \text{nm} \). When \( w \) is more than a few \( l_F \), lateral gating only produces an edge effect and the core of the nanowire behaves as a simple conductance.

As \( v_d \) increases, the conductivity begins to decrease as a consequence of velocity saturation. Since the nanowires are highly resistive relative to the ohmic contacts and access resistances, the majority of the voltage drop due to an applied bias occurs over the length of the wire \( (l = 1.1 \mu \text{m}) \). The onset of velocity saturation in intercalated graphene occurs at an electric field of \( \mathcal{E}_{\text{sat}} \approx 20 \text{kV/cm} \) (Table 3.1). In the fabricated devices, \( \mathcal{E}_{\text{sat}} \) is reached at approximately 2.2V, and coincides with the observed current compression and decrease in conductivity at high bias.

Responsivity and NEP are measured using a large signal network analyzer (LSNA) up to 49GHz. A low-frequency responsivity (NEP) of 250V/W(50pW/√Hz) is observed in
the 30nm GND detector. The GND responsivity is observed to be relatively constant as a function of frequency with the exception of a gradual drop which may be attributed to capacitive and resistive losses in the substrate. Despite the parasitic effect, a flat responsivity (NEP) of $80 \text{V/W}(170 \text{pW}/\sqrt{\text{Hz}})$ is observed in the 30nm GND detectors at 49GHz.\textsuperscript{120} This represents a substantial improvement over initial results of $3.9 \text{V/W}(2200 \text{pW}/\sqrt{\text{Hz}})$ on intercalated bilayers and $-4.2 \text{V/W}(8200 \text{pW}/\sqrt{\text{Hz}})$ in native monolayers reflecting improvements in material quality and processing techniques.\textsuperscript{119} The results are promising, and suggest that GND devices in hydrogen intercalated bilayers could facilitate efficient detection to frequencies $> 100\text{GHz}$. 
Chapter 6

Material Growth and Processing Techniques

Graphene science is a wide ranging field, and many methods of sample preparation have been introduced including exfoliation, transfer, and epitaxy. Epitaxial growth techniques on SiC are of particular interest as they allow material to be prepared on large area substrates. This is an important step forward for realizing graphene based electronics as it allows for integration within existing fabrication frameworks. With the development of growth techniques, Raman spectroscopy and reflectance mapping have become a preferred methods for analyzing the material properties as they are non-destructive. Reflectance data can be used to obtain a rapid characterization of the number of layers and overall surface morphology in large area material, and Raman data can reveal additional details regarding crystallinity, defect density, strain etc. Additionally, significant improvements have been made with regard to fabrication techniques allowing for the development of electron devices and integrated circuits in graphene.

6.1 Graphene Growth

Epitaxial graphene is grown on commercially available semi-insulating (SI) 4H-SiC or 6H-SiC substrates. Graphene growth on SiC is achieved either by high temperature sublimation or by chemical vapor deposition (CVD). During sublimation growth, the substrate itself behaves as a carbon source. Silicon atoms are sublimated from the SiC substrate at high temperature and graphene is formed by the remaining carbon atoms resulting in a reduction of the surface energy of the system. During CVD growth, process gasses introduced into the growth chamber decompose at high temperature to form graphene layers.

Graphene is grown by both methods on the (0001) face of SiC in horizontal hot wall CVD reactor. The reactor itself consists of a quartz tube which is circumscribed with a large inductor coil. The sample itself is mounted on graphite susceptor which is coated with poly-SiC or TaC. Ordinary CVD reactors have only a single susceptor plate, where as the horizontal hot wall design consists of a susceptor plate placed in an enclosure of poly-SiC covered graphite. This gives improved temperature(pressure) control and helps to manage thermal gradients within the reactor. When RF is applied to the heating coil, eddy currents are induced in the susceptor generating heat. The temperature is monitored via a blackbody
radiation thermometer, and a feedback controller is used to dynamically modulate the input power thereby sustaining the desired temperature. Typical RF power ranges are on the order of 20kW. Process gasses are then introduced into the reactor a specified pressure to etch/grow material.

All growth processes require an “in-situ etching” (i.e. surface preparation) step, the purpose of which is to remove native oxide and to provide an atomically smooth surface for graphene growth.\textsuperscript{199} In-situ etching is carried out in a background pressure of H\textsubscript{2} at a low pressure (10mbar) and relatively low temperature (1550K) for about 10min. SiC etching in H\textsubscript{2} begins to occur around 1420K. After in-situ etching, the reactor chamber is cooled to 1000K and purged with a flow of Ar gas at 300mbar to remove any residual H\textsubscript{2} in the chamber. The advantage of the low temperature (pressure) method is that it minimizes surface step-bunching during graphene growth and completely eliminates the formation of micro-pits around threading screw dislocations (TSDs).\textsuperscript{199}

Growth may be performed in vacuum (10^{-3} mbar) or in a background pressure of Ar (20-50mbar).\textsuperscript{200} During vacuum growth, the residual background pressure is due to sublimation of Si and desorption of material from the reactor walls. The higher pressures in Ar growth function to reduce the Si sublimation rate and consequently the growth rate. The growth temperature varies depending on the process and is typically of order 1600-1700K. The time needed for a sublimation run is approximately 20min.

The high temperatures needed for graphene growth are consequent to the poor solubility of silicon and carbon in SiC. Also, sublimation growth is a self limiting process since it becomes more difficult for silicon to diffuse out of the SiC as the number of graphene layers increases. From stoichiometry alone, growth of a single graphene layer must deplete 3.19 bilayers of the hexagonal SiC structure such that graphene growth tends to generate a significant Si background pressure.\textsuperscript{4} Due to the fact that a non integer number of SiC bilayers is required for each graphene layer, partial bilayers of SiC must remain at the graphene/SiC interface. This generates significant surface step bunching leading to terraced surface that is typical in epitaxial samples. Incidentally, terrace edges provide nucleation sites for graphene growth such that monolayer (bilayer) samples demonstrate bilayer (multilayer) coverage on terrace edges.\textsuperscript{104}

Another viable technique for the growth of epitaxial graphene on SiC is chemical vapor deposition. CVD growth is fundamentally different than sublimation growth as carbon is deposited on the substrate. As with sublimation growth, CVD graphene also requires an initial surface preparation step. Following surface preparation, the process chamber is heated to 1600K and propane gas is introduced at a pressure of 10mbar.\textsuperscript{201} At high temperature, the propane molecules decompose to form carbon-hydrogen radicals. These radicals then adsorb onto the substrate and react to form sp\textsuperscript{2} bonded graphene layers. As this process is deposition based, it is not self limiting as is the case for the sublimation technique. The CVD process usually requires a carrier gas (usually Ar at a pressure of 50mbar) to deliver the chemical species to the substrate. It is important to note that the growth temperature for the CVD process is somewhat lower than what is required to initiate sublimation such that no sublimation occurs during a typical CVD growth run. However, some surface step bunching still occurs at high temperature leading to the terraced substrate morphology.

When performing graphene growth by sublimation or CVD, a carbon buffer layer (CBL) forms at the graphene/SiC interface. Intercalation can be performed either in-situ or in
6.2. CHARACTERIZATION TECHNIQUES

Many techniques are available for the characterization of epitaxial graphene. Most material characterization is aimed at determining the number of layers in the graphene, qualitatively evaluating the defect density, and assessing the large area uniformity of graphene samples. To this end, samples are characterized via Raman spectroscopy and reflectance mapping. Scanning electron microscopy (SEM), and atomic force microscopy (AFM) may also be used to gain a detailed picture of the surface prior to device fabrication.

In order to count the number of layers, several techniques have been applied including low energy electron microscopy (LEEM)\textsuperscript{202} *, scanning electron microscopy (SEM),\textsuperscript{203} phase contrast atomic force microscopy (AFM),\textsuperscript{204} and Kelvin probe force microscopy (KPFM).\textsuperscript{94, 205, 206} The SEM and AFM techniques may be used to probe surface morphology and determine the number of layers in few layer graphene, and LEEM has been shown to be reliable up to approximately 10 layers.

\*In LEEM, the number of layers is determined by observing contrast in transmission of a low energy (0eV ≤ \(e_e\) ≤ 12eV) electron beam. By observing changes in the resonant reflection of low energy electrons and comparing results with the band structure in few layer systems, the number of layers can be determined.

Figure 6.1: [left] A 45µm\textsuperscript{2} reflectance showing surface morphology of graphene bilayers grown by sublimation.\textsuperscript{104, 127} The map of is calibrated to the number of layers via Eq. 6.2. Uniform bilayers are observed on terraces, while trilayer and multilayer growth appears on terrace edges. [right] A collection of Raman spectra taken from bilayer and trilayer regions within the framed region. The G, 2D, and D Raman lines indicated.

a secondary process run. Epitaxial graphene may be intercalated by exposing samples to hydrogen at a temperature(pressure) of 1100K(50mbar) for approximately 10min. If native growth produces only the CBL, a quasi free standing monolayer will be obtained after intercalation. Similarly, if native growth produces a CBL plus a monolayer, bilayer material will be obtained after intercalation. Intercalation can be reversed by heating the sample to 1100K in vacuum.
Reflection mapping may be used to achieve high throughput determination of the number of layers in large area samples. The technique is inspired by the optical absorption properties of exfoliated graphene flakes on SiO$_2$. The reflectance of a single layer of graphene on SiC is given by the following relation.

$$R(1) = \frac{|n_{SiC} + \sigma(\omega)/(\epsilon_0c) - 1|^2}{|n_{SiC} + \sigma(\omega)/(\epsilon_0c) + 1|^2}$$ (6.1)

Here $n_{SiC} \approx 2.77$ is the refractive index of SiC, and $\sigma(\omega)$ is the optical conductance of a single graphene layer. At optical frequencies, $\sigma(\omega)$ can be replaced by the conductance quantum $e^2/4\hbar$ such that $\sigma(\omega)/(\epsilon_0c) \approx \pi\alpha$ where $\alpha$ is the fine structure constant. In the case of $N$ graphene layers, each layer contributes $\pi\alpha$ to the total conductance such that the relation above reduces to the following

$$R(N) \approx \frac{|n_{SiC} + N\pi\alpha - 1|^2}{|n_{SiC} + N\pi\alpha + 1|^2} \approx R_{SiC}\left(1 + \frac{4\pi\alpha N}{n_{SiC}^2 - 1}\right)$$ (6.2)

The total reflectance of $N$ epitaxial graphene layers on SiC is approximated as $R(N) \approx R_{SiC}(1 + 0.017N)$ such that each graphene layer contributes 1.7% to the total observed reflectance.\textsuperscript{103}

Raman spectroscopy can also be used to determine the number of layers by examining the position and linewidth of the G and 2D peaks. Layer determination via Raman spectroscopy should be correlated with reflection data since doping and strain generate spectral distortion. The ratio of the D and G peak intensities is also relevant as it allows for a qualitative estimation of defect density and crystallinity. The D peak in particular correlates to the breathing modes of sp$_2$ bonded rings which are forbidden in defect free graphene.\textsuperscript{207–209}

The reflectance map and associated Raman spectra shown in Fig. 6.1 are representative epitaxial graphene on SiC. Terraces demonstrate bilayer coverage, while trilayer graphene is seen on terrace edges. In the framed bilayer region, the Raman G, 2D, and D lines appear at 1590cm$^{-1}$, 2700cm$^{-1}$, and 1350cm$^{-1}$ respectively. In the trilayer region, the G(2D) lines are shifted to 1597(2720)cm$^{-1}$. The $I_D/I_G$ ratio in the framed region of the reflection map averages at approximately 0.06 and has a maximum at 0.18. This measurement in conjunction with the G peak position at $\approx 1590$cm$^{-1}$ indicates a lowly defected bilayer as interpreted by the amorphization trajectory available in Ferarri et. al. [209]. An analysis of Fig. 6.1 also reveals a relationship between D line intensity and broadening/bifurcation in the G line suggesting uniaxial strain in the lattice.\textsuperscript{210}

### 6.3 Processing Graphene

The fabrication of devices and test structures in epitaxial graphene layers is challenging owing to the sensitivity of the graphene layers to process environments and handling. In this work, process flows have been developed for electron beam lithography (EBL), deep ultraviolet lithography (DUV) and standard photo-lithography (PL). From a technological perspective, the PL process is desirable from the perspective of maximizing throughput and scaling. However, the low field transport properties in graphene exhibit moderate degradation in PL
processes due to contamination with resist residues. PL resist residues are very difficult to remove when processing graphene because standard O\textsubscript{2} plasma treatments etch graphene. For this reason, EBL processing is used for lithography steps on unpassivated graphene.

The core transistor process consists of the following steps: alignment metalization, contact metalization (Ohmic), electrical isolation (mesa), dielectric deposition, dielectric etching, gate metalization, and pad metalization. Several strategies exist with regard to the implementation of each step, and the order of the first few steps is somewhat interchangeable allowing for some design flexibility. The first process flow consists of performing the deposition of the dielectric first in order to encapsulate the graphene. This is then followed by contact metalization and mesa isolation. A second process flow consists of performing alignment and contact metalization in a single step and following with mesa isolation and dielectric deposition. The third process flow consists of performing an initial alignment metalization followed by mesa isolation and contact metalization. In all process flows, a final polymer or dielectric deposition step may be performed in order to encapsulate the devices.

### 6.3.1 Ohmic Contacts

In order to minimize parasitic resistances in devices, the formation of highly conductive Ohmic contacts is essential. Following lithography, the metal is deposited by electron beam evaporation and subsequent liftoff. The contact metalization typically consists of either Ti/Pt/Au(10/10/70nm) or Ti/Pd(1/30nm) metal stacks. The contacts are then annealed at 400°C under a high flow of Ar for 15min in order to improve the contact resistance.

One fundamental challenge when processing graphene is the poor adhesion of metal to the active layer such that the contacts have a tendency to delaminate during later process steps.\(^{211}\) In order to circumvent the adhesion problem, the mesa first arrangement is desirable as it allows the contact metalization to be anchored to the SiC substrate. However, this comes at the cost of introducing an additional process step for alignment metalization and opens potential avenues for contamination of the graphene layer. While performing the Ohmic contact prior to mesa isolation precludes the anchored contact strategy, it allows for the combination of alignment and Ohmic steps saving a lithography step.

It is useful to outline the choice of metals used in Ohmic contacts. In both cases, the Ti layer serves as an adhesion layer to both the graphene and the substrate. However, the function of the platinoids is somewhat different in the Ti/Pd stack versus the Ti/Pt/Au stack. In the Ti/Pd case, a Ti contact is formed initially. However, upon annealing at 400°C in Ar, the thin Ti layer is consumed by the Pd via diffusion along grain boundaries in the metal resulting in a Pd contact.\(^{212,213}\) In the Ti/Pt/Au process, the Ti layer forms the contact and the Pt layer serves as a diffusion barrier. Interdiffusion also occurs in the Ti/Pt system forming a Ti\textsubscript{3}Pt intermetallic. However, the thickness of this interfacial layer is only of order 10 Å.\(^{214}\)

The choice of metal for contacting graphene is a subject of debate, and several notable studies have addressed the issue.\(^{211,215-218}\) Density functional theory (DFT) studies have shown a variation in the binding energy depending on the selection of the metal. In the case of Al, Cu, Ag, and Pt(111) a low binding energy of 0.04 eV per carbon atom is calculated, while in the case of Ni, and Pd(111) a higher binding energy of 0.1 eV is obtained. In the case of high binding energy metals, the graphene/metal chemisorption destroys the K valleys in
Figure 6.2: [left] A scanning electron micrograph of a completed 0.5μm Hall bar with Pd contact metalization in monolayer intercalated graphene. The active area lies entirely on a single terrace. Note the large inclusions of bilayer material [right] Extracted TLM data from two H-intercalated monolayer samples grown on 4H-SiC and 6H-SiC respectively with Pd contact metalization. Points represent the mean resistances measured for each gap, and errorbars represent the standard deviation in measurement data. Performing the TLM extraction, a $\rho_{sh}$ of 220(269Ω/sq) and $\rho_c$ 148(101Ω·μm) is obtained for the 4H(6H) samples respectively.

the graphene band structure resulting in a metallic interface which incidentally serves as a good contact. When the chemisorption interaction is weak, low work function metals induce an n-type doping in the graphene (Al, Ag, Cu), while high work function metals induce p-type doping (Au, Pt).

Despite these considerations, several metals have been used to successfully contact graphene with values of $\leq 100\,\text{μΩ} \cdot \text{μm}$ being reported. In this work, both Pd and Ti/Pt contacts have been used, and contact resistances of $\leq 200\,\text{μΩ} \cdot \text{cm}$ are routinely achieved in monolayer and bilayer transistor processes.

6.3.2 Measuring Contact Resistance

The measurement of the contact resistance is done via the Transfer Length Method (TLM). Graphene mesas are fabricated and the length is varied between the contacts. The IV characteristic is measured at low voltages in order to extract the total resistance of each structure. Ohm’s law gives

$$v = i \left[ 2r_c + r_m(l) \right]$$  \hspace{1cm} (6.3)

where $l$ is the distance between the contacts and $r_m(l)$ is the mesa resistance. When performing TLM measurements in graphene, the standard assumption that the sheet resistance ($\rho_{sh}$) is constant across all structures is usually not valid (see Fig. 3.6). In this case, the contact resistance may be obtained via least squares fitting to data obtained from multiple TLM structures. Expressing Eq. 6.3 in terms of sheet resistance, one finds.

$$r = \left( 2r_c + \rho_{sh} \frac{l}{w} \right)$$  \hspace{1cm} (6.4)
Eq. 6.4 describes a linear dependence of total resistance on the distance between the contacts. The slope of the IV characteristic with respect to $l$ gives the sheet resistance, while the ordinate intercept ($l = 0$) gives the contact resistance.

$$\frac{\partial r}{\partial l} = \frac{\rho_{sh}}{w}$$

The contact resistivity is typically defined in units of $\Omega \cdot \mu m$ such that $\rho_c = r_c w$ where $w$ is the width of the contact. It is convenient to express the IV characteristic in terms of $\rho_c$, $\rho_{sh}$, and aspect ratio ($s \equiv l/w$).

$$r = 2\rho_c/w + \rho_{sh}s$$

The slope and ordinate intercept are then be obtained by plotting resistance versus aspect ratio and performing linear least squares regression.

### 6.3.3 Dielectric Deposition and Characterization

Since the graphene layers are grown directly on the SI SiC substrate, top gating approaches are needed in order to affect charge control. This is in contrast to graphene on homoepitaxial SiC and transferred graphene on SiO$_2$ where back gating approaches are also applicable. Many dielectrics have been utilized in graphene devices including SiO$_2$, HfO$_2$, Al$_2$O$_3$ and polymer layers (PMMA). In this work, Al$_2$O$_3$ is used exclusively as the dielectric as it is a high-$\kappa$ material and exhibits adequate band alignment for MOS capacitors and transistors (Fig. 4.1).

Many dielectric deposition processes involve high temperatures and plasma processing which are incompatible with graphene. For this reason, low temperature dielectric processes are needed. Several techniques exist to grow low temperature oxides on graphene including atomic layer deposition (ALD), hotplate oxidation of aluminium, and direct electron beam evaporation of amorphous Al$_2$O$_3$. In the ALD method, Al$_2$O$_3$ is deposited via the thermal decomposition of Al$_2$(CH$_3$)$_6$ in an atmosphere of H$_2$O at 300$^\circ$C. Generally, the adsorption of the Al$_2$(CH$_3$)$_6$ precursor on graphene is poor such that a pure ALD process generally results in incomplete coverage which is inadequate for large area structures. To circumvent this, a seed layer of Al$_2$O$_3$ may be deposited prior to ALD. The seed layer is deposited via electron beam evaporation and subsequent hotplate oxidation at 200$^\circ$C of a thin (1nm) layer of aluminium metal for 5min. In the case of thin Al$_2$O$_3$ layers, repeated deposition and hotplate oxidation of thin aluminium layers is found to be sufficient. All low temperature films exhibit substantial surface roughness as shown in Fig. 6.3.

In conjunction with process development in graphene, the hotplate, seeded ALD, and evaporated oxides were characterized on 4H-SiC. Circular MOS capacitors with a diameter 200$\mu$m were fabricated on n-type 4H-SiC homoepitaxial layers. CV measurements were then performed at room temperature in order to assess hysteresis, leakage, and dielectric breakdown (Fig. 6.4). Of the three oxides shown, Al$_2$O$_3$ grown by cyclic evaporation/oxidation of thin aluminium films is the most promising. The static dielectric constant of the hotplate oxide on SiC may be estimated at $5.7 \leq \kappa \leq 7.1$. This should be compared with the $5.4 \leq \kappa \leq 5.7$ observed in identical oxides grown on epitaxial graphene (see Chapter 4). In the hotplate oxide, breakdown occurs at a voltage(field) of 8.0V(5.16MV/cm). Though both
Figure 6.3: [top] SEM and AFM images of monolayer intercalated graphene prior to oxidation. The rightmost image represents an on-terrace AFM scan. Note the visible inclusions of bilayer material exhibiting hexagonal symmetry. [bottom] The same sample after hotplate oxidation. The AFM images reveal the amorphous nature of the resulting oxide layer.

$\kappa$ and the breakdown field are considerably less than the case of $\alpha$-$\text{Al}_2\text{O}_3$, ($\kappa \approx 10$, $E_{br} \approx 10\text{MV/cm}$), the hotplate oxides are promising with regard to leakage.

All three oxides demonstrate a severe hysteresis of clockwise orientation suggesting a high density of electron acceptors in the films. Upon repeated sweeps, the hotplate oxide demonstrates a complete hysteresis collapse whereas the seeded ALD and evaporated oxides demonstrate partial collapse. In all three cases, the hysteresis collapses towards the lower/return branch indicating that negative charge becomes fixed in the oxide layer when sweeping to positive bias. These features should be compared with the hysteresis and drift of $v_D$ towards positive bias seen in room temperature graphene MOS measurements (Fig. 4.8). In this way, the SiC MOS results serve as an independent verification that poor quality dielectrics are a major source of hysteresis and bias dependent instability in graphene MOS devices.

6.4 Electron Beam Lithography

The EBL patterning steps are all performed with the JEOL JBX-9300FS EBL system. Metalization steps are performed with via patterning of a bilayer MMA(EL10)/PMMA(A2) (80/500nm) resist stack. Both layers are deposited by spin coating at 2000rpm and curing at 170° C for 5min. After exposure, the pattern is developed in a 1:4 solution of IPA:H20. Alternatively, a 1:1 MIBK:IPA solution may be used.
for 30s and cured at 110°C for 60s. After an exposure dose of 235μC/cm² the pattern is developed in ma-D 525 for 60s. The graphene layer is then etched in a 50W O₂ plasma for 15s at a pressure of 250mTorr.

Oxide etch patterning is typically done via patterning of UV-60:0.75(750nm). The resist is deposited by spin coating at 3000rpm and subsequent softbaking at 130°C for 60s. Following an exposure dose of 40μC/cm² a post exposure bake at 130°C for 60-90s is required prior to a 60s development in MF-CD-26 or MF24-A. Finally, oxide layers may be etched in a dilute 1:10 solution of BOE:DI or 2% HF. Typical etch rates depend on the oxide quality and type and are of order 10 nm/s. If should be noted that UV-60:0.75 can reliably withstand oxide etch times of up to 10s. For thicker oxides, an alternative hard masking/plasma etching process (e.g. 150W Cl/Ar ICP) is required.

Gates are deposited in a high resolution EBL process. A bilayer AR 6200-2:1:1/UV60:0.75 (150/650nm) resist stack is deposited via spin coating at 2000/4000rpm respectively. Both resist layers are cured at 170°C following spin coating. Gates with T and Γ geometry are then patterned using multiple EBL shot ranks. When the bilayer is exposed with a high dose, the underlying AR 6200-2:1:1 will match design dimensions whereas the UV 60-0.75 will be severely overexposed resulting in a profiled opening. The required dose may very depending on the substrate material and design requirements, though values of 550μC/cm² are typical. After exposure a post exposure bake is performed at 130°C for 90s for the UV-60:0.75 layer. The UV60:0.75 is then developed in MF-CD-26 for 60s. A subsequent ashing in 50W/250mTorr O₂ plasma often required in order to fully expose the underlying AR 6200-2:1:1 layer. Finally, the AR 6200-2:1:1 is developed in o-Xylene 120-150s to expose the oxide. An additional 5s low pressure directional ashing step (50W/10mTorr) may be performed in order to remove resist residue from the oxide surface prior to metal deposition. It should be noted that this final step requires some degree of caution. Gate metalization is then performed via electron beam evaporation and subsequent liftoff of a Al/Pd(300/10nm) metalization stack.

**Figure 6.4:** CV(GV) measurements at 100kHz on three different 15nm low temperature oxides grown on n-type 4H-SiC homoepitaxial layers. [left] 200°C hotplate oxide [center] seeded ALD oxide [right] evaporated oxide. Measurements consist of two repeated hysteresis sweeps. The first sweep is shown dashed, while the second is shown solid. All hysteresis loops are of clockwise orientation.
6.5 Photolithography

Photolithography (PL) may be used to positive effect when a process begins with a dielectric deposition or passivation step. PL offers a high throughput process, but comes at the cost of having to accommodate the initial oxide layer throughout the process. Otherwise, PL processing occurs in direct analogy to EBL processing. The alignment marks, mesa, Ohmic, dielectric etch, and contact metalization steps are all performed via PL. If gated devices are needed, then the patterning done via EBL. In this work, all photolithography steps are carried out with a KS MJB3-UV 400 contact photolithography system.

As SI-SiC substrates are transparent, scattered light can cause significant parasitic exposure of photoresist. Thus, patterning of a Ti anti reflection frame via PL and liftoff is needed to maintain $2\mu m$ resolution. Additionally, every PL step must be accompanied by an edge removal step in order to obtain good contact between the pattern mask and the active area of the sample. Metalization steps begin by spin coating AZ-5214E image reversal photoresist at 5000rpm for 60 s. The resist is then cured at 110°C for 75 s. The pattern is exposed with a dose(time) of 5 mW/cm$^2$(2.5 s). The sample is then quickly baked at 120°C for 75 s in order to reverse the image. Following this step is a flood exposure for 60 s and development in a dilute 1:5 solution of AZ-351B developer:D I for 30 s. Note that AZ-351B etches low temperature Al$_2$O$_3$ layers at a rate of order 1nm/min such that some caution is required in process design. Alignment marks and pads can then be deposited directly on the oxide via evaporation or DC sputtering. For Ohmic contacts, the passivation layer must be etched in order to expose the graphene prior to metalization. In all cases the metal layers are identical to those of the EBL process. Mesa isolation is performed by utilizing AZ-5124 in positive mode with an exposure dose(time) of 5 mW/cm$^2$(10 s). Prior to the plasma etching of graphene, the gate oxide must be etched (1:10 BOE:DI or 2% HF).

6.6 DUV Lithography

Deep ultraviolet lithography (DUV) is presented as a potential alternative to PL processing. DUV lithography proceeds along identical lines to PL processing with the exception that different resist layers are used. It should be noted that quartz plates must be used for masking during DUV processing owing to their enhanced transparency in deep ultraviolet (248nm).

Positive mode lithography is performed using UV-60 0:0.75 resist. The resist is deposited via spin coating at 5000rpm for a 620nm thickness and soft baking at 130°C for 90 s. The optical sensitivity of UV-60:0.75 is 8.5 mJ/cm$^2$ such that exposure times tend to be of order 4 s in standard DUV systems. The short exposure times present a difficulty in performing DUV lithography in UV-60:0.75 with regard to resolution. When liftoff processes are needed, thicker layers may be deposited by performing multiple spin coatings. Although it is difficult to achieve a reliable liftoff profile using UV-60:0.75, slight overexposure and overdevelopment may improve results. However, liftoff processes in UV-60:0.75 should only be used in cases where only thin metalization layers are needed. For processes requiring negative mode lithography, ma-N 2401 is used. The optical sensitivity of ma-N 2401 is of order 260 mJ/cm$^2$ such that exposure times of order 120 s are required. For both positive mode and negative mode DUV lithography, development proceeds as in the EBL case.
Scattering Theory

The process of calculating scattering lifetimes involves three steps. First, one must ascertain the dynamics of scattering between two quantum states in the material. As electrons in graphene monolayers and bilayers are chiral, anisotropic scattering must be accounted for. Next, one must evaluate the matrix element for a given scattering potential, and calculate the transition rate using Fermi’s Golden Rule. Finally, one must integrate over all possible scattering events in momentum space.

In a description of scattering, the Hamiltonian is considered to consist of the sum of the Hamiltonian in the absence of scattering (Eq. 2.9) and a spatially varying potential \( V(r) \) which couples states of momentum \( k \) to states of momentum \( k' \).

\[
\mathcal{H} = \mathcal{H}_0 + V(r) \tag{A.1}
\]

The transition rate \( \Gamma_{k'}^k \) can be calculated via perturbation theory (i.e. Fermi’s Golden Rule).

\[
\Gamma_{k'}^k = \frac{2\pi}{\hbar} \sum_{k \rightarrow k'} |\langle \psi_{k'} | V(k - k') | \psi_k \rangle|^2 \Delta(\epsilon, \epsilon') \tag{A.2}
\]

Here, the quantity \( V(k - k') \) represents the Fourier transform of the position space potential, and the term \( \Delta(\epsilon, \epsilon') \) indicates conservation of energy. The matrix element which describes the amplitude of scattering from \( k \) to \( k' \) is given by

\[
\langle \psi_{k'} | V(k - k') | \psi_k \rangle = A^{-1} \int \Psi_{k'}^* V(k - k') \Psi_k dk 
\tag{A.3}
\]

Calculation of \( \tau \) is then given by summing over all possible ways of transitioning from a state of momentum \( k \) to a state of momentum \( k' \).

\[
\frac{1}{\tau} = \sum_{k'} \Gamma_{k}^{k'} [1 - \cos(\theta_{kk'})] \tag{A.4}
\]

The trigonometric term in (A.4) is derived from the Boltzmann transport equation. The term \( \theta_{kk'} \) represents the scattering angle between the initial and final momentum states.


A.1 Scattering in a General Scalar Potential

Calculation of the momentum relaxation time requires one to evaluate the matrix element (A.3). In the case of electron-phonon scattering and impurity scattering, the scattering potential is simply represented by a scalar field. In calculating the matrix element in the case of a scalar field, one sees the effect of the chiral property of carriers in graphene monolayers and bilayers. First, it is useful to diagonalize the Hamiltonian by unitary transformation. The transformation matrix $U$ is simply constructed from the eigenvectors of the untransformed Hamiltonian (2.9).

\[
U_{\delta k} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ e^{i\theta_k} & -e^{i\theta_k} \end{bmatrix}
\]

(A.5)

After transforming $\mathcal{H} \rightarrow U^\dagger \mathcal{H} U$, the Hamiltonian takes the following form

\[
\mathcal{H} = \pm v_f |\delta p| \sum_s \xi_s^\dagger \xi_s
\]

(A.6)

The effect of this transformation is to express the Hamiltonian in the basis of conduction and valence states as opposed to the basis of the $a$ and $b$ sublattices. The $\xi_s^\pm$ now represent the creation and annihilation operators for electrons (+) and holes (−). It is instructive to see how the states themselves transform.

\[
|\Xi^+_{k}\rangle = U_{\delta k}^\dagger |\psi^+_k\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]

\[
|\Xi^-_{k}\rangle = U_{\delta k}^\dagger |\psi^-_k\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

(A.7)

Generally, one is free to multiply the $|\Xi^\pm_k\rangle$ by a constant phase factor, while leaving the Hamiltonian unchanged. Such a gauge invariance arises as a symmetry of the spinor field in graphene. Considering such a gauge transformation $|\Xi^\pm_k\rangle \rightarrow e^{-i\theta_k/2} |\Xi^\pm_k\rangle$ the transformation matrix becomes.

\[
U_k = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\theta_k/2} & e^{-i\theta_k/2} \\ e^{i\theta_k/2} & -e^{i\theta_k/2} \end{bmatrix}
\]

(A.8)

After this change of basis, it is straightforward to calculate the matrix element (A.3) by direct substitution.

\[
\langle \psi^+_k | V(k - k') \psi^+_k \rangle = \langle \Xi^+_k | U_{k'}^\dagger V(k - k') U_k | \Xi^+_k \rangle
\]

\[
= A^{-1} V(k - k') \cos(\theta_{kk'}/2)
\]

(A.9)

Here $\theta_{kk'}$ represents the scattering angle between initial and final states, and $A$ is the normalization of the inner product. Defining the transferred momentum $q = k - k'$ and substituting into Fermi’s Golden Rule yields the following for the transition rate.

\[
\Gamma^{k'}_k = \frac{2\pi}{\hbar} \frac{1}{A^2} \sum_q |V(q)|^2 \cos^2(\theta_{kk'}/2) \Delta(\epsilon, \epsilon')
\]

(A.10)

The chirality electrons in a monolayer is introduced $\Gamma^{k'}_k$ via the $\cos^2(\theta_{kk'}/2)$ term (see Eq. 2.21). In the event where $\theta_{kk'} = \pi$ the $\Gamma^{k'}_k = 0$ such that pure backscattering is
suppressed. Substituting and converting the sum to an integral yields the following general formula

$$\frac{1}{\tau} = \frac{A}{(2\pi)^2} \int d\mathbf{k}' [1 - \cos(\theta_{\mathbf{kk}'})] \left\{ \frac{2\pi}{\hbar} \frac{1}{A^2} \sum_q |V(q)|^2 \cos^2(\theta_{\mathbf{kk}'} / 2) \Delta(\epsilon - \epsilon') \right\} \quad (A.11)$$

Repeating the entire analysis for a bilayer results in the simple transformation $\theta_{\mathbf{kk}'} \rightarrow 2\theta_{\mathbf{kk}'}$ for the chiral term in Eq. A.10. In the following few sections, neutral impurity scattering, acoustic phonon scattering and charged impurity scattering will be considered in graphene. In all cases, $V(q)$ will be defined as a scalar potential, and the scattering rate will then be calculated via a straightforward application of Eq. A.10. The calculations will be carried out for the case of a monolayer. Analogous results for a bilayer are also be shown. It is useful to note the differential relation for monolayers and bilayers.

$$|\mathbf{k}|d|\mathbf{k}| = (\hbar v_f)^{-2} \epsilon d\epsilon$$

$$|\mathbf{k}|d|\mathbf{k}| = (\hbar v_f)^{-2} (\gamma_{\perp}/2) d\epsilon$$

### A.2 Neutral Impurity Scattering

Consider the case where the scattering potential is simply constant $|V(q)|^2 = V_0^2$. Such a potential would correspond to that of neutral impurities as obtained by the short range approximation (see charged impurity scattering). The scattering is considered elastic such that $\Delta(\epsilon, \epsilon') = \delta(\epsilon - \epsilon_f)$. In this case, the scattering rate in (A.11) evaluates to.

$$\Gamma_{\mathbf{k}} = \frac{2\pi}{\hbar} \frac{1}{A^2} \sum_{\mathbf{k} \rightarrow \mathbf{k}'} V_0^2 \cos^2(\theta_{\mathbf{kk}'} / 2) \delta(\epsilon - \epsilon_f) \quad (A.13)$$

In the case the sum over all possible transitions is simply the total number of impurities $N_i = An_i$ where $n_i$ is the number of neutral impurities per unit area. Canceling the normalization terms and substituting into (A.11) yields the following for $\tau$.

$$\frac{1}{\tau} = \int \frac{dk'}{(2\pi)^2} \frac{2\pi}{\hbar} [1 - \cos(\theta_{\mathbf{kk}'})] n_i V_0^2 \cos^2(\theta_{\mathbf{kk}'} / 2) \delta(\epsilon \epsilon_f) \quad (A.14)$$

Evaluating the integral leads to the following for $\tau$

$$\frac{1}{\tau} = \left( \frac{|\epsilon_f|}{4\hbar^2 v_f^2} \right) n_i V_0^2$$

(A.15)

The bilayer result may be expressed by transforming $\epsilon_f \rightarrow \gamma_{\perp}$ in Eq. A.15. In the case of neutral impurities, the momentum relaxation time scales inversely with the impurity density. In a monolayer, $\tau_n^{-1}$ carries a linear dependence on $\epsilon_f$, whereas in a bilayer, $\tau_n^{-1}$ is constant.
A.3 Acoustic Phonon Scattering

It is also useful to examine the dependence of $\tau$ in the case of acoustic phonon scattering. Incidentally, the calculation of momentum relaxation time in the case of acoustic phonon scattering is very similar to the case of neutral impurity scattering shown in the previous section. Here we consider transitions from momentum state $k$ to momentum state $k'$ via scattering with an acoustic phonon of momentum $q$. In this case, the matrix element is given by:

$$|V(q)|^2 = \left( \frac{D^2 \hbar |q|}{2A \rho_m v_{ph}} \right)$$

(A.16)

Here $D$ represents the deformation potential coupling constant, $\rho_m$ the mass density of graphene, and $v_{ph}$ the phonon velocity. Substituting into Eq. A.10 yields for the scattering rate.

$$\frac{1}{\tau} = \int \frac{dk'}{(2\pi)^2} \left[ 1 - \cos(\theta_{kk'}) \right] \left\{ \frac{2\pi}{\hbar} \sum_q \left( \frac{D^2 \hbar |q|}{2\rho_m v_{ph}} \right) \cos^2(\theta_{kk'}/2) \Delta(\epsilon, \epsilon') \right\}$$

(A.17)

In the case of phonon scattering, the conservation of energy term takes the following form.

$$\Delta(\epsilon, \epsilon') = N_q \delta(\epsilon - \epsilon_f + \hbar v_{ph}|q|) + [N_q + 1] \delta(\epsilon - \epsilon_f - \hbar v_{ph}|q|)$$

(A.18)

Here $N_q$ is the phonon occupation number. As phonons are bosons, the occupation number is given by the Bose-Einstein distribution.

$$N_q = \frac{1}{\exp(\hbar \omega_q/k_bT) - 1}$$

(A.19)

The first and second terms indicate absorption and emission of a phonon with energy $\hbar v_{ph}|q| = \hbar \omega_q$ respectively. In the limit of high temperature $k_bT \gg \hbar v_{ph}|q|$ the above relation may be simplified to read.

$$\Delta(\epsilon, \epsilon') = \frac{2k_bT}{\hbar v_{ph}|q|} \delta(\epsilon - \epsilon_f)$$

(A.20)

To simplify the matter of calculating $\Gamma_k$, the sum over all phonon modes is often replaced with a single effective phonon mode $q_{eff}$ thus eliminating the need to evaluate the sum. Combining results one has.

$$\frac{1}{\tau_{ph}} = \left( \frac{D^2}{\rho_m v_{ph}^2} \right) k_bT \int \frac{dk'}{(2\pi)^2} \left[ 1 - \cos(\theta_{kk'}) \right] \cos^2(\theta_{kk'}/2) \delta(\epsilon - \epsilon_f)$$

(A.21)

Integrating one finds that scattering time evaluates to the following:

$$\frac{1}{\tau_{ph}} = \left( \frac{\epsilon_f}{4\hbar^3 v_f^2} \right) \left( \frac{D^2}{\rho_m v_{ph}^2} \right) k_bT$$

(A.22)

Note that the form of Eq. A.22 here identical to that of Eq. A.15. As before, the bilayer result is achieved via $\epsilon_f \rightarrow \gamma_\perp$ in Eq. A.22. In the case of acoustic phonon scattering, the mobility should behave as $(k_bT)^{-1}$. 
A.4 Charged Impurity Scattering

Charged impurity scattering is highly relevant in the case of graphene, and it is essential to analyze the properties of $\tau$ in the case of a charged impurity density. Treating a charged impurity as point charge, one has the bare Coulomb potential.

$$\phi(r) = \frac{1}{4\pi \kappa} \frac{e^2}{|r|}$$  \hspace{1cm} (A.23)

In a semiconductor, a charged impurity will attract mobile carriers thus causing local perturbations in the carrier density $n \rightarrow n + \delta n$. These perturbations will give rise to a perturbation in the potential $\phi_0 \rightarrow \phi_0 + \delta \phi$. In absence of any screening and external electric fields, $n$ and $\epsilon_f$ may be approximated as constant such that the potential as locally flat. In this case only the perturbations need be considered. As is the situation in the low field transport regime. At low field, the perturbation due to a charged impurities will vary much more strongly than the applied field near the impurity. To calculate the effective screened potential around a charged impurity, one must solve the Poisson equation (i.e. Gauss’ Law).

$$\nabla^2 \delta \phi(r) = -\frac{e \delta n(r)}{\kappa}$$  \hspace{1cm} (A.24)

Here $\kappa$ represents the dielectric constant, and $e \delta n(r)$ represents the perturbation in charge density due to a charged impurity. First a relation must be found between $\phi(r)$ and $\rho(r)$. At thermal equilibrium the following approximation may be made.

$$\frac{e \delta n(r)}{\kappa} \approx k_F^2 \delta \phi(r)$$  \hspace{1cm} (A.25)

Here $\kappa$ represents the dielectric constant of the material. The constant introduced $k_F = l_F^{-1}$ represents the characteristic screening length in the material. This can be taken to be the Debye length or the Thomas-Fermi length depending on the system under consideration. The Debye length arises when one considers electrons to obey Maxwell Boltzmann statistics, while the Thomas-Fermi length arises when the system is considered to be at a constant chemical potential. In graphene, the Thomas-Fermi screening length is the relevant quantity.

$$k_F = \alpha k_f$$  \hspace{1cm} (A.26)

Here, $\alpha = e^2/\kappa \hbar v_f \approx 2.2/\kappa$ is the fine structure constant in graphene, and $k_f = \sqrt{4\pi n_s g_s g_v}$ is the Fermi-wavevector.\textsuperscript{230} Solving the Poisson equation, one finds the Yukawa potential.

$$\delta \phi(r) = \frac{1}{4\pi \kappa} \frac{e^2}{|r|} e^{-k_F |r|}$$  \hspace{1cm} (A.27)

The calculation indicates that a charged impurity will generally attract mobile carriers in the graphene such that the potential profile will decay more quickly than $|r|^{-1}$. It is interesting to consider the case of a pure Coulomb potential where $k_F \approx 0$. Taking the Fourier transform of Eq. A.27 with $k_F \approx 0$, one has one has for $|V(q)|^2$ of Eq. A.11

$$|V(q)|^2 = \left( \frac{2\pi e^2}{\kappa |q|} \right)^2$$  \hspace{1cm} (A.28)
In the case where screening is strong, \( k_F \to \infty \), the radial dependence may be treated as a delta function \( \eta \delta(r) \). This is known as the short range approximation.

\[
\delta\phi(r) \approx \frac{e^2 \eta}{4\pi \kappa} \delta(r) = V_0 \delta(r) \quad (A.29)
\]

Taking the Fourier transform of Eq. A.29, one recovers the case of neutral impurity scattering \( |V(q)|^2 = V_0^2 \). Substituting Eq. A.28 into Eq. A.2 one has for the transition rate

\[
\Gamma_{kk'} = \frac{2\pi}{\hbar} a^{-1} n_c \left( \frac{2\pi e^2}{\kappa |q|} \right)^2 \cos^2(\theta_{kk'/2}) \delta(\epsilon - \epsilon_f) \quad (A.30)
\]

Substituting into for \( \tau \) gives the following

\[
\frac{1}{\tau_c} = \int \frac{dk'}{(2\pi)^2 \hbar} n_c \left( \frac{2\pi e^2}{\kappa |q|} \right)^2 \left[ 1 - \cos(\theta_{kk'}) \right] \cos^2(\theta_{kk'/2}) \delta(\epsilon - \epsilon_f) \quad (A.31)
\]

In this case, the integral retains a dependence on \( |q| \) which did not appear in the case of neutral impurity scattering or acoustic phonon scattering. By trigonometry, one has that \( |q| = 2|k| \sin(\theta_{kk'/2}) \) such that the integral reduces to the following.

\[
\frac{1}{\tau_c} = \frac{\hbar}{2\pi} \left( \frac{\pi e^2}{\kappa} \right)^2 n_c \int 2 \cos^2(\theta_{kk'/2}) (\hbar |k|)^{-2} \delta(\epsilon - \epsilon_f) dk' \quad (A.32)
\]

Collecting terms and integrating yields the following result

\[
\frac{1}{\tau_c} = \frac{n_c}{\hbar} \left( \frac{\pi e^2}{\kappa} \right)^2 \frac{1}{|\epsilon_f|} \quad (A.33)
\]

The bilayer result is obtained by transforming \( n_c \to n_c/2 \) in Eq. A.33. In the case of charged impurity scattering, the momentum relaxation times in monolayers and bilayers carry a linear dependence on \( \epsilon_f \).\(^{195,231}\)
Throughout the course of this work, modeling results have been presented in the context of measurement data. In order to preserve the textual integrity of the work, comments on modeling strategies have been omitted. Modeling devices in graphene is computationally challenging due to the presence of many interacting nonlinearities. This is particularly the case for the modeling of CV and hysteresis curves observed in GFET data. In the case of the CV data, a statistical model was introduced in order to account for surface potential fluctuations (Eq. 4.13). From a computational perspective, this introduces a Monte Carlo simulation into an already highly nonlinear problem (Eq. 4.8). In the case of hysteresis modeling, the need to evaluate Preisach kernels implies an infinite dimensional problem (Eq. 5.6). Additionally, the relations governing behavior observed in Figs. 4.3 and 5.3 are highly parameterized such that many iterations are needed in order to arrive at convergent solutions. In general, a traditional CPU based implementation is not viable with regard to evaluation time even if efficient algorithms are implemented.

In order to model CV and hysteresis data, a massively parallel computation scheme was implemented on graphics processing units (GPUs). This strategy takes advantage of the parallel architecture of GPU processors whereby simple instruction sets are implemented in a highly threaded computing environment. In the GPU scheme, each processor core evaluates a single thread and results are stored in shared memory on the device. When a solution is obtained, the result is then copied to the hosting CPU.\textsuperscript{232}

In order to illustrate the fundamental difference between the CPU and GPU approaches, consider the case of calculating the square each element in a vector $v$ of length $N$ and storing the result in another vector $r$. In a CPU implementation, one has the following:

```c
void square(float* v, float* r, int N){
    for(int i = 0; i < LEN, i++){
        r[i] = v[i]*v[i];
    }
}
```

Here, the code loops through each element of \( v \) and stores the result in \( r \) such that the evaluation efficiency is \( O(n) = n \). Contrast this to the GPU code fragment shown below.

```c
__global__ void square(float* v, float* r)
{
    const int tid = threadIdx.x;
    r[tid] = v[tid]*v[tid];
}

square<<<1, N>>>(v, r);
```

In this case, the square of each element is evaluated on a separately indexed thread, which corresponds to a separate core on the GPU. Note that the GPU code does not contain a loop instruction. Instead, \( N \) individual threads are launched via the `<<<1, N>>>(v, r);` command. All threads run simultaneously in the context of the GPU kernel such that the evaluation efficiency is \( O(n) = 1 \).

Properly implemented GPU code can run several orders of magnitude faster than an equivalent CPU implementation. Such a scheme is highly valuable in the case of scientific computing and physical modeling where fast element-wise applications are often required. This is particularly useful in the case where numerical integration, iterative non-linear solving, or averaging is involved. GPU implementation is not suited towards every kind of numerical problem. For example, problems which require communication between elements(threads) are not straightforward to implement in a GPU framework. A classic example of this is the case of taking the discrete derivative of a vector \( v \). Further, GPUs do not have stack memory such that recursive algorithms cannot be implemented.

Modeling of the CV and hysteresis data is implemented in three parts: a control script, a GPU kernel, and a fitting engine (`ndfit`). The control script is written in python and serves to invoke the GPU kernel and `ndfit`. The GPU kernel contains optimized functions relevant to the simulation. Functions which are implemented on the GPU include the calculation of \( \rho(\epsilon) \), \( n(\epsilon) \), \( \Delta v(\epsilon_f) \), \( C_{\text{tot}}(v) \), \( D_{\text{it}}(v) \), \( \mathcal{P}[^] \), etc. The kernel is written in the compute unified device architecture (CUDA), which is a C-like interface that facilitates programmatic access to the GPU via the graphics driver.

The GPU kernel serves as a fit function by which model parameters are optimized via `ndfit`. `ndfit` is written as a C extension for python, and is based on a design philosophy which allows for large parameter sets and generic fit functions of arbitrary complexity. Relevant model parameters consist of a set of physical constants of the problem in question and include quantities such as \( \delta\epsilon_f \), \( \epsilon_g \), \( \epsilon_0 \), \( \epsilon_\delta \), \( \alpha \), \( \mu \) etc. The model parameters are passed to `ndfit` as a vector \( p \). `ndfit` creates a matrix \( M \) of test vectors around \( p \) given an increment vector \( dp \). During each iteration, all vectors in the matrix \( M \) are evaluated against the fit function in order to determine a new test vector. This new test vector \( p \) is taken to be the vector in \( M \) which minimizes the sum of the square differences between the modeled curve obtained from the GPU kernel and measured data. The algorithm then proceeds iteratively until adequate convergence is achieved. During the optimization process, `ndfit` scales the increment vector \( dp \) dynamically in order to minimize the number of iterative steps required to achieve convergence.

This modeling and optimization routine serves as the primary motivation for the GPU scheme. In the case of CV data, the simulation of a single smooth CV curve involves solving Eqs. 4.8 and 4.4 of order \( 10^4 \) times for noisy \( \epsilon_f \) data. Each iteration of the fitting engine then
requires the simulation of order $2^n$ smooth curves where $n$ is the number of model parameters. Agreement between the model and measured data is only reached after a sufficient number of iterations ($10^3$). Thus, without efficient simulation strategies, a quantitative analysis of measurement data in the context of theoretical results becomes intractable.
Summary and Outlook

In this work, epitaxial graphene on 4H(6H)-SiC has been assessed for potential applications in high frequency electron devices through electron transport and charge control measurements. The experimental results have been used in conjunction with a thorough theoretical treatment to interpret the observed behavior in field effect devices. Throughout the work, the graphene-substrate and graphene-oxide interfaces are found to command significant influence in the characteristics observed in graphene devices and test structures.

Low field measurements demonstrate that intercalated layers offer superior transport properties when compared to native material, and mobilities as high as 6000(2500)cm²/V·s have been measured in large area monolayers(bilayers) respectively. Epitaxial graphene is observed to transition from electron conduction to hole conduction upon intercalation due to the spontaneous polarization of the 4H(6H)-SiC substrate (ΔP). Additionally, the substrate generates velocity saturation (v_sat) in epitaxial graphene which is relevant as v_sat determines the upper limit on the intrinsic frequency performance in field effect devices. The dominant scattering channel giving rise to velocity saturation is remote polar optical phonons in the substrate (ε_max). Transport considerations show that the saturation velocity v_sat ∝ ε_max. In both 4H(6H)-SiC the surface optical mode has a relatively high energy of ε_max ≈ 115meV which translates to an acceptable saturation velocity of order 2 · 10⁷ cm/s.

Measurements of the CV characteristic in graphene MOS suggest that charge control is more effective in bilayer material. This is counter intuitive, as monolayer material should demonstrate superior charge control properties. This discrepancy is attributed to the opening of a narrow energy gap in bilayer material (ε_g) as consequence of ΔP. This reinforces the notion that the role of the substrate is critical when assessing epitaxial graphene. The CV measurements also demonstrate that low temperature dielectrics may be used to gate graphene, and an interface state density (Dit) of order 2 · 10¹² eV⁻¹cm⁻² is determined. Additionally, the CV measurements highlight a temperature dependent hysteresis in graphene MOS structures which is related to charge injection in the dielectric. The charge control experiments also estimate the RMS of surface potential fluctuations (δε_f) in graphene to be of order 80-90meV. This has important consequences with regard to a device as it sets a limits on the effectiveness of charge control. Even in the case of a bilayer with a narrow energy gap, the presence of surface potential fluctuations can undermine current modulation.

Epitaxial monolayers are semi-metallic whereas epitaxial bilayers may be considered a pseudo-semiconductor. Due to these fundamental properties, charge control is intrinsically weak when compared with other semiconductor materials. This is compounded by the constellation of issues explored in this work and manifests as a modest frequency performance.
in field effect devices when compared to other semiconductor materials. The substrate induced velocity saturation in conjunction with compromised charge control forcibly imply limitations in transit frequency \( f_t \) and unity current frequency \( f_{max} \) for active devices.

In light of these results, several advancements in material growth and fabrication techniques are needed in order to achieve extrinsic values of \( f_t(f_{max}) > 100 \text{GHz} \). The SiC polytypes offer perhaps the best opportunity for realizing high speed electronic devices in graphene owing to the ability to grow epitaxial layers of controlled thicknesses, the option of intercalation, the possibility for engineering material systems, and the relatively high \( \epsilon_{\Delta}^{max} \). In the context of this study, epitaxial bilayers on 6H-SiC represent the most promising avenue with regards to technological applications.

With regard to transport, some improvement is likely to come with substrate engineering. In intercalated layers on SiC, the degree of hole conduction is proportional to the degree of hexagonality of the substrate. To this end, 3C-SiC may be of interest as it is feasible to produce quasi-free standing layers with \( \epsilon_f \approx 0 \). Additional flexibility is afforded by the possibility of growing graphene on homoepitaxial layers. Other directions of interest may be transferred graphene on diamond or hexagonal BN. Hysteresis and a high \( D_{it} \) represent a major technological challenge for graphene and implore further investigations into improving dielectric quality. Experiments show that significant improvements are required regarding the deposition of thin dielectric films on graphene. Possible solutions could consist of an optimized atomic layer deposition process for Al\(_2\)O\(_3\). Other high-\( \kappa \) dielectrics such as HfO\(_2\) or Y\(_2\)O\(_3\) should also be considered.

It is also interesting to investigate alternative applications in order to procure a position for graphene in the competitive field of high frequency electronics. Graphene devices are unique insofar as they exhibit very high current densities such that even a small amount of current modulation translates into a comparably large transconductance. In this way, active devices in graphene behave more as voltage controlled resistances than transistors. Therefore, avenues utilizing the nonlinear transfer characteristics of graphene MOS devices may provide the way forward. Possible applications for graphene MOS might include systems which can operate comfortably above \( f_{max} \) such as zero bias power detectors and high frequency mixers.
Acknowledgement

I would like to extend my greatest gratitude to all who have helped with the work. Firstly, to N. Rorsman for his methodical approach and his appreciation for tact, diligence, and completeness. Next, to E. Ö. Sveinbjörnsson in Reykjavik for his telescopic support of the work, his help with the CV curves, and his insightful skepticism. To O. Habibpour for his help with the devices and processing, to A. Westlund for his collaboration on nanowire diodes, and to M. Thorsell for help with measurements. To C. Melios, O. Kazakova, and my other colleagues at NPL in London for their help with AFM techniques, and to I. Ivanov for his help with the Raman spectroscopy. I would also like to thank those who provided material for these studies including W. Strupinski in Warsaw, and E. Janzén and J. Hassan in Linköping. And finally to H. Zirath for facilitating the work and for supporting my development as a research scientist. This work has been supported by the Swedish Foundation for Strategic Research (SSF), the Knut och Alice Wallenberg Foundation (KAW), the European Science Foundation (ESF) and the Graphene Flagship.

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Appended Publications

**Article A:** A temperature dependent measurement of the carrier velocity vs. electric field characteristic for as-grown and H-intercalated epitaxial graphene on SiC


The velocity field characteristic in native and intercalated graphene monolayers is measured using pulsed current voltage techniques. Velocity saturation in epitaxial graphene is found to depend critically on the energy of the surface optical mode ($\epsilon_{SO}$) in the SiC substrate. These results set fundamental limitations on the frequency performance that may be expected in high speed transistor in graphene. For native(intercalated) material, a saturation velocity ($v_{sat}$) of 2.3(1.4)·$10^7$ cm/s is extracted from the measurements. Additionally $v_{sat}$ is found to vary linearly with $\epsilon_{SO}$ and inversely with $\sqrt{n}$ where $n$ is the carrier density.

**Article B:** Charge Control in Graphene MOS Capacitors

*Submitted Manuscript*, 2016

Charge control in intercalated monolayer and bilayer MOS capacitors with an Al$_2$O$_3$ field oxide is investigated via temperature dependent measurements of the capacitance voltage (CV) characteristic. From the CV measurements, the density of interface states ($D_{it}$) is found to be of order 1.75(1.50)·$10^{12}$ eV$^{-1}$cm$^{-2}$ in the monolayer(bilayer) structures respectively. The CV measurements also allow for an assessment of surface potential fluctuations ($\delta\epsilon_f$) and material anisotropy. Important differences are observed between the materials. Most notably, a surface potential induced energy gap $\epsilon_g$ is assessed for the bilayer material. The CV results provide a foundation for the analysis of graphene FETs in intercalated material.

**Article C:** Hysteresis modeling in graphene field effect transistors


Hysteresis is a fundamental issue in graphene field effect transistors as it introduces bias dependent stability and is observed when performing measurements of the gate voltage ($v_g$) versus drain current ($i_d$). In this work we present an empirical model of hysteresis in GFETs based on a modified Preisach kernel. Optimized hysteresis curves are then compared with measured GFET data in order to investigate the origin of the hysteresis and to extract several material parameters which are relevant for device design. Quasi-static and low frequency measurements of the $i_d(v_g)$ characteristic demonstrate rate dependence in the hysteresis, which is interpreted as a measure of the charging effect responsible for hysteresis generation.
**Article D:** Assessment of H-intercalated graphene for microwave FETs through material characterization and electron transport studies  

Hydrogen intercalated graphene bilayers on SiC are a promising candidate for high frequency applications. Epitaxial graphene is grown in a horizontal hot wall chemical vapour deposition (CVD) reactor. The material is then characterized by micro-Raman and reflection mapping at 532nm. 2x50μm coplanar field effect transistors with a gate length of 1μm are fabricated along with supplementary test structures. S-parameters are measured up to 67GHz, and an extrinsic $f_t(f_{max})$ of 20(13)GHz is observed. Supplementary measurements of the low field transport properties $\mu$, $\sigma$, and $n_{sh}$ are also presented.

**Article E:** Graphene self-switching diodes as zero-bias microwave detectors  

Graphene nanowire diodes represent a novel approach to zero-bias high frequency detection. Self-switching diodes (SSDs) achieve rectification by modulating the carrier density in a slotted nanoscale channel via a lateral field effect. SSDs are fabricated in native and hydrogen intercalated graphene grown by sublimation and responsivity is measured over 1-67GHz. As-grown and H-intercalated samples demonstrate a responsivity(NEP) of $-4.2V/W(8.2nW/\sqrt{Hz})$ and $3.9V/W(2.2nW/\sqrt{Hz})$ respectively. The change of sign in responsivity is reflects electron and hole conduction in the native and intercalated samples respectively.

**Article F:** High frequency electromagnetic detection by nonlinear conduction modulation in graphene nanowire diodes  

Nanowire diodes are fabricated in hydrogen intercalated graphene bilayers in order to investigate the sources of nonlinearity responsible for detection via scaling of the nanowire width. Two nonlinearities are characterized: a zero-bias conductance minimum attributed to modulation of the carrier density via lateral gating, and a high bias conductance slope attributed to velocity saturation in the nanowire channel. Responsivity and NEP are investigated via large signal measurements, and a peak responsivity(NEP) of $250V/W(50pW/\sqrt{Hz})$ is found at 1GHz in the 30nm nanowire diodes. Responsivity is observed to scale as an inverse exponential with nanowire width due to screening of the lateral field effect. This paper is a continuation of the work presented in Article E.
Article G: Quasi-free-standing monolayer and bilayer graphene growth on homoepitaxial on-axis 4H-SiC(0001) layers


Homoepitaxial SiC layers of varying conductivities are grown on semi-insulating (SI) 4H-SiC substrates in a horizontal hot wall CVD reactor. Graphene monolayers and bilayers are then grown in a subsequent step and in-situ intercalated with hydrogen. The graphene is found to be of similar quality to identically grown material directly on (SI) 4H-SiC via fabrication and electrical characterization of test structures. A material analysis is also performed via Raman spectroscopy and reflection mapping. Such advanced epitaxial structures may provide additional flexibility in the design of graphene based technologies.
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A TEMPERATURE DEPENDENT MEASUREMENT OF THE CARRIER VELOCITY VS. ELECTRIC FIELD CHARACTERISTIC FOR AS-GROWN AND H-INTERCALATED EPITAXIAL GRAPHENE ON SiC

M. Winters, J. Hassan, H. Zirath, E. Janzén, and N. Rorsman

A temperature dependent measurement of the carrier velocity vs. electric field characteristic for as-grown and H-intercalated epitaxial graphene on SiC

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A technique for the measurement of the electron velocity versus electric field is demonstrated on as-grown and H-intercalated graphene. Van der Pauw, coplanar microbridge, and coplanar TLM structures are fabricated in order to assess the carrier mobility, carrier concentration, sheet resistance, and contact resistance of both epi-materials. These measurements are then combined with dynamic IV measurements to extract a velocity-field characteristic. The saturated electron velocity measurements indicate a value of $2.33 \times 10^7$ cm/s for the as-grown material and $1.36 \times 10^7$ cm/s for the H-intercalated material at 300 K. Measurements are taken as a function of temperature from 100 K to 325 K in order to estimate the optical phonon energy $E_{OP}$ of 4H-SiC by assuming an impurity scattering model. The extracted values of $E_{OP}$ are 97 meV for the as-grown sample and 115 meV for the H-intercalated sample. The H-intercalated result correlates to the anticipated value of 116 meV for 4H-SiC, while the as-grown value is significantly below the expected value. Therefore, we hypothesize that the transport properties of epitaxial graphene on SiC are influenced both by intercalation and by remote phonon scattering with the SiC substrate.

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I. INTRODUCTION

Graphene on SiC has generated a great deal of interest in both the electronics and materials physics community as theoretical calculations and experimental measurements indicate exemplary electronic, mechanical, and thermal properties. Epitaxial graphene on SiC wafers is of particular interest as it potentially provides a route to large scale processing of graphene based devices.

The ability of a device to function at high frequency is limited by the drift velocity ($v_d$) of charge carriers at high-electric fields: $v_d = \langle \mathbf{k} \cdot \mathbf{E} / m^* \rangle$. Here, $m^*$ is the effective mass of the charge carriers, $\mathbf{k}$ is the wavevector, and $\mathbf{E}$ is the unit vector which points in the direction of the electric field. Drift velocity is limited by scattering events in the material. Carriers in graphene may scatter via impurities, phonons in the substrate, phonons in the graphene, and via Coulomb interactions. The Ensemble Monte Carlo approach is particularly suited to the modelling of carrier scattering in graphene.

The most common way to measure the velocity-field characteristic is by a dynamic current voltage measurement. Short pulses are used in order to minimize resistive self heating effects, which may interfere with a proper interpretation of the temperature dependence. This method has been applied to measurements on silicon, silicon carbide, and other materials. Additionally, a capacitive probe method has been used in order to obtain the velocity-field characteristic in semiconductor materials. In another approach, the velocity-field characteristic of GaAs was measured via the injection of electrons into the material with an electron beam. Velocity-field-characterization has also been thoroughly explored on graphene on SiO$_2$ by Dorgun et al. An impurity scattering limited saturation velocity of $>3 \times 10^7$ cm/s is reported for sheet carrier densities $n < 10^{12}$ cm$^{-2}$. The corresponding optical phonon energy $E_{OP}$ for SiO$_2$ is reported to be 36 meV from temperature dependent measurements.

Here, we measure the velocity-field characteristic of graphene to determine potential applications for high-frequency devices. Such a characterization lends valuable physical insight into the transport of charge carriers in two-dimensional structures. As-grown and H-intercalated epitaxial graphenes are prepared on the Si-face of semi-insulating (SI) 4H-SiC wafers with the intention of measuring the field dependence of carrier velocity as a function of temperature. Van der Pauw structures, coplanar transfer length method (TLM) structures, and coplanar microbridge structures are fabricated using standard processing techniques. The Van der Pauw structures are used to motivate an empirical relationship between carrier concentration and sheet resistance. TLM structures are measured to estimate the contact resistance of graphene-metal contacts. Pulsed IV measurements are performed as a function of temperature to obtain an IV characteristic for both materials. These measurements are combined to extract the carrier velocity versus electric field characteristics. These are then fitted to a standard velocity field model in order to determine the saturated electron velocity in both materials.

II. METHODS

A. Material growth

Epitaxial graphene was produced by sublimation of carbon in a CVD reactor by heating SiC. Depending on the growth conditions, monolayer, bi-layer, and multilayer graphenes may be formed on the surface of the SiC wafer. However, there are many challenges associated with such an
approach including material uniformity and the existence of a complex terraced substrate surface morphology. A horizontal hot-wall CVD reactor was used for the growth of graphene in vacuum \((1 \times 10^{-5} – 1 \times 10^{-8} \text{ mbar})\) on the Si-face of chemomechanically semi-insulating nominally on-axis 4H-SiC substrates. In order to minimize surface degradation in the form of surface step-bunching and defect selective etching on the Si-face, graphene growth was performed at an optimized temperature of 1400 °C.11 Two sets of samples were grown under the same growth conditions. In one set of samples, only graphene was grown, while the other set of samples was in situ intercalated with hydrogen.

The existence of a buffer layer of graphene-like carbon bound to silicon at the SiC/graphene interface has been known for some time.12 The buffer layer consists of lattice matched \(6\sqrt{3} \times 6\sqrt{3}\)R30 carbon atoms with a high density of dangling bonds, which are a result of high temperature processing. Sheet carrier densities in epitaxial graphene tend to be quite high \(10^{12} – 10^{13}\)12,13 Hydrogen intercalation converts the interface carbon buffer layer into the first graphene layer and transforms epitaxial graphene into quasi free-standing graphene on the substrate.12,14 The efficacy of the H-intercalation process may be demonstrated using a variety of techniques such as Raman spectroscopy, SEM, LEEM, XPS, and Angle Resolved Photo Electron Spectroscopy (ARPES). H-intercalated material tends to be p-type with higher carrier concentrations and average carrier mobility, while as-grown material tends to be n-type with lower carrier concentrations and carrier mobility.14

B. Device fabrication

Graphene test structures are produced using standard processing procedures used for semiconductor device fabrication. First, alignment marks are patterned via photolithography, DC sputtering of Ti/Au, and liftoff in acetone. Next, the graphene mesa layer is patterned via photolithography and dry etching in oxygen plasma.15 The formation of Ohmic contacts is a critical step in the graphene fabrication procedure. The surface is first cleaned using a standard acetone/methanol/isopropyl alcohol (IPA) degreasing. A subsequent cleaning in CHCl3 is then performed in order to remove as many organic contaminants and residues from previous processing steps as possible from the surface. Then, Ohmic contacts are patterned using photolithography, DC sputtering of Ti/Au, and liftoff. An additional DC sputtering of Ti/Au and liftoff are done for the formation of contact pads. The contact resistance is measured to be \(2.2 \Omega\) mm and \(1.2 \Omega\) mm in as-grown and H-intercalated graphene, respectively. For this extraction, the contact resistance is assumed to be constant over the range of electric field applied to the structure.

Prior to passivation, the samples are annealed in a mixture of atmospheric H2/Ar in a 1:9 ratio at 300 °C in order to remove residues from previous photolithography steps. Passivation is achieved using a layer of benzocyclobutene (BCB) diluted in [1,3,5] trimethylbenzene in a 1:1 ratio.16 The BCB layer is spun onto the substrate and then patterned via photolithography. A curing step is performed at 250 °C for 2 h. After curing, the thickness of the BCB passivation layer is \(~2 \mu m\). BCB has been selected because it improves the large-area uniformity of transport properties. The sheet resistance versus carrier concentration both before and after passivation with BCB for one H-intercalated sample. Statistics are gathered from 40 identical \(100 \mu m \times 100 \mu m\) Hall structures fabricated on a single chip.

C. Measurement technique

Measurements are carried out using a four part setup consisting of a Tabor 8500A pulse generator, a HP85120A pulse head, an HP6625A two channel supply, and a TDS7104 oscilloscope. Pulse parameters are controlled via a Python script. The pulse generator serves as a clock to generate pulses from the pulse head. The magnitude of the pulse is controlled via setting the voltage on the DC supply, while the pulse width (1 μs), rise time (100 ns), and duty cycle

![Graphene (H-intercalated)](image)

FIG. 1. Plots showing the Hall statistics before and after passivation with BCB for one H-intercalated sample. Statistics are gathered from 40 identical \(100 \mu m \times 100 \mu m\) Hall structures fabricated on a single chip.

![SEM image of H-intercalated graphene microbridge](image)

FIG. 2. A SEM image of an H-intercalated graphene microbridge structure used for velocity-field measurements before the fabrication of Ohmic contacts. The image shows the surface morphology of H-intercalated graphene, as well as corner rounding due to photolithography.
(1 ms) are controlled with the pulse generator. Voltage pulses are applied to the microbridge structures, and the output current waveform is measured via a Hall effect probe. The voltage pulses are also monitored using the oscilloscope. The pulse magnitude is swept from 0 V up to the onset of breakdown effects in steps of 1 V. Breakdown effects are observed generally for voltage pulses with $V > 30$ V. The output current pulse ladder for one measurement is shown in Fig. 3.

The center of a square wave pulse in the time domain may be found using the convolution method:

$$\frac{d}{dt} \left( \int V(t) V(t - \tau) d\tau \right) = 0,$$

$$\frac{d}{dt} \left( \int I(t) V(t - \tau) d\tau \right) = 0.$$

The solution to the above equations gives the center of the voltage and current pulses in time ($t_c$ and $t_i$). The corresponding $V(t_i)$ and $I(t_i)$ are taken to be a single point in the IV characteristic. Repeating for all voltage steps gives the full IV characteristic. This method is valid as the current pulses observed are of constant amplitude for each applied voltage. Furthermore, it has the advantage of efficiently finding the correct pulse amplitude in noisy signals.

The following non-linear model may be applied to the extracted IV characteristics with great accuracy.\(^{17}\)

$$I = I_0[1 + \lambda V] \tanh(\beta V),$$

where $I_0$ indicates the location of the onset of saturation in the IV characteristic, $\lambda$ is the channel length modulation parameter, and $\beta$ is the current saturation parameter.\(^{17}\) The extracted values from Eq. (1) are $I_0 = 28.4$ mA, $\lambda = 0.0166 V^{-1}$, and $\beta = 0.0825 V^{-1}$ for the IV curve shown in the bottom plot of Fig. 3. Pulsed IV measurements are taken as a function of temperature from $T = 100$ K to $T = 325$ K in a closed cycle Helium cryostat under vacuum conditions.

### III. THEORY

A graphene mesa may be considered as a charge carrying sheet. The electron drift velocity may be determined by the following relation:

$$v_d = \frac{I}{en_{sh}w_{ch}},$$

where $e$ is the fundamental charge, $n_{sh}$ is the sheet carrier concentration, and $w_{ch}$ is the width of the sheet. The determination of the carrier concentration is of fundamental importance for the extraction of the electron velocity from dynamic IV measurements.

The sheet carrier density $n_{sh}$ is estimated via the sheet resistance $R_{sh}$. $R_{sh}$ is obtained from dynamic IV measurements and knowledge of the geometry of the charge carrying graphene mesa. $n_{sh}$ may be calculated from $R_{sh}$ via the following relation:

$$R_{sh} = \frac{1}{e\mu_{sh}\\\left(\\right)}.$$

Hall measurements were performed at $T = 300$ K to obtain the average mobility $\mu$, allowing for a direct calculation of the carrier density $n_{sh}$ from the measured field sheet resistance $R_{sh}$. Hall data are used to generate statistics on the relationship between carrier concentration $n_{sh}$ and sheet resistance $R_{sh}$.

On both as-grown and H-intercalated materials, 40 individual $100\, \mu m^2$ Van der Pauw structures are measured (Fig. 4).\(^{13}\) The measured Hall data are then fitted to Eq. (3) via a least squares method. Highly asymmetric structures and structures, which have poor Ohmic contacts, were rejected from the data. The result of the fit is the average carrier mobility for the chip ($\bar{\mu}$).

The measured Pearson correlation for fitted Hall data (Fig. 4) is $\rho = -0.96$ for as-grown material and $\rho = 0.74$ for H-intercalated material after the deposition of passivation. The average mobility ($\bar{\mu}$) for the as-grown material is $877 \, cm^2/V\, s$ and the H-intercalated material is $1042 \, cm^2/V\, s$. These values agree with microwave reflectivity measurements.
of the mobility, which give $835 \text{ cm}^2/\text{V s}$ for the as-grown material and $1143 \text{ cm}^2/\text{V s}$ for H-intercalated material. The microwave reflectivity measurements are performed after material growth and prior to any fabrication of devices. The distribution of the measured mobility data for both materials is shown in Fig. 5.

Equation (2) indicates that $v_d$ depends on $n_{sh}$, which is itself a function of temperature. In order to account for this, the Fermi energy at $300 \text{ K}$ is calculated for both materials given the carrier density $n_{sh}(T = 300 \text{ K})$. Assuming a Dirac cone model for the graphene band structure and non-degenerate Fermi-Dirac statistics, the Fermi level may be related to the carrier concentration via the Fermi Dirac integral:

$$n = N_g \int_0^\infty \frac{u}{1 + e^{u-\eta_f}} du,$$

$$p = N_g \int_0^\infty \frac{u}{1 + e^{u+\eta_f}} du.$$  

The quantity $N_g$ represents the effective sheet density of states and is given by the following relation:

$$N_g = \frac{g_s g_v}{2\pi} \frac{(k_b T)^2}{\hbar v_f}.$$  

Here, $g_s$ and $g_v$ are the spin and valley degeneracies in graphene. Each carrier in graphene can have positive or negative spin polarization $g_s = 2$, such that each state can be occupied by two carriers with opposite spin polarization. In monolayer graphene, there are two inequivalent conical valleys in the first Brillouin zone ($K$ and $K'$) giving rise to a valley degeneracy $g_v = 2$. It should be noted that the valley degeneracy is higher for multilayer sheets of graphene. The variable $\eta_f$ represents the Fermi energy $E_f$ normalized to the thermal energy $k_b T$ when the Dirac point $E_D$ is taken to be zero energy. The exponential term evaluates to the following:

$$u \pm \eta_f = \frac{E \pm E_f}{k_b T}.$$  

The variable of integration is thus energy normalized to thermal energy $u = E/k_b T$. These relations should be understood in conjunction with the energy-momentum dispersion relation in graphene: $E - E_d = \hbar v_f |k|$, where $k$ is the wavenumber and $v_f = 10^6 \text{ cm/s}$ is the Fermi velocity in graphene. Due to the high carrier concentration, $E_f = \text{constant}$ over the measured temperature range. The Fermi level is found to be 250 meV for the as-grown material and 520 meV for the H-intercalated material. Given the Fermi level at $T = 300 \text{ K}$, it is possible to calculate carrier concentration as a function of temperature across the measured temperature range for both materials by Eq. (4) (Table I).

The electric field $E$ applied to the charge carrying sheet is calculated from dynamic IV measurements, TLM measurements of the contact resistance, and knowledge of the

TABLE I. A calculation of the sheet carrier concentration ($\text{cm}^{-2}$) based on the measured data at $300 \text{ K}$ for various temperatures. Values are normalized to $10^{12} \text{ cm}^{-2}$. The (+/−) indicates the sign of charge carriers for each material.

<table>
<thead>
<tr>
<th>$n_{sh}$ (cm$^{-2}$)</th>
<th>100K</th>
<th>200K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown (−)</td>
<td>4.61</td>
<td>4.66</td>
<td>4.75</td>
</tr>
<tr>
<td>H-intercalated (+)</td>
<td>19.8</td>
<td>19.9</td>
<td>20.0</td>
</tr>
</tbody>
</table>
geometry of the sheet. For a given measurement, one can express the measured voltage \( V \) as a function of the measured current \( I \), the contact resistance \( R_c \), and the total microbridge resistance \( R_{\text{mesa}} \). If the measured voltage drop and measured current are \( V \) and \( I \), then by Ohm’s law

\[
V = I[2R_c + R_{\text{mesa}}].
\]

The voltage drop across the mesa is then

\[
V_{\text{mesa}} = V - 2IR_c = IR_{\text{mesa}}.
\]

Given the effective voltage drop across the mesa \( V_{\text{mesa}} \), it is possible to calculate its sheet resistance \( R_{sh} \). The width \( w \) of the mesa is generally not constant due to process accuracies such that \( w = w(l) \). The mesa may be considered to be composed of an infinite number of series resistors with resistance \( dR_{\text{mesa}} \). If the sheet resistance of the microbridge is assumed to be constant, the voltage drop across the mesa \( V_{\text{mesa}} \) may be calculated by integration.

\[
V_{\text{mesa}} = IR_{sh}\int_0^l \frac{dl}{w(l)}.
\]

The geometry of the patterned microbridge graphene mesas in Fig. 2 is approximated as shown in Fig. 6.

The solid lines represent the geometry which may be used for calculation. The rounded corners shown in dashed lines indicate the true geometry from photolithography. This approximation yields the following for the sheet resistance:

\[
V_{\text{mesa}} = IR_{sh}
\]

\[
\left[4\int_0^{l_{\text{end}}} \left(w_{\text{end}} + \frac{w_{\text{end}} - w_{\text{ch}}}{l_{\text{end}}} l\right)^{-1} dl + \frac{l_{\text{ch}}}{w_{\text{ch}}} \right].
\]

Carrying out the integration, one may solve for the mesa sheet resistance

\[
R_{sh} = R_{\text{mesa}} \left[2\left(\frac{\log\left(\frac{w_{\text{end}}}{w_{\text{ch}}}ight)}{\tan \theta}\right) + \frac{l_{\text{ch}}}{w_{\text{ch}}} \right]^{-1},
\]

where

\[
\tan \theta = \frac{2l_{\text{end}}}{w_{\text{end}} - w_{\text{ch}}}.
\]

The term \( \theta \) is the current spreading angle describing the effect of the mesa geometry.\(^5\) In the low field region, the dynamic IV characteristic is linear such that the differential sheet resistance is approximately constant.

\[
R_{sh} = \frac{dV}{dl}_{\mid_{V=0}} = \text{constant}.
\]

Using the above relations, it is possible to obtain \( R_{sh} \). This value of \( R_{sh} \) may then be combined with Hall data in order to obtain the corresponding sheet carrier density \( n_{sh} \). Finally, the carrier density may be combined with measured current and channel width giving the corresponding carrier velocity. The electric field may then be obtained by considering the voltage drop across the channel region.

\[
R_{\text{mesa}} = 2R_{\text{end}} + R_{ch}.
\]

The resistances associated with \( l_{\text{end}} \) and \( l_{ch} \) are denoted as \( R_{\text{end}} \) and \( R_{ch} \), respectively. These resistances are obtained from Eq. (7). The magnitude of the electric field in the graphene bridge is

\[
\mathcal{E} = \frac{V_0 - 2I_0[R_{\text{end}} + R_{ch}]}{l_{ch}}.
\]

Given dynamic IV data, measurements of the contact resistance, and Hall measurements, it is possible to obtain the velocity-field characteristic of a graphene microbridge. Accurate determination of the end geometry is critical, as it is found to have a non-negligible effect on the velocity-field extraction. The geometry is measured using SEM imaging.

**IV. RESULTS**

To model the velocity-field behaviour, the following empirical model is applied:\(^4\)

\[
v_s(\mathcal{E}) = \frac{\mu \mathcal{E}}{\left[1 + \left(\frac{\mathcal{E}}{\mathcal{E}_{\text{sat}}}\right)^{\alpha}\right]^{\frac{1}{\alpha}}},
\]

Here, \( v_s \) is the saturated electron velocity, \( \mu \) is the local mobility, and \( \alpha \) is a fitting parameter, which describes the rate of saturation. The electric field above which the electron velocity is saturating is given by \( \mathcal{E}_{\text{sat}} = v_{sat}/\mu.\(^5\) The temperature dependent velocity-field data are fitted to Eq. (11) via a non-linear log-log least squares fit method. This gives \( v_{sat} \), \( \mu \), and \( \alpha \) for each temperature. The measured
and modeled velocity-field curves for both materials and for temperatures ranging from 100 K to 325 K are shown in Fig. 7 (Table II).

The saturation field $E_{\text{sat}}$ for graphene is measured to be between that of silicon and SiC. For fields of magnitude below $E_{\text{sat}}$, the velocity-field characteristic is linear and $v_d = \frac{E}{C^2}$. 

V. DISCUSSION

The extracted $\mu$ and $v_{\text{sat}}$ from the velocity-field measurements may be plotted as a function of temperature (Fig. 8). There are two dominant models for the temperature dependence of the electron mobility $\mu(T)$ in epitaxial graphene. First is a model in which the temperature dependence of carrier velocity is dominated by acoustic phonon scattering within the graphene. This model demonstrates a steep linear increase in the mobility for decreasing temperature.3,22 There is also a constant mobility model ($\mu(T) = \text{const}$) in which carrier velocity is determined by impurity scattering.8 In reality, both acoustic phonon scattering and impurity scattering will occur such that the measured mobility should demonstrate characteristics of both models.

With the assumption of the impurity scattering model ($\mu(T) \sim \text{const}$), it is possible to estimate the energy of the surface phonon $E_{SO} = \hbar\omega_{SO}$ in 4H-SiC with the Illinois equation.8,23,24

$\mu(T) = \mu_0 + A_1\ln(T) + A_2T^2$  \hspace{1cm} (12)

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$\mu(T) = \mu_0 + A_1\ln(T) + A_2T^2$  \hspace{1cm} (12)
Here, $N_{OP}$ represents the occupation statistics of the optical phonon mode in SiC for a given temperature. The phonon occupation $N_{OP}$ is given by non-degenerate Bose-Einstein statistics.

$$N_{OP} = \frac{1}{e^{\frac{\epsilon}{kT}} - 1}. \quad (13)$$

Thus, as $T$ increases, $N_{OP}$ increases such that the number of optical phonons increases. Higher phonon densities increase the probability of scattering events between carriers and phonons. This has the effect of decreasing the saturation velocity, $v_{sat}$.

The expected temperature dependence for $v_{sat}$ assuming the impurity scattering model (Eq. (12)) is shown in Fig. 8. By fitting the data to Eq. (12), it is possible to extract the surface phonon energy $E_{SO} = \hbar \omega_{SO}$ for the 4H-SiC of 97 meV from the as-grown measurements and 115 meV from the H-intercalated measurements.

It is useful to describe these results in connection with the dielectric properties of the 4H-SiC substrate. The relative permittivity of a dielectric will vary with frequency $\epsilon = \epsilon(\omega)$ in the following way: $^{25}$

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_{0} - \epsilon_{\infty}}{1 - (\omega/\omega_{TO})^2}. \quad (14)$$

From the electrodynamic perspective, phonons are related to waves of electrostatic polarization, which exist in the presence of an oscillating electromagnetic field.

$$P(\omega) = \epsilon_{0}[\epsilon(\omega) - 1]|E(\omega)|.$$

It can be shown that the frequencies of polarization waves in electrodynamic derivations may be related to the frequencies of phonon oscillations derived from lattice mechanics $\omega_{TO}$ and $\omega_{LO}$. $^{26}$ In this way, optical phonons are directly related to dielectric properties arising from the polarizability of the substrate lattice. $^{23}$ The existence of optical surface phonons arises when one considers the form of the electric field at the boundary between a material with permittivity $\epsilon(\omega)$ and vacuum $\epsilon_{vac} = 1$. Solving for the electromagnetic boundary equations in this problem gives the following dispersion relation $^{25-27}$

$$\omega^2(k) = \frac{1}{2}(\omega_{k}^2 + \omega_{LO}^2) - \frac{1}{2}\left[\left(\omega_{k}^2 + \omega_{LO}^2\right)^2 - 4\omega_{k}^2\omega_{LO}^2\right]^\frac{1}{2}. $$

Here the phonon frequencies $\omega_{LO}$ and $\omega_{SO}$ are the longitudinal and surface optical phonon frequencies. They can be expressed in terms of the dielectric constant of the material $\epsilon$ and the transverse optical phonon frequency $\omega_{TO}$. Here, $\omega_{k} = \sqrt{(\epsilon_{\infty} + 1)/\epsilon_{\infty}ck}$

$$\omega_{LO} = \sqrt{\frac{\epsilon_{0}}{\epsilon_{\infty}}\omega_{TO}}, \quad \omega_{SO} = \sqrt{\frac{\epsilon_{0} + 1}{\epsilon_{\infty} + 1}\omega_{TO}}.$$ 

<table>
<thead>
<tr>
<th>4H-SiC</th>
<th>HÕTO</th>
<th>HÕSO</th>
<th>HÕLO</th>
</tr>
</thead>
<tbody>
<tr>
<td>HREELS</td>
<td>98.7</td>
<td>115.9</td>
<td>119.9</td>
</tr>
<tr>
<td>$\nu(E)$</td>
<td>96.5</td>
<td>115.0</td>
<td>117.6</td>
</tr>
</tbody>
</table>

Here, $\epsilon_{0}$ is the static $\omega = 0$ dielectric constant and $\epsilon_{\infty}$ is the high frequency $\omega \rightarrow \infty$ dielectric constant. The relation between $\omega_{TO}$ and $\omega_{LO}$ is known as the Lyddane-Sachs-Teller (LST) relation. From the above relations, it is clear that $\omega_{TO} < \omega_{SO} < \omega_{LO}$ because $\epsilon_{0} > \epsilon_{\infty}$. For 4H-SiC and 6H-SiC, $\epsilon_{0} = \sqrt{\epsilon_{\infty} - \epsilon_{\infty}^{\parallel}} = 9.812$ and $\epsilon_{\infty} = \sqrt{\epsilon_{\infty}^{\perp} \epsilon_{\infty}^{\parallel}} \approx 6.609,28,29$ These calculations account for the anisotropy of $\epsilon$ in the 4H-SiC and 6H-SiC polytypes. Table III summarizes the measurements of the phonon energies in 4H-SiC by high-resolution energy loss spectroscopy (HREELS) by Nienhaus et al. as well as our measurement of $\hbar\omega_{SO}$ in the case of H-intercalated material.

The extracted value of $\hbar\omega_{SO} = 115$ meV is reasonably close to the accepted value of 115.9 meV (Refs. 28 and 30) in the measurements on H-intercalated graphene. The H-intercalated result suggests that impurity scattering determines the transport properties. Furthermore, the transport properties of epitaxial graphene are strongly influenced by the substrate. Given that the mobility is constant in the H-intercalated measurement, it is reasonable that the H-intercalated material may be used to estimate the surface phonon energy in SiC in accordance with the impurity scattering model. The Fermi level in H-intercalated material is much higher than the phonon mode energy such that the temperature dependence in model is very weak. Furthermore, the hypothesis that H-intercalation somehow decouples graphene layers from the substrate must be considered alongside the observation that carriers in the H-intercalated graphene interact with substrate surface optical phonons.

The value obtained for as-grown graphene $\hbar\omega_{SO} = 97$ meV in this measurement is non-physical based on Eq. (15). There are many potential reasons for this. The as-grown measurements demonstrate a weak linear increase in the mobility with decreasing temperature. This suggests that the transport properties in as-grown material are influenced by both acoustic phonon scattering and impurity scattering. In this way, the as-grown sample may be a poor candidate for estimating $\hbar\omega_{SO}$ as such an estimation via Eq. (12) requires that $\mu(T)$ is constant. Additionally, the influence of the buffer layer on transport properties in as-grown graphene is largely unknown. As-grown material also shows a much wider variation in the measured carrier density indicating that the epitaxial graphene layer is highly non-uniform. In the as-grown material, the Fermi level is lower, and the phonon coupling is stronger, giving a stronger dependence in the measured electron velocity with temperature.

The fundamental weakness in this method lies in the non-uniformity of epitaxial graphene, which produces statistical variation in the observed Hall data. This translates...
directly into experimental error. Thus, it is necessary to examine the possibility of a more advanced structure design and processing strategy such that Hall measurements may be performed in situ with dynamic IV measurements.

VI. CONCLUSIONS

A method of measuring the electron velocity in graphene mesas has been presented. The saturated electron drift velocity has been measured to be $2.33 \times 10^7 \text{cm/s}$ in as-grown epitaxial graphene and $1.36 \times 10^7 \text{cm/s}$ in H-intercalated epitaxial graphene. The extraction is performed by calculating the sheet resistance of microbridge structures based on measured data. From this value, one can infer the carrier concentration from Hall statistics gathered from a number of Van Der Pauw structures. The contact resistance is also measured and mesa geometry is considered. Temperature dependent measurements are used in order to extract an optical phonon energy for 4H-SiC assuming an impurity scattering model resulting in a measured surface phonon energy of $E_{SO} \approx 115 \text{meV}$. This correlates well with the accepted value of $\sim 115.9 \text{meV}$ and seems to support an impurity scattering hypothesis. The direct corollary to this observation is that the transport properties of epitaxial graphene are strongly influenced by the substrate.

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ARTICLE B

CHARGE CONTROL IN GRAPHENE MOS CAPACITORS

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Charge Control in Graphene MOS Capacitors

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Capacitance-voltage (CV) measurements are performed on planar MOS capacitors fabricated in hydrogen intercalated monolayer and bilayer graphene grown on 6H-SiC as a function of frequency and temperature. A quantitative model of charge control in graphene MOS systems is presented in conjunction with the measured data. By modeling the CV data, an interface state density of order $2 \cdot 10^{12} \text{eV}^{-1}\text{cm}^{-2}$ is found in both material systems. Surface potential fluctuations of order 80-90meV are also assessed in the context of measured data. In bilayer material, a narrow bandgap of 260meV is observed consequent to the spontaneous polarization in the substrate. A hysteresis in the CV data observed in both materials with increasing temperature indicates a thermally activated charge trapping mechanism at the graphene/dielectric interface.

I. INTRODUCTION

The potentially outstanding electron transport properties of graphene monolayers and bilayers has generated significant interest, and high speed field effect devices have been demonstrated in both materials.1-2. Intercalated layers grown by epitaxy on SiC are particularly promising as they demonstrate adequate uniformity and transport properties.3-4. However, transistors in graphene often demonstrate poor current modulation, bias dependent instability, and hysteresis effects which compromise device performance.5-7. In order to understand the observed device characteristics, an investigation of charge control in graphene metal oxide semiconductor (MOS) systems is needed.

Capacitance-voltage (CV) measurements have facilitated an understanding of charge control in MOS systems in a variety of material contexts including silicon, SiC8-9, and III/V heterostructures9. The CV technique indirectly probes the interaction of the electronic band structure with other aspects of the MOS system such as interface states ($D_{it}$), surface potential fluctuations ($\delta \epsilon_f$), material non-uniformity, and substrate polarization ($\Delta P$).

Charge control in graphene MOS systems has been investigated previously, and recent studies have sought to quantify the quantum capacitance ($C_q$) of monolayers and bilayers in top gated field effect devices10. Surface potential fluctuations ($\delta \epsilon_f$) were later addressed in the context of graphene monolayers and bilayers, and results were treated phenomenologically as a broadening of the density of states in graphene11. In exfoliated monolayers on SiO2, Dröschet al. attribute poor current modulation in top gated structures to surface potential fluctuations of order 100meV12. In [13], charge control is investigated in monolayers transferred onto SiO2 with an Al2O3 gate dielectric grown by atomic layer deposition (ALD). Results demonstrate dispersion in the CV curves associated with interface states ($D_{it}$), and temperature dependence is attributed to thermally activated charge trapping in the dielectric.

It is also necessary to consider substrate induced effects in graphene MOS systems. In epilaxial graphene on 4H(6H)-SiC in particular, the spontaneous polarization of the substrate $\Delta P$ is responsible for the hole conductivity observed in intercalated monolayers and bilayers14. Additionally, $\Delta P$ is known to open a narrow energy gap ($\epsilon_g$) in epilaxial bilayers, which has important consequences for modeling charge control15,16.

Here, we present a quantitative physical model of charge control in graphene monolayers and bilayers in conjunction with temperature dependent CV measurements performed on planar MOS capacitors fabricated in hydrogen intercalated epitaxial monolayers and bilayers grown on 6H-SiC. CV modeling allows for the extraction of a number of relevant device parameters including the density of interface states and the magnitude of surface potential fluctuations, and the presence of a narrow energy gap in bilayers induced by the spontaneous polarization of the substrate. Hysteresis and charge injection effects are also discussed in the context of the temperature dependent data.

II. THEORY

An analysis of charge control in a MOS capacitor begins by considering the modulation of the Fermi energy $\epsilon_f$ by an applied voltage $v$. The total capacitance response observed in a CV measurement may be expressed as

$$\frac{1}{C_{tot}(\epsilon_f)} = \frac{1}{C_{ox}} + \frac{1}{e^2 \rho(\epsilon) + e^2 D_{it}(\epsilon)}$$

(1)

In Eq. 1, $C_{ox}$ represents the oxide capacitance, $C_q = e^2 \rho(\epsilon)$ the quantum capacitance in graphene, and $C_{it} = e^2 D_{it}(\epsilon)$ the capacitance due to interface states17,18. Eq. 1 implies the following relation between $\epsilon_f$ and $v$19

$$\frac{1}{e} \frac{d\epsilon}{dv} = \frac{C_{ox}}{C_{ox} + e^2 \rho(\epsilon) + e^2 D_{it}(\epsilon)}$$

(2)
Integrating equation Eq. 2 over \( \epsilon \in [0, \epsilon_f] \) and \( v \in [v_D, v] \) yields the following expression.

\[
\Delta v - \frac{e^2}{C_{ox}} \int_{v_D}^{v} D_{it}(v) dv = \frac{\epsilon_f}{e} + \frac{e}{C_{ox}} n(\epsilon_f) \quad (3)
\]

In Eq. 3, \( \Delta v = v - v_D \) where \( v_D \) is the Dirac voltage (\( \epsilon_f = 0 \)). Eq. 3 is the equivalent of the Berglund integral in graphene MOS\(^{20}\). The electron density may be calculated via the Fermi-Dirac integral.

\[
n_e(\epsilon_f) = \int_0^\infty \rho(\epsilon; \epsilon_f, k_b T) d\epsilon \quad (4)
\]

In Eq. 4, \( k_b \) is Boltzmann’s constant and \( T \) is the absolute temperature. The occupation statistics are given by the Fermi-Dirac distribution \( f(\epsilon; \epsilon_f, k_b T) = [1 + e^{(\epsilon - \epsilon_f)/k_b T}]^{-1} \). The hole density \( n_h(\epsilon_f) \) may be obtained by transforming \( \epsilon_f \rightarrow -\epsilon_f \) and integrating over \( \epsilon \in [0, -\infty) \). The total carrier density is then given by \( n = n_e + n_h \). When \( \epsilon_f \gg 0 \) electron density dominates and when \( \epsilon_f \ll 0 \) hole density dominates. An ambipolar condition occurs near \( \epsilon_f \approx 0 \), as both electron and hole density contribute to the total carrier density. The monolayer and bilayer density of states relations are

\[
\rho_m(\epsilon_f) = \frac{g_s g_v}{2\pi} \frac{|\epsilon_f|}{(\hbar v_f)^2} \quad (5)
\]

\[
\rho_b(\epsilon_f) = \frac{g_s g_v}{2\pi} \frac{|\epsilon_f| + \gamma_{\perp}/2}{(\hbar v_f)^2} \quad (5)
\]

where, \( g_s, g_v \) are the twofold spin(valley) degeneracies respectively, \( v_f \approx 1 \cdot 10^6 \text{cm/s} \) is the Fermi velocity in graphene, and \( \hbar \) is the reduced Plank constant. In the case of bilayer graphene, the density of states in Eq. 5 is approximated as the sum of the density of states at low and high energy. The quantity \( \gamma_{\perp} \approx 0.4eV \) represents the interlayer coupling constant in Bernal stacked bilayers\(^{21}\).

In order to accurately model CV curves, it is necessary to account for interface states \((D_{it})\). Generally, the effect of a large \( D_{it} \) is to compromise charge control in the channel by screening \( C_q \). A common approach to estimate \( D_{it} \) is to compare the capacitive response of the MOS structure at low and high frequency\(^9\).

\[
eD_{it}^f(v) = \left( \frac{C_{ox}C_0}{C_{ox} - C_{it}} - \frac{C_{ox}C_{\infty}}{C_{ox} - C_{\infty}} \right) \quad (6)
\]

When a MOS capacitor is biased at low frequency, the total capacitance \( C_{\text{tot}}^0 \) will contain contributions from \( C_{ox} \), \( C_q \), and \( C_{it} \). As the frequency of the test signal is increased, interface states will contribute less to the total capacitance observed. In the case of very high frequencies only \( C_q \) and \( C_{ox} \) will contribute to the observed capacitance \( C_{\text{tot}}^\infty \). This dispersive effect in the \( C_{it} \) is due to the finite capture and emission lifetimes \( (\tau_{c,e}) \) of trap states. In the majority of dielectric/semiconductor systems, \( \tau_e \gg \tau_c \) such that the dominant contribution to frequency dependence in \( C_{\text{tot}} \) is \( \tau_c \).

Eq. 6 tends to underestimate \( D_{it} \) especially when \( C_q \gg C_{it} \). In order to account for this, the effective \( D_{it} \) may be estimated by multiplying Eq. 6 by a scaling factor \( D_0 \). The dispersive effect due to the finite lifetimes of trap states is well described by a simple exponential where \( \omega = 2\pi f \) is the angular frequency.

\[
D_{it}(v, \omega) = D_0D_{it}^*(v)e^{-\omega\tau_c} \quad (7)
\]

The movement of charge in and out of interface states gives rise to a small signal conductance \( G_{it} \) such that \( D_{it} \) can be estimated by examining the frequency dependence of \( G_{it} \).

\[
\left( \frac{G_{it}}{\omega} \right) = \frac{e\omega\tau_c D_{it}}{1 + (\omega\tau_c)^2} \quad (8)
\]

Eq. 8 exhibits a maximum in conductance when interface states are in resonance with the test signal.

When analyzing CV data, it is also necessary to account for surface potential fluctuations \((\delta \epsilon_f)\). Surface potential fluctuations describe a spatial variation in \( \epsilon_f \) due to charge inhomogeneities at the graphene/substrate and graphene/oxide interfaces. In graphene, surface potential fluctuations are especially relevant near \( \epsilon_f = 0 \) as they generate localized islands of electron and hole conduction\(^{22–24}\). In order to model surface potential fluctuations, it is useful to introduce a random variable to describe the Fermi energy \( \tilde{\epsilon}_f \).

\[
\tilde{\epsilon}_f = \mathcal{N}(\epsilon_f) \quad (9)
\]

The distribution \( \mathcal{N} \) represents the statistics which describe the spatial variations of \( \epsilon_f \). Typically, \( \mathcal{N} \) may be assumed to be normally distributed.

\[
\mathcal{N}(\epsilon ; \epsilon_f, \delta \epsilon) = \exp \left( -\frac{(\epsilon - \epsilon_f)^2}{2(\delta \epsilon)^2} \right) \quad (10)
\]

In Eq. 10 the terms \( \epsilon_f \) and \( \delta \epsilon \) represent the mean and standard deviation of the Fermi energy statistics \( \tilde{\epsilon}_f \).

\[
\delta \epsilon = \delta \epsilon_f \exp \left( -\frac{\epsilon_f^2}{2(\delta \sigma_f)^2} \right) \quad (11)
\]

\( \delta \epsilon_f \) represents the root mean square (RMS) value of surface potential fluctuations near the Dirac point. Eqs. 10 and 11 describe a case where the magnitude of the surface potential fluctuations decays with standard deviation \( \delta \sigma_f \) as one moves further from \( \epsilon_f = 0 \). Generally the term \( \delta \sigma_f \) is found to be of order 100meV such that \( \delta \epsilon \approx \delta \epsilon_f \) near the Dirac point. When \( |\epsilon_f| \gg 0 \), surface potential fluctuations have little effect on the behavior of the CV characteristic.

In this work, we propose the following method to model CV-curves in graphene. First, \( D_{it}^f \) may be estimated via Eq. 6. As this is known to be an underestimation, the scale parameter \( D_0 \) is then introduced and the corresponding \( D_{it} \) may be included. If a negative \( D_0 \) is required to obtain accurate high frequency capacitance curves, then the measurement data must be...
Corrected for inductance. Typically, an inductance correction is only needed for measurement frequencies exceeding 1MHz. Using $D_{ll}(v, \omega)$, one may obtain $\epsilon_f(v, \omega)$ via Eq. 3 via nonlinear optimization methods. In order to obtain proper capacitance curves, it is necessary to account for surface potential fluctuations. This is accomplished via a kind of Monte Carlo simulation in which noisy $\epsilon_f(v, \omega)$ curves are generated via Eqs. 10 and 11. These are then used to calculate noisy capacitance curves via Eq. 1. Results are then averaged in order to obtain a final model.

III. METHODS

CV(GV) measurements are performed as a function of temperature on 10 000µm${}^2$ planar MOS capacitors using an Agilent E4980A LCR meter. The geometry of the MOS capacitors is shown in Fig. 2. In the CV measurements, the applied bias is swept quasistatically from -2 to 2V, and the capacitive(conductive) responses of the device to a 10mV test signal are measured at several frequencies $f \in [1, 10, 100, 200, 500, 1000]$kHz. All measurements consist of a forward and reverse sweep in order to track hysteretic effects in the devices.

The monolayer and bilayer samples were grown on semi-insulating (SI) 6H-SiC by chemical vapour deposition (CVD) and in-situ intercalated with hydrogen.$^{25,26}$ Upon intercalation, both monolayers and bilayers exhibit hole conduction ($\epsilon_f < 0$) as a consequence of the spontaneous polarization of the substrate.$^{14}$ Prior to device fabrication, the samples were characterized via microwave reflectivity measurements and scanning electron microscopy (SEM) in order to assess material quality and the number of layers. The microwave reflectivity measurements yielded mobilities of 4500(3000)cm$^2$/V·s and carrier densities of 0.95(0.87)$\cdot 10^{13}$cm$^{-2}$ for the monolayer(bilayer) samples.

The Al$_2$O$_3$ dielectric was deposited by repeated evaporation and subsequent hotplate oxidation at 200°C of 1nm aluminium metal films. In both samples, a target oxide thickness ($t_{ox}$) of 15nm was chosen in order to ensure adequate coverage of the terraced morphology of the SiC substrate. In addition to the planar MOS devices, ancillary van der Pauw (vdP) structures and Transfer Length Method (TLM) structures are included to assess the low field transport properties and contact resistance after processing. From these structures, mean mobilities of 1601(2028)cm$^2$/V·s and carrier densities of 1.05(0.79)$\cdot 10^{13}$cm$^{-2}$ are obtained for the monolayer(bilayer) samples. Measurements on the TLM structures indicated a contact resistance of 300(200)Ω·µm for the monolayer(bilayer) samples.

The temperature sweep is carried out in a liquid N$_2$ cryostat, and the temperature is swept linearly from 77K to 280K. Additional measurements are performed at room temperature in order to investigate charge in-
FIG. 3: [left] The extraction of the $\tau_e$ via the exponential decay of $D_0 D_{it}$ with increasing frequency (Eq. 7). [inset] The estimated $D_0 D_{it}$ as calculated from the difference of high frequency and low frequency capacitances. [right] The estimation of $\tau_e$ from Eq. 8. [inset] The CV curves measured corresponding to the CV curves shown in Fig. 1. Low and high frequency curves are shown solid, while intermediate frequencies are shown dotted.

<table>
<thead>
<tr>
<th></th>
<th>$C_{ox}$ (pF)</th>
<th>$\kappa$</th>
<th>$v_D$ (V)</th>
<th>$D_0$</th>
<th>$D_{it}$</th>
<th>$\tau_e$ (ps)</th>
<th>$\delta\epsilon_f$ (meV)</th>
<th>$\delta\sigma_f$ (meV)</th>
<th>$\epsilon_f$ (meV)</th>
<th>$\sigma_f$ (meV)</th>
<th>$p$(% ML)</th>
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</thead>
<tbody>
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<td>1.51(1.50)</td>
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<td>78</td>
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<td>260</td>
<td>80</td>
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</table>

TABLE I: A table summarizing the model parameters for the 77K CV curves shown in Fig. 1. The density of interface states ($D_{it}$) is reported in units of $10^{12}$eV$^{-1}$cm$^{-2}$ for $\epsilon_f = 0$, and parentheses represent extractions from CV(GV) curves respectively. Note that the $\epsilon_f$ and $\sigma_f$ values in monolayer material apply only to its 20% bilayer component. The quantities are grouped according to their relevant effect.

jection effects in connection with the hysteresis observed in the devices. In order to obtain figures for $D_{it}$ and $\delta\epsilon_f$, the low frequency conductance must be negligible over the applied bias range. In all CV curves presented in this work, a low frequency conductance of <1nS is observed.

In order to assess material uniformity, work function ($\phi_g$), and surface potential fluctuations ($\delta\epsilon_f$) in epitaxial graphene, frequency modulated Kelvin Probe Force Microscopy (KPFM) is performed on small 25nm$^2$ van der Pauw (vdP) structures$^{27}$. As KPFM is only sensitive to the surface of a material, it was necessary to fabricate samples without the gate oxide present. Prior to performing KPFM, AFM cleaning was performed in contact mode to remove contaminants and residues from the surface. As graphene is sensitive to atmospheric and polymer contaminants, it is necessary to perform the KPFM measurements in a controlled atmosphere$^{28–30}$. Prior to scanning, the chamber was evacuated and then subsequently filled with $N_2$ at room temperature. Finally, the atmosphere was saturated to a relative humidity of 30%. The work function calibration was done using $\phi_g = \phi_{probe} - eV_{cpd}$ where $V_{cpd}$ is the measured surface potential. The probe work function ($\phi_{probe}$) was calibrated against the an Au contact electrode within the scan area.

Modeling the CV curves is computationally difficult as a combination of Monte Carlo methods, nonlinear methods, and parameter optimization is required. For this reason, an efficient CV simulation kernel was implemented on a graphics processor (GPU). GPU processing offers the flexibility of a massively parallel computation scheme in a highly threaded environment allowing for efficient Monte Carlo simulations.

IV. CV CHARACTERISTICS IN GRAPHENE MOS CAPACITORS

The measured and modeled low frequency CV characteristics at 77K are shown in Fig. 1 for both monolayer and bilayer material. $\epsilon_f(v_g)$ as calculated from Eq. 3 is also shown. Both materials exhibit a minimum in capacitance which corresponds to $\epsilon_f = 0$. As both materials are intercalated, $v_D > 0$ indicating hole density at zero bias. Moving away from $v_D$ in either direction, the capacitance increases and then saturates indicating accumulation of carriers at the graphene/oxide interface. In the saturation regions, $C_q \gg C_{ox}$ such that the oxide capacitance and dielectric constant may be estimated $\kappa = C_{ox}/\varepsilon_0$. Additionally, the CV curves are approximately symmetric around $v_D$, which reflects the symmetric behavior of $\rho_{m,b}(\epsilon_f)$ around $\epsilon_f = 0$.

All parameters for the modeled monolayer and bilayer capacitance curves of Fig. 1 are shown in Table I. In the following sections, details are presented with respect to the implementation and interpretation of modeling results shown in Table I. First, a commentary on $D_{it}$ is provided. Next, surface potential fluctuations and mate-
served in AlGaN/GaN heterostructures with a low temperature ALD Al₂O₃ gate dielectric. For comparison, values as low as 5·10¹⁰eV⁻¹cm⁻² and 10¹¹eV⁻¹cm⁻² have been achieved in silicon and SiC MOS devices respectively with high temperature SiO₂ dielectrics.

From Fig. 1, the monolayer material exhibits the larger swing in Fermi energy with ɛ_f ∈ [-0.32, 0.28eV] over the applied bias range. Thus, the measurement only probes an energy interval at the dielectric/graphene interface over 0.60eV near the middle of the dielectric band gap. The D₀ for such a limited energy range are in most cases rather flat (e.g. for SiO₂ and Al₂O₃ on SiC and Si) such that the peak in D₀ near v_D is an artifact of the extraction. When v is far from v_D, C_q is large such that a estimation of D₀ by Eq. 7 is difficult. For this reason, the maximum density of interface states Dₘₐₓ occurring at ɛ_f = 0 is taken to estimate the true D₀.

B. Surface Potential Fluctuations

The effect of surface potential fluctuations is to generate a distributed capacitance minimum in the CV characteristics. In the case of a monolayer, C_q(ɛ_f) → 0 when ɛ_f = 0 such that C_q of the measured value occurs near v_D. The fact that such a minimum is not seen in measurement data demonstrates the effect of surface potential fluctuations (δɛ_f). Modeling the CV characteristics in monolayers and bilayers yields values of 92(78)meV for δɛ_f. This should be compared with values of 100meV, 25-40meV and 30-100meV in graphene, Si, and SiC MOS devices respectively.

The results of KPFM imaging are shown in Fig. 4. The magnitude of the surface potential fluctuations in pristine graphene may be compared with those extracted from CV measurements. The work function data is normally distributed for the monolayer(bilayer) regions within a 25-40meV and 30-100meV range. The results of KPFM imaging are shown in Fig. 4. The magnitude of the surface potential fluctuations in pristine graphene may be compared with those extracted from CV measurements. The work function data is normally distributed for the monolayer(bilayer) regions within a 25-40meV and 30-100meV range. The results of KPFM imaging are shown in Fig. 4. The magnitude of the surface potential fluctuations in pristine graphene may be compared with those extracted from CV measurements. The work function data is normally distributed for the monolayer(bilayer) regions within a 25-40meV and 30-100meV range.

C. Material Uniformity

The SEM and KPFM images of Figs. 2 and 4 show that the large area monolayer MOS capacitors have bilayer inclusions which have an effect on the CV characteristics. These inclusions are a consequence of the growth mechanism. During epitaxy, graphene growth nucleates at step edges and propagates over the terrace. On monolayer(bilayer) samples, bilayer(multilayer) graphene is common on terrace edges respectively. Additionally, inclusions of monolayer(bilayer) material in bilayer(monolayer) samples may also appear on terraces.
FIG. 5: [left/centre] Temperature dependence of $v_D$ in the CV curves for monolayer (black) and bilayer (red) MOS capacitors respectively. A hysteresis in the CV characteristic opens in both materials around 160K suggesting an additional trap related effect. Arrows for the bilayer curve indicate the clockwise orientation of the hysteresis. [right] $v_D$ plotted as a function of temperature for the forward(dashed) and reverse(solid) sweeps.

It is straightforward to account for inclusions in CV modeling by considering the density of states as linear combination of the monolayer and bilayer relations (Eq. 5).

$$\rho_{e\cdot f}(\epsilon) = p\rho_m(\epsilon) + (1 - p)\rho_b(\epsilon)$$  \hspace{1cm} (12)

In Eq.12, the quantity $p$ represents the mixing ratio of monolayer area to the total area of the device. In order to estimate $p$, SEM imaging was performed on monolayer and bilayer material. Terraces and terrace edges are clearly visible on the surface of the substrate. In Fig. 2, low contrast regions correspond to monolayer material while high contrast regions correspond to bilayer material. Values of 0.8(0.1) were obtained from imaging monolayer(bilayer) material respectively.

### D. Energy Gaps in Bilayer MOS

Although the CV characteristic observed in monolayer and bilayer is qualitatively similar, the physical origin of the capacitance minimum is different. This may be seen by returning to the expression for the total capacitance (Eq. 1). At high frequency, $D_{it} \approx 0$ such that the total capacitance is simply $C_{tot} = \left[C_q^{-1} + C_{ox}^{-1}\right]^{-1}$. In both monolayer and bilayer material, a minimum in $C_{tot}$ is expected at $\epsilon_f = 0$. However, in a bilayer $C_q \neq 0$ when $\epsilon_f = 0$. Evaluating the quantum capacitance in a bilayer, a value of 4.170pF/cm$^2$ is obtained at $\epsilon_f = 0$. For the $A = 10000\mu$m$^2$ bilayer capacitors $C_qA = 471pF$. By contrast, the observed oxide capacitance $C_{ox}A \approx 33pF$. Thus, the minimum expected capacitance at high frequency is $C_{tot}^{min} = 30.8pF$.

By this analysis, the minimum high frequency capacitance observed in the bilayer data (23.2pF) is lower than expected the 30.8pF. In order to describe the observed behavior it is necessary to introduce an energy gap $\epsilon_g$ into the density of states relation near $\epsilon_f = 0$.

$$\rho_b(\epsilon) = \rho_b^0(\epsilon)\rho_g(\epsilon : \epsilon_g, \sigma_g)$$  \hspace{1cm} (13)

The notion of an energy gap in graphene bilayers is well understood, and results in a symmetry breaking of the bilayer Hamiltonian which occurs when the individual layers are at different potential energies\cite{15,16}. In bilayer MOS, there are two sources of such potential which function to open a gap: the high density of interface states at the graphene/oxide interface $D_{it}$, and the spontaneous polarization of the 6H-SiC substrate $\Delta P$. In both cases the sheet charge density involved is of order $10^{12}$cm$^{-2}$ at minimum, such that a symmetry breaking of the bilayer Hamiltonian is realistic. The notion of an energy gap is additionally supported by the fact that the 1kHz CV curve in bilayer material exhibits a significantly deeper capacitance minimum than the monolayer case despite comparable $D_{it}$ and $\delta \epsilon_f$.

The presence of surface potential fluctuations (80-90meV) reflects that the charge densities involved are not uniform. In this case, the magnitude of the energy gap will vary locally from point to point within the bilayer MOS structure such that an empirical model is needed for $\rho_g(\epsilon : \epsilon_g, \sigma_g)$.

$$\rho_g(\epsilon : \epsilon_g, \sigma_g) = 1 - \frac{1}{2}\text{erfc}\left(\frac{\epsilon + \epsilon_g/2}{\sqrt{2}\sigma_g}\right) + \frac{1}{2}\text{erfc}\left(\frac{\epsilon - \epsilon_g/2}{\sqrt{2}\sigma_g}\right)$$  \hspace{1cm} (14)

The effect of Eq. 14 is to cut a smoothed notch out of the bilayer density of states relation in (Eq. 5). Here $\epsilon_g$ represents the mean value of the energy gap, while $\sigma_g$ characterizes its dispersion. Results from CV modeling suggest an energy gap of 260meV in the case of the bilayer sample, and a value of 274meV for the bilayer component of the monolayer sample. These values are in qualitative agreement with experiments in dual gated field effect transistors, in which a narrow energy gap of $\epsilon_g = 250$meV has been observed\cite{38,39}. Polarization induced gaps of order $\epsilon_g = 150$meV have also been observed epitaxial bilayers on SiC\cite{40}.
FIG. 6: [left] A demonstration of the sensitivity of modeled CV curves on surface potential fluctuations for bilayer material. \( \delta \varepsilon_f \) is scaled linearly from 0meV to the 80meV arrived at by modeling. [right] A similar demonstration regarding \( \varepsilon_g \) sensitivity in bilayers. In both plots the measured CV curve is shown in red while modeled curves are shown in black.

E. Graphene MOS Band Diagrams

The energy band diagram for the graphene MOS system as shown in Fig. 7 provides a useful context to understand CV measurements. The mean work function of \( \phi_g = 4.8 \) eV for graphene estimated from the KPFM measurements is in relative agreement with literature values\(^{28,41,42} \). The estimation of the \( \phi_g \) from KPFM is calibrated relative to the work function of the Au contact metalization.

As the amount of mobile charge in the semi-insulating SiC is negligible, there should be minimal band bending in the SiC bulk. Thus, \( \varepsilon_f \) passes through the midgap such that the band offset between the conduction band in the SiC and the \( \varepsilon_f \) in the graphene is \( \varepsilon_{gSiC} = \frac{1}{2} \). The band gap in 6H-SiC is \( \varepsilon_{gSiC} \approx 3.0 \) eV resulting in a band offset of 1.5eV\(^{14,43} \).

The band gap in Al\(_2\)O\(_3\) oxide \( \varepsilon_{gAl2O3}^z \) has been shown vary with the phase of the material and its quality. Values for high quality crystalline films range from 8.8eV in \( \alpha-Al_2O_3 \) to 7.1-8.0eV in \( \gamma-Al_2O_3 \). For lower quality amorphous films, values of 5.1-7.1eV are reported\(^{44,45} \). Measurements for the conduction band offset between the amorphous Al\(_2\)O\(_3\)/SiC system yield values of 2.06eV such that the charge neutrality point in the graphene lies near the midgap in the Al\(_2\)O\(_3\)\(^{46-48} \). For this reason, Al\(_2\)O\(_3\) is an ideal dielectric for graphene MOS on SiC.

V. DISCUSSION

The quantitative nature of the CV model becomes evident when considering sensitivity with regard to the parameters of Table I. A particular sensitivity is observed with respect to \( \delta \varepsilon_f \) and \( \varepsilon_g \) as summarized in Fig. 6. Further, all parameters introduced into the model are physical with the possible exception of \( \delta \sigma_f \). In the Si and SiC cases, the magnitude of the surface potential fluctuations is typically independent of bias such that \( \delta \sigma_f \rightarrow \infty \). In the context of the CV model, \( \delta \sigma_f \) effectively corrects for the artificial profile of \( D_{it} \) obtained from Eq. 6.

When measuring the CV characteristic as a function of temperature, several additional effects are observed which are not considered in the CV model (Fig 5). First, a hysteresis of anti-clockwise orientation opens in both samples for temperatures(thermal energies) greater than 160K(13.7meV). Hysteresis is a common problem in the context of graphene field effect transistors and has been attributed to a plurality of mechanisms\(^{49-51} \). The orientation of the hysteresis is significant and suggests a charge injection effect\(^{52,53} \).
By comparing the extracted forward ($v^f_D$) and reverse ($v^r_D$) sweep Dirac points a similar trend appears in both materials. Generally, $v^f_D$ is constant, while $v^r_D$ increases suggesting that charge injection occurs only when $\epsilon_f > 0$. In monolayer(bilayer) a $v^f_D - v^r_D$ of 0.43(0.52V) is observed at 280K indicating similar levels of charge injection in both materials. Repeated CV sweeps of increasing amplitude reveal a drift of the capacitance minima towards positive bias indicating permanent injection of negative charge into the oxide layer. In addition to hysteresis, a monotonic increase in the zero bias capacitance is observed with increasing temperature. In\textsuperscript{13} similar trends in graphene MOS capacitors are attributed to a thermally activated trap mechanism.

The effect of oxide charging tends to be deleterious to effective charge control as the lagging of $\epsilon_f$ behind $v$ generates a more shallow slope accompanied with additional broadening in the CV characteristic on either side of $v_D$. The charge injection hysteresis is observed at all frequencies owing to the fact that it is a DC effect. The frequency relevant to charge injection is the sweep rate of the applied bias rather that of the test signal.

The effectiveness of charge control can be estimated by considering the ratio of the carrier density in accumulation $n_{acc}$ to the intrinsic carrier density. From modeling CV data, the maximal $\epsilon_f$ is approximately 320(-220)meV for monolayer(bilayer) material. This corresponds to a carrier density of approximately 0.78(1.03)$ \times 10^{13} \, \text{cm}^{-2}$. The intrinsic electron densities are given by the following relations\textsuperscript{24}

\begin{equation}
\begin{align*}
n^e_m(0) &= \frac{\pi (k_B T)^2}{6 (\hbar v_f)^2} \\
n^b_e(0) &= \frac{\log(2)}{\pi} \frac{\gamma \cdot k_B T}{(\hbar v_f)^2}
\end{align*}
\end{equation}

Counting both electrons and holes, the above relations evaluate to 0.16(2.79)$ \times 10^{12} \, \text{cm}^{-2}$ at 77K. This suggests a ratio $n_{acc} / n_{tot}(0)$ of 469(36) in monolayer(bilayer) material suggesting that charge control should be much more effective in the monolayers. However, in the presence of surface potential fluctuations, the RMS carrier densities become 0.51(2.86)$ \times 10^{12} \, \text{cm}^{-2}$ such that a reduced ratio of 15(3.6) is expected at 77K. Modulation of the carrier density in both cases is further limited by the presence of $D_{it} \approx 2 \times 10^{12} \, \text{eV}^{-1} \, \text{cm}^{-2}$. In the case of monolayer material, $D_{it}$ destroys the remaining modulation of carrier density at low frequency. In bilayer material, some charge control is preserved due to $\epsilon_g \approx 260\,\text{meV}$.

VI. CONCLUSIONS

A method to model measured CV data in graphene MOS structures has been described. With accurate models, it is possible to estimate the density of interface states $D_{it}$, the magnitude of surface potential fluctuations $\delta \epsilon_f$, the effect of material anisotropy, and the presence of a narrow energy gap $\epsilon_g$ in bilayer material. The density of interface states is significant in both materials, and values of order $2 \times 10^{12} \, \text{eV}^{-1} \, \text{cm}^{-2}$ are extracted from measurement data. An analysis of the $D_{it}$ results yields an emission lifetime $\tau_e$ of several hundred nanoseconds for the trap states. In both materials, surface potential fluctuations of order 80-90meV are found to generate a distributed capacitance minimum. Similar values are obtained from KPFM measurements, and surface potential fluctuations are found to be correlated with inclusions of monolayer(bilayer) material. An narrow energy gap of order 260meV is obtained for the bilayer constituents of both materials consequent to the spontaneous polarization of the substrate. An anti-clockwise hysteresis effect is observed due to a thermally activated trap in the oxide. The hysteresis is found to be temperature dependent, and a thermal barrier of about 160K(13.7meV) is deduced from temperature dependent CV data. The hysteresis has a deleterious effect on charge control, and generates considerable broadening in the CV characteristics of both MOS systems.

These results are of interest from a physical and technological perspective as they suggest a need to improve dielectric quality in graphene MOS. The effect of $D_{it}$ and $\delta \epsilon_f$ substantially compromise charge control in graphene MOS systems. Monolayer material exhibits poor charge control characteristics as a direct consequence of these effects. In bilayers, some degree of charge control is maintained due to the opening of a narrow energy gap. This suggests that monolayers and bilayers should be investigated in conjunction with further studies in dielectric films with equal interest.

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Hysteresis modeling in graphene field effect transistors

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Hysteresis modeling in graphene field effect transistors

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Graphene field effect transistors with an Al2O3 gate dielectric are fabricated on H-intercalated bilayer graphene grown on semi-insulating 4H-SiC by chemical vapour deposition. DC measurements of the gate voltage \( v_g \) versus the drain current \( i_d \) reveal a severe hysteresis of clockwise orientation. A capacitive model is used to derive the relationship between the applied gate voltage and the Fermi energy. The electron transport equations are then used to calculate the drain current for a given applied gate voltage. The hysteresis in measured data is then modeled via a modified Preisach kernel. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4913209]

I. INTRODUCTION

Graphene has attracted a great deal of interest from diverse range of disciplines due to its unique band structure and electron transport properties. A wide range of graphene based technologies, including electrochemical sensors,1 infrared detectors,2 and field effect transistors (FETs), have been presented. Particular interest has been directed towards the development of a graphene based technology for high frequency electronic devices. Though frequently observed,3–7 a theoretical treatment of field effect hysteresis in graphene FETs has not yet been presented in the context of experimental data.

The field effect hysteresis is not unique to graphene. Gate hysteresis has been observed in a variety of semiconductor materials, such as AlGaAs/GaAs heterostructures,8,9 AlGaInN/GaN MOS heterostructures,10 and (4,6)H-SiC MOS structures.11,12 The hysteresis in MOS structures is usually attributed to charge trapping at the semiconductor/dielectric interface, ion drift within the insulator, or space charge effects related to dielectric polarization. Charge trapping generates a hysteresis of anti-clockwise orientation,9,13 whereas polarization and space charge effects generate a hysteresis with clockwise orientation.14 Technology development often aims at the elimination of hysteretic phenomena for the purpose of reducing bias dependent instabilities. In addition to providing insight into the origin of the hysteresis effect, an accurate model based on first principles provides a deeper understanding into the device physics and electron transport properties of MOS structures.

Hysteresis is observed in graphene field effect transistors (GFETs) of many types, including exfoliated flakes,4,15 transferred large area layers on SiO2 and SiO2/Si3N4,16 and as-grown layers SiC grown by chemical vapour deposition (CVD)17 and sublimation. In this work, a drain hysteresis of similar character is clearly seen in H-intercalated CVD bilayer GFETs when measuring the drain current \( i_d \) as a function of gate voltage \( v_g \). In the absence of hysteresis, the drain current density \( J \) may be calculated from the electron \( n \) and hole \( p \) densities by the following equation:

\[
J = e[n\mu_n + p\mu_p]\mathbf{E}. \tag{1}
\]

The electron and hole densities are themselves a function of the Fermi energy \( \epsilon_f \). During FET operation, \( \epsilon_f \) is modulated by \( v_g \). In Eq. (1), \( e \) is the fundamental charge, \( \mu_n, \mu_p \) are the electron and hole mobilities, and \( \mathbf{E} \) is the electric field applied between source and drain.

The objective of this work is to extend Eq. (1) to include a hysteretic effect and to apply quantitative hysteresis models to GFET data. In Sec. II, the metal/oxide/semi-metal (MOSm) system is modeled as a capacitive divider, and a relation expressing the dependence of \( \epsilon_f \) on \( v_g \) is presented. The current saturation observed in graphene is modeled by considering Fermi level pinning interface effects. In Sec. III, the hysteresis is introduced by considering a hysteretic Fermi energy \( \mathcal{P}[\epsilon_f] \). The operator \( \mathcal{P} \) is a modified Preisach kernel which generates a hysteresis on \( \epsilon_f \). Given \( \mathcal{P}[\epsilon_f] \), it is straightforward to calculate the hysteretic current density via substitution of \( \mathcal{P}[\epsilon_f] \) for \( \epsilon_f \) in Eq. (1). Details regarding device fabrication and material/device characterization are presented in Sec. IV. Additional details regarding the computational implementation of the Preisach kernel and hysteresis optimization are also presented. In Secs. V and VI, this model is applied to DC and low-frequency (LF) hysteresis measurements on the GFETs, and the resulting non-linear GFET models obtained from hysteresis optimization are shown. In Sec. VII, the physical origin of the hysteresis is discussed in the context of the experimental results.

II. CAPACITANCE MODELING

To generate \( \mathcal{P}[\epsilon_f] \), it is necessary to find the relationship between the Fermi energy and gate voltage. A common approach is to model the MOSm structure as a capacitive divider (Figure 1).18 Here, \( C_{ox}, C_a, C_q \) represent the oxide, density of states (i.e., quantum), and interface charge capacitances per unit area, respectively.

The following relation follows from voltage division:

\[
\frac{\partial v_g}{\partial \epsilon_f} = \frac{C_{ox}}{C_{ox} + C_a + C_q}. \tag{2}
\]
Here, $v_g = e\varepsilon_f$ represents the voltage at the graphene dielectric interface. $C_q$ is obtained by differentiating the carrier density with respect to energy ($C_q = \partial Q = e\partial (en)$). 

$$e^2\partial n = e^2\partial_\varepsilon [\rho(\varepsilon)]^2 \partial(\varepsilon ; \varepsilon_f, \beta) d\varepsilon 
\approx e^2 \rho(\varepsilon) \partial(\varepsilon - \varepsilon_f) d\varepsilon 
= e^2 \rho(\varepsilon_f).$$

In Eq. (3), the carrier density $n(\varepsilon_f)$ is expressed as the product of the density of states in graphene $\rho(\varepsilon)$ and the Fermi Dirac distribution $f(\varepsilon ; \varepsilon_f, \beta)$, where $\beta = (k_B T)^{-1}$. The integral is evaluated via the zero temperature approximation such that $\partial f(\varepsilon ; \varepsilon_f, \beta) \approx \delta(\varepsilon - \varepsilon_f)$.

In AB-stacked bilayer graphene, the density of states is calculated from a tight binding Hamiltonian with one interlayer coupling term $(\gamma)$. The case of monolayer graphene is obtained by considering $\gamma = 0$. Taking the total density of states to be the sum of the low and high energy approximations gives the following:

$$\rho(\varepsilon) = \frac{g_s g_v}{2\pi} \left[ \varepsilon_f + \frac{\gamma}{2} \right].$$

Here, $\hbar$ is the reduced Planck constant, $g_s,g_v$ are the spin and valley degeneracies, $v_f = 10^6$ cm/s is the Fermi velocity in graphene, and $\gamma \approx 0.4$ eV is the interlayer coupling constant. In graphene, the ideal $C_q$ exhibits a linear dependence on $\varepsilon_f$. It is useful to introduce a constant for the prefactor in Eq. (4)

$$\eta = \frac{g_s g_v}{2\pi} \left( \frac{\hbar v_f}{2} \right).$$

The capacitance due to interface charge may be obtained similarly by $C_{it} = \partial_\varepsilon Q_{it} = e^2 D_{it}(\varepsilon_f)$. Substituting for $C_q$ and $C_{it}$ in Eq. (2) leads to the resulting differential equation

$$\frac{\partial \varepsilon}{\partial_\varepsilon} = e^2 \left( 1 + \frac{e^2}{C_{ox}} \rho(\varepsilon_f) + D_{it}(\varepsilon_f) \right).$$

Substituting for $\rho(\varepsilon)$ and integrating over $\varepsilon \in [0, \varepsilon_f]$ and $v \in [v_f, v_f]$ yields the following relation between the Fermi energy and the applied gate voltage:

$$\Delta \varepsilon_v = \varepsilon_f + \frac{e^2}{2 C_{ox}} \left( \varepsilon_f^2 + \varepsilon_f \gamma \right) + \frac{e^2}{2 C_{ox}} \int_0^{\varepsilon_f} D_{it}(\varepsilon_f).$$

Where, $\Delta \varepsilon_v = e(v_g - v_D)$, where $v_D$ is the Dirac voltage (i.e., the gate voltage where $\varepsilon_f = 0$). In Secs. II A and II B, two solutions to Eq. (7) are presented. In Sec. II A, the case of a constant $D_{it}$ is examined, and in Sec. II B, the case of an empirically modeled $D_{it}$ is considered. The empirically modeled case is selected to generate Fermi level pinning.

**A. Constant $D_{it}$**

In order to obtain a closed form solution to Eq. (7), it is useful to select a $D_{it}(\varepsilon_f)$ to be a constant $D_{it}^0$. In this case, it is possible to obtain an analytic expression for Fermi energy as a function of gate voltage $v_g$:

$$\Delta \varepsilon_v = \left[ 1 + \frac{e^2}{C_{ox}} \left( \frac{\eta \gamma}{2} + D_{it}^0 \right) \right] \varepsilon_f + \left[ \frac{e^2}{2 C_{ox}} \right] \varepsilon_f^2.$$  

Solving for $\varepsilon_f$ yields the following quadratic relation:

$$\varepsilon_f = \frac{1}{2a} \left[ \pm \sqrt{4a \Delta \varepsilon_v + b^2} - b \right],$$

where the constants are given by the following:

$$a = \frac{e^2}{2 C_{ox}},$$

$$b = \left[ 1 + \frac{e^2}{C_{ox}} \left( \frac{\eta \gamma}{2} + D_{it}^0 \right) \right].$$

The effect of the quantum capacitance is to introduce a $\varepsilon_f \propto \sqrt{\Delta \varepsilon_v}$ such that there is a weak saturating behavior in $\varepsilon_f$. The Dirac voltage introduces a shift into the function and can be estimated from experimental data. Reducing $C_{ox}$ and increasing $D_{it}^0$ have the same effect of increasing $b$, which results in reduced gate control over $\varepsilon_f$.

**B. The Lorentz-$\delta$ model**

Experimental results suggest that the saturation of $\varepsilon_f$ is much stronger than $\sqrt{\Delta \varepsilon_v}$ for large gate voltages. This Fermi level pinning effect can be introduced by considering a charge density at the graphene dielectric interface $\sigma_{it}(\varepsilon_f) = e \int_0^{\varepsilon_f} D_{it}$. The interface charge density is modeled by a Lorentzian distribution centered at $\epsilon_f^0$ and $\epsilon_f^0 < 0$. The distributions have additional broadening which is also modeled by a Lorentzian distribution

$$D_{it} = \sum_{n,p} D_{it}^D \mathcal{F}(\varepsilon_f ; \epsilon_f^0, \gamma_0^2) + D_{it}^D \mathcal{F}(\varepsilon_f ; \epsilon_f^0, \gamma_0^2).$$

Here, $\mathcal{F}(\varepsilon_f ; \epsilon_f^0, \gamma_0^2)$ is a Lorentzian distribution centered on $\epsilon_f^0$ with a width of $\gamma_0^2$ and $\gamma_0^2 > 0$. The distribution has additional broadening which is also modeled by a Lorentzian distribution

$$\mathcal{F}(\varepsilon_f ; \epsilon_f^0, \gamma_0^2) = \frac{1}{\pi \gamma_0^2} \left[ 1 + \left( \frac{\varepsilon_f - \epsilon_f^0}{\gamma_0^2} \right)^2 \right].$$

FIG. 1. The capacitive divider model for the graphene MOS$_m$ system.
The sum in Eq. (11) extends over two indices, \( n \) and \( p \), representing pinning during electron (\( \epsilon_f > 0 \)) and hole conduction (\( \epsilon_f < 0 \)), respectively. With the Lorentz-\( \delta \) model, Eq. (7) becomes a transcendental equation which must be solved numerically. To achieve the Lorentz-\( \delta \) effect, one requires that \( \gamma_{\epsilon_f}^p \ll \gamma_{\epsilon_f}^f \). This model is generally considered to be valid if the following holds for a given time varying gate voltage:

\[
\epsilon_f^0 < \epsilon_f < \epsilon_f^p.
\] (13)

When \( v_g \) becomes large, the narrow Lorentzian distributions cause a rapid increase in \( D_H \). This forces \( \epsilon_f \) to plateau near \( \epsilon_f^0 \) and \( \epsilon_f^p \) (Figure 2). The saturating behavior of \( \epsilon_f \) manifests as a saturation in the electron and hole densities generating current saturation in the device. The choice of the Lorentz-\( \delta \) model implies that the source of \( D_H \) is a resonant process. In particular, the two narrow peaks are associated with discrete energy levels at which fixed charge is generated. Although the Lorentz-\( \delta \) model is semi-empirically motivated, a context can be provided (see Sec. VII B).

### III. HYSTERESIS MODELING

Given \( D_H \), it is possible to calculate the Fermi energy \( \epsilon_f \) and drain current density \( J \) as a function of gate voltage. The hysteresis is then introduced into \( J \) by considering a hysteretic Fermi energy. This is done by evaluating a Preisach kernel \( P \) on the non-hysteretic Fermi energy. Let \( \epsilon_f^0 \in [0,1) \) represent a time varying Fermi energy in absence of hysteresis. A hysteretic Fermi energy is then represented by

\[
\epsilon_f = P[\epsilon_f^0].
\] (14)

Such an operator was first introduced by Preisach in 1935 to describe the hysteresis in the magnetization as a function of the applied magnetic field.\(^{24}\)

#### A. The functional relay

In modeling the graphene FET, the Preisach kernel \( P \) is constructed via a linear superposition of functional relays \( R_{\epsilon-\epsilon+} \):

\[
R_{\epsilon-\epsilon+}[\epsilon_f^0 : x] = A \left\{ \begin{array}{ll} x\epsilon_f^0 - 1, & \text{if } \epsilon < \epsilon_- \\ x\epsilon_f^0 + 1, & \text{if } \epsilon > \epsilon_+ \\ x\epsilon_f^0 + \kappa, & \text{otherwise} \end{array} \right.
\] (15)

Here, \( \kappa = -1 \) if \( \epsilon_f^0 \) crosses the threshold \( \epsilon_- \), \( \kappa = 1 \) if \( \epsilon_f^0 \) crosses the threshold \( \epsilon_+ \), and \( A \) is a scaling parameter such that \( R_{\epsilon-\epsilon+}[\epsilon_f^0 : x] \) is defined over the same range as \( \epsilon_f^0 \). The introduction of the term \( x\epsilon_f^0 \) is a divergence from the traditional Preisach model for \( x > 0 \). The effect of \( x \) is to build the behavior of \( \epsilon_f^0 \) into the relay operator. As \( x \rightarrow \infty \), \( R_{\epsilon-\epsilon+}[\epsilon_f^0 : x] \rightarrow \epsilon_f^0 \). The action of the functional relay on a given \( \epsilon_f^0 \) is shown in Figure 3. Here, \( \epsilon_f^0 \) is a solution to Eq. (7) in the case of a Lorentz-\( \delta \) model obtained from measured GFET data (Fig. 4).

The functional relay operator is alternatively defined in terms of its mean value \( \epsilon_0 = (\epsilon_- + \epsilon_+)/2 \) and half width \( \epsilon_0 = (\epsilon_+ - \epsilon_-)/2 \). This form of the relay is what commonly appears in the Preisach kernel

\[
R_{\epsilon-\epsilon+}[\epsilon_f^0 : x] = \epsilon_0 + A \epsilon_0 + \epsilon_0 + x = \epsilon_0 + A \epsilon_0 + \epsilon_0 + x.
\] (16)

#### B. The Preisach kernel

The Preisach kernel is obtained by integrating over an infinite number of functional relay elements of mean value \( \epsilon_0 \) and half width \( \epsilon_0 \).\(^{25,26}\) The functional relay parameter \( x \) is considered to a constant of the kernel\(^{25,26}\)

\[
P[\epsilon_f^0] = \int_{-\infty}^{\infty} \omega(\epsilon_0, \epsilon_0) R_{\epsilon-\epsilon+}[\epsilon_f^0 : x] d\epsilon_0 d\epsilon_0.
\] (17)

The kernel is evaluated by breaking the time varying Fermi energy \( \epsilon_f^0(t) \) into monotonically increasing \( \epsilon_f^0(t) \) and decreasing \( \epsilon_f^0(t) \) steps. In order for the model to be fully determined, it is necessary to select a weighting function \( \omega(\epsilon_0, \epsilon_0) \) (see Sec. III C)

\[
P[\epsilon_f^0] = A \int_{\epsilon_f^0} \left[ x\epsilon_f^0 + 1 \right] \omega(\epsilon_0, \epsilon_0) d\epsilon_0 d\epsilon_0
\]

\[
+ A \int_{\epsilon_f^0} \left[ x\epsilon_f^0 - 1 \right] \omega(\epsilon_0, \epsilon_0) d\epsilon_0 d\epsilon_0
\] (18)

---

FIG. 2. \( \epsilon_f \) shown as a function of \( v_g \) in the absence of the Lorentz-\( \delta \) effect (blue) and in the Lorentz-\( \delta \) model (red) for a sinusoidal gate voltage with an amplitude of 2 V (dashed). The blue curve demonstrates the \( \sqrt{2\pi x} \) dependence of \( \epsilon_f \) on \( v_g \), while the red curve shows a Fermi level pinning effect which is symmetric about \( \epsilon_f = 0 \).

FIG. 3. The characteristic of a functional relay operator (\( x = 20.0 \)) on a typical \( \epsilon_f^0(\epsilon_f) \) in \( [\epsilon_f^0, \epsilon_f^0] \) plane for \( \epsilon_0 = 0 \) mV and \( \epsilon_0 = 40 \) mV. (Inset) The same relay plotted in the \( [\epsilon_f^0, \epsilon_f^0] \) plane (red) and the analogous case of a pure Preisach relay \( x = 0.0 \) (dashed). Arrows indicate the direction of traversal for monotonically increasing/decreasing inputs.
The integrals over monotonically increasing and decreasing sections of $e_j/\varepsilon_j$ yield the lower and upper branches of the hysteresis, respectively. This allows for an intuitive interpretation of the behavior of $\mathcal{P}(e_j)$. Generally, $\mathcal{P}(e_j)$ describes nested hysteresis loops with ascending and descending branches. Note that the scaling factor $A$ is selected such that the endpoints of ascending and descending branches of $\mathcal{P}(e_j)$ are equivalent to those of $e_j/\varepsilon_j$. Once the hysteretic Fermi energy is found, it is possible to calculate the channel carrier density as a function of gate voltage
\[ n = \eta \int_0^\infty \left[ \epsilon + \frac{\gamma_1}{2} \right] f(e; \epsilon_j, \beta) \, d\epsilon. \] (19)

The hole density $p$ is obtained via transforming $(\epsilon, \epsilon_j) \rightarrow (-\epsilon, -\epsilon_j)$ and performing integration over $\epsilon \in [0, -\infty)$. Given the carrier density, it is possible to calculate the current density
\[ J = e[\mu_n n(\mathcal{P}(e_j)] + \mu_p p(\mathcal{P}(e_j)] + \mu_r p_r] E. \] (20)

Here, $\mu_n$ and $\mu_p$ are the electron and hole low field mobilities. Since the electron and hole densities inherit hysteretic behavior via $\mathcal{P}(e_j)$, it follows that the current density is also hysteretic. The current density in absence of hysteresis is recovered by substituting $e_j/\varepsilon_j$ for $\mathcal{P}(e_j)$ in Eq. (20). The current density relationship also includes a parasitic source/drain conductance term $\sigma_r = e\mu_r p_r$, where $p_r$ is the parasitic carrier density.\(^{29}\)

C. The weighting function $\omega(e_0, \epsilon_3)$

The behavior of the hysteresis operator is determined by the weighting function $\omega(e_0, \epsilon_3)$. The purpose of $\omega(e_0, \epsilon_3)$ is to assign a normalized weight to the functional relay located at $R_{e_0 - \epsilon_3, e_0 + \epsilon_3}$. In most hysteretic models, the density function is assumed to be an analytic function in the $[e_0, \epsilon_3]$ plane. Common choices include the elliptic Gaussian,\(^{28}\) the Lorentz distribution,\(^{26}\) and the Derivative Arc Tangent (DAT) function.\(^{30}\) Discrete density functions have also been successfully used to describe hysteretic systems.\(^{31}\) In this work, a novel approach based on error functions is used. The Preisach measure is assumed to obey the separation ansatz
\[ \omega(e_0, \epsilon_3) = \omega_0(e_0) \omega_3(\epsilon_3). \] (21)

The terms $\omega_0$ and $\omega_3$ describe how the functional relays are distributed in terms of energy and half-width. The $\omega_0$ term describes where the dominant contribution to the hysteresis is in energy, while $\omega_3$ along with the functional relay parameter $\alpha$ describes the degree of hysteresis opening. For GFET hysteresis modeling, the difference of two Gaussian cumulative distribution functions is chosen for $\omega_0$ and $\omega_3$
\[ \omega_{0,3} = \frac{1}{2} \left[ \text{erf} \left( \frac{e_0 - e_0^0}{\sqrt{2}\sigma_{0,3}} \right) - \text{erf} \left( \frac{e_3 - e_3^0}{\sqrt{2}\sigma_{0,3}} \right) \right]. \] (22)

It is important that $e_0^0$ and $\sigma_{0,3}$ are selected such that $0 < \omega(e_0, \epsilon_3) < 1$ for all $e_0$ and $\epsilon_3$. This ensures that all relays in the Preisach kernel have the same orientation.

IV. METHODS

Graphene monolayers plus a carbon buffer layer are grown on semi-insulating 1 cm$^2$ 4 H-SiC substrates in a CVD reactor by thermal decomposition of $\text{C}_3\text{H}_8$.\(^{32}\) The samples are then in-situ intercalated with hydrogen to produce quasi-standing bilayer graphene.\(^{33}\) GFETs are then fabricated via electron beam lithography (EBL) as shown in Figure 4.\(^{34}\) The most relevant step in the fabrication in this work is the deposition of the $\text{Al}_2\text{O}_3$ gate dielectric. Atomic layer deposition (ALD) of $\text{Al}_2\text{O}_3$ is performed via thermal decomposition of $\text{Al}_2(\text{CH}_3)_{12}$ and $\text{H}_2\text{O}$. Deposition begins with electron beam evaporation and subsequent oxidation at 180°C of 1–2 nm of Al metal. This yields a nucleation layer $\approx 2–3$ nm in thickness. This step is needed in order to provide adequate nucleation for the subsequent ALD growth.\(^{35}\) The process then continues with the deposition of an additional 10 nm of $\text{Al}_2\text{O}_3$ by ALD at 300°C. Generally, this method produces a low quality $\text{Al}_2\text{O}_3$ film which is polycrystalline to amorphous in nature. In this work, Al was chosen as a gate metal in order to minimize the gate leakage current $i_g$.

All measurements are performed at low drain bias in order to probe the low field regime. Measuring at low drain bias also reduces the stress on the device during measurement, and minimizes the coupling effect between the gate and drain biases. H-intercalated devices are typically p-type and exhibit carrier densities on the order of $1 \times 10^{12}$ cm$^{-2}$. Measurements on six separate 100 $\times$ 100 μm$^2$ Van der Pauw structures are performed using a Biorad HL5500PC Hall System in order to determine the average low field Hall mobility $\mu_h$ and carrier density $n_p$ of the material. The contact resistance $r_c$ is obtained by measuring several transfer length method (TLM) structures fabricated on the same chip. The intrinsic electric field is then calculated by accounting for nonzero $r_c$ (Eq. (23))
\[ |E| = \frac{v_d - i_d \left( \frac{r_c}{w_{ch}} \right)}{l_{ch}}. \] (23)

The relative permittivity of the oxide is estimated ($\epsilon_r$) via MOS capacitance measurements on identically grown $\text{Al}_2\text{O}_3$ films on Si. The dimensions of the devices measured in this work along with several other important parameters are

![FIG. 4. A scanning electron micrograph of an Al gated 2 $\times$ 50 μm co-planar GFET used for DC/LF hysteresis measurements and modeling.](image-url)
shown in Table I. It is important to note that there is a degree of non-uniformity in the device properties. The minimum (maximum) mobility of the Hall structures was 1760(2200) cm²/V s, and the minimum(maximum) carrier density was 0.96 × 10¹³(1.09 × 10¹³) cm⁻². Similar variations were observed in other parameters.

Hysteresis modeling and parameter optimization are computationally challenging. Each iteration in the optimization routine consists of testing 2⁹ complete hysteresis curves against measured data, where n ≥ 9 is the total number of parameters in the optimization. Furthermore, the generation of each hysteresis curve requires the summing over a large number (≥ 16⁵) of functional relays. In order to overcome these challenges, a massively parallel computation scheme employing a graphics processor (nVidia GeForce 640GT GPU) was developed. The Preisach operator (Eq. (18)), hysteresis scaling, and calculation of the carrier densities (Eq. (19)) are implemented in single CUDA (Compute Unified Device Architecture) kernel. A tail recursive entropy minimizing optimization algorithm is implemented using a custom built Python C extension. Each step in the optimization routine involves 2⁵ calls to the CUDA kernel.

Standard routines seek to optimize α along with the eight constants of ω(ε₀, ε₆). Using this method, each recursive step in the standard optimization routine is of order 5 s and adequate convergence is typically achieved in <100 iterations. The GPU implemented kernel offers a speed improvement of ≈ 1000× compared to traditional CPU implementations, thus allowing for rapid optimization cycles despite the large number of parameters in the model and the complexity of the Preisach kernel. Once optimized values are obtained, the same CUDA kernel is used to generate high precision hysteresis curves with ≥ 16⁵ functional relays in ≤ 500 ms.

V. DC HYSTERESIS MODELING

DC hysteresis measurements are performed on bilayer graphene FETs using a semiconductor parameter analyzer (HP-4156B) at 300 K with an integration time of 20 ms per bias point. The gate bias is swept repeatedly in the forward and reverse direction, and the extremum of the sweep are increased from ±1 V to ±6 V in intervals of 1 V, and the sweep rate is held constant at 4.87 V/s for all hysteresis curves. The drain bias (vₓ) is kept at a low constant value of 50 mV. The DC measurements are made in order to determine whether the observed hysteresis consists of nested loops, such as those described by a Preisach operator. Each measurement consists of multiple sweeps in order to probe the reversibility of the physical process which generates hysteresis. From these measurements, it is also possible to estimate the parameters of Dₓ and to assess the general behavior of ω(ε₀, ε₆, δ). Other parameters, such as the majority/minority carrier mobilities μₓ and μᵣ, the parasitic conductivity σₓ, and the Dirac Voltage vₓ, are also extracted via accurate models of measured data.

To generate a hysteresis model, ω(ε₀, ε₆, δ) and J are first calculated in the absence of the hysteresis for an initial Dₓ (Eqs. (7) and (20)). By comparing these results to measured data, μₓ, σₓ, vₓ, and Dₓ can be estimated prior to hysteresis optimization. Generally, a Lorentz-δ model is assumed for Dₓ. An optimization routine is performed on J in order to find appropriate values for ω(ε₀, ε₆, δ) and α. The optimization process usually includes modifications to μₓ, σₓ, and vₓ from the initial modeling in absence of hysteresis. This modeling procedure is repeated for each curve in the data set for a fixed Dₓ.

Once an accurate fit has been achieved for each measured hysteresis curve, a final model can be obtained by averaging over the parameters of each modeled curve. This final averaged model then serves as a general model of the device in the absence of hysteretic effects. The hysteresis is then included by considering ω(ε₀, ε₆, δ) and α from the optimization of each curve. The parameters extracted from hysteresis modeling of the measured data shown in Figure 5 are given in Table II. The model parameters define lₓ(εₓ) in the absence of hysteretic effects.

Using the parameter values from Table II and the density functions obtained from the optimization of each hysteresis curve, the hysteretic/non-hysteretic Fermi energy and current density are calculated as shown in Figure 6. The Preisach kernel generates nested hysteresis loops in the Fermi energy which in turn leads to hysteretic current loops which closely resemble the measured data shown in Figure 5.

The shape of ω(ε₀, ε₆, δ) indicates which functional relays are most active in the Preisach kernel. Figure 7 shows ω(ε₀, ε₆, δ) for the [−6, 6] V DC hysteresis sweep shown in Figure 5. It should be noted that all hysteresis sweeps in Figure 5 are modeled using similar ω(ε₀, ε₆, δ). The shape of ω(ε₀, ε₆, δ) indicates strong hysteretic activity when εₓ = 0 changes sign indicating that the hysteresis is maximally open near vₓ.

The mean Dirac voltage (vₓ) extracted from the hysteresis curves in Fig. 5 is 1.77 V. This global vₓ defines the point of minimum conduction in absence of hysteresis. In the DC data, the extracted vₓ generally falls between the two minima of the measured hysteresis curves. In the modeling of individual hysteresis curves, a drift of the Dirac point towards negative bias is observed for increasing sweep amplitude. This drift is attributed to the accumulation of positive charge at the graphene/dielectric interface. The hole mobility μᵣ obtained from the extraction is consistent with the Hall measurements obtained from separate Van der Pauw

<table>
<thead>
<tr>
<th>Device</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>lₓ</td>
<td>1.0 (µm)</td>
</tr>
<tr>
<td>lₚₓ</td>
<td>2.5 (µm)</td>
</tr>
<tr>
<td>wₓ</td>
<td>50 (µm)</td>
</tr>
<tr>
<td>lₚₒ</td>
<td>13.0 (nm)</td>
</tr>
<tr>
<td>εₓ</td>
<td>6.0</td>
</tr>
</tbody>
</table>
structures. An electron mobility of $\mu_n = 1100 \text{ cm}^2/\text{Vs}$ is also obtained from the modeled data. This conduction asymmetry between majority and minority carriers in graphene is also observed in other work.\textsuperscript{36,37}

VI. LOW FREQUENCY MEASUREMENTS

The field effect hysteresis in GFETs often depends on the rate at which $\epsilon_f$ changes. In this case, the Preisach kernel $P[\epsilon_f, \omega]$ includes a dependence of frequency $\omega$. Many hysteretic physical systems are not rate independent, and measurements performed as a function of sweep rate may be used to probe the underlying physics of hysteresis generation.

In order to assess the rate dependent properties of the observed hysteresis in graphene FETs, low frequency large signal measurements are performed. The gate bias is swept using a large signal (10 V peak to peak) sinusoid via a signal generator (Agilent 33250 A). The time varying gate voltage $v_g(t)$ and drain current $i_d(t)$ are then monitored using an oscilloscope (Agilent MSO6034A). Hysteresis curves are generated by plotting the voltage waveform against the current waveform. The rate dependence of the hysteretic effect is

**TABLE II.** The mean parameter values for the device model extracted for the DC hysteresis curves shown in Figure 5. Values for $D_{p,m}$ and $D_{n,m}$ are given in $10^{13} (\text{cm}^{-2})$. The maximum opening of the modeled hysteresis $\Delta_v$ of the $[-5,5]$ V curve is also tabulated.

<table>
<thead>
<tr>
<th>$D_{p,m}$</th>
<th>$D_{n,m}$</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_0^p$</td>
<td>$\epsilon_0^n$</td>
<td>102 (meV)</td>
</tr>
<tr>
<td>$\epsilon_0^p$</td>
<td>$\epsilon_0^n$</td>
<td>20 (meV)</td>
</tr>
<tr>
<td>$\gamma_p^0$</td>
<td>$\gamma_n^0$</td>
<td>1.4 (meV)</td>
</tr>
<tr>
<td>$D_{p,0}$</td>
<td>$D_{n,0}$</td>
<td>2.25 (cm$^{-2}$)</td>
</tr>
<tr>
<td>$D_{p,\delta}$</td>
<td>$D_{n,\delta}$</td>
<td>2.75 (cm$^{-2}$)</td>
</tr>
</tbody>
</table>

FIG. 5. Measured and modeled hysteresis curves for hysteretic $v_g$ sweeps of increasing amplitude for a bilayer GFET. Each panel shows the measured data (black), the result of hysteresis modeling and optimization (red), and the calculated current in the absence of hysteretic effects (blue). The extrema of the sweeps range from $\pm 1$ V (top left) to $\pm 6$ V (bottom right). The drain bias is maintained at a constant 50 mV for the entire data set. Arrows indicate the orientation of the hysteretic effect, and all hysteresis curves are obtained at a constant sweep rate of 4.87 V/s.

FIG. 6. The calculated behavior of the Fermi energy $\epsilon_f$ as a function of gate voltage with (black) and without (red) the hysteretic effect. The model is generated with the parameters shown in Table II. (Inset) The current density is calculated from $\epsilon_f$ with (black) and without (red) the hysteretic effect.

FIG. 7. A plot of the optimized density function $\omega(\epsilon_0, \epsilon_D)$ for the $[-6, 6]$ V DC hysteresis sweep shown in Figure 5.

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observed by increasing the frequency of the applied gate voltage from 10 mHz to 1 kHz. In these experiments, a large constant bias of 250 mV is applied to the drain in order to obtain acceptable resolution in the current waveform. All measurements are performed at 300 K. The large signal response of a second GFET is shown in Figure 8, and each hysteresis curve is modeled in a similar manner as was done for the DC measurements.

The parameters obtained from modeling of LF hysteresis curves measured on the second GFET are shown in Table III. The results from hysteresis modeling indicate graphene with a hole/electron mobility of 2548(1100) cm²/V s. Upon comparison with the device shown in Table II, this GFET demonstrates a higher mobility, a reduced Fermi level pinning effect, and remarkable symmetry in the DC measurements. As in the DC case, this shift in the DC hysteresis measurements are performed at 300 K. The large signal response of a second GFET is shown in Figure 8, and each hysteresis curve is modeled in a similar manner as was done for the DC measurements.

FIG. 8. Measured (black) and modeled (red) hysteresis curves. The plots show a weakly rate dependent hysteretic response of the drain current for an applied sinusoidal gate voltage with an amplitude of 5 V for several frequencies ranging from 10 mHz to 1 kHz. The calculated hole/electron mobilities are 2548(1100) cm²/V s. The applied drain bias is 250 mV for all sweeps.

This represents a major divergence from the case of electrolyte gated graphene flakes on SiO₂ where very strong rate dependence is observed with top gating. In Ref. 4, hysteresis collapse leading to orientation reversal is observed with decreasing sweep rate from 62.5 mHz to 4.2 mHz. In Ref. 4, the hysteresis is attributed to competing charge transfer to and from the graphene layer which describes very slow time constants. In the case of the devices presented in this work, hysteresis narrowing occurs gradually over five orders of magnitude in frequency. This property of weak rate dependence, consistent orientation, and approximate symmetry in Dₛ suggests a different physical mechanism for hysteresis generation.
VII. DISCUSSION

The hysteresis curves presented in this work are representative of what is observed in many graphene FETs. It is significant that the drain hysteresis appears in many GFET designs on various materials and substrates to varying degree. In order to generate a hysteretic Fermi energy, there must be a hysteretic charge density $\sigma_d$ at the graphene/dielectric interface. The hysteresis in graphene FETs is commonly attributed to the accumulation of charge at the graphene/dielectric interface due to trap states. Other possible mechanisms include a leakage current induced hysteresis or a space-charge induced hysteresis. In Secs. VII A and VII B, these physical mechanisms behind the weakly rate dependent hysteresis are explored in the context of measurement data.

A. Gate current measurements

Measurements of the gate leakage current $i_g(v_g)$ are performed in order assess whether the leakage current contributes to the hysteretic behavior observed in the $i_d(v_g)$ curves. $i_g(v_g)$ measurements are performed using a Keithley 4200 SCS parameter analyzer. In order to obtain high current resolution, a current preamplifier is used to measure $i_g$, $i_d(v_g)$ hysteresis curves are simultaneously measured at $v_d = 50\,\text{mV}$. All curves are measured with and without microscope illumination (Figure 9). A strong dependence of the magnitude gate current is observed between illuminated and un-illuminated measurements, while the $i_d(v_g)$ hysteresis curves show no such dependence.

The $i_d(v_g)$ hysteresis curves indicate that the gate leakage in the device is a predominantly a photoinduced effect. At negative bias, photons of energy $\epsilon_f = h\omega_0$ generate hot electrons in the gate metal which are then injected into the conduction band of the dielectric due to the applied electric field. These electrons are either scattered into trap states in the dielectric or tunnel through the oxide. When positive bias is applied, the trapped carriers are released by the light. Additionally, the $i_g(v_g)$ do not demonstrate closure indicating that negative charge has accumulated in the dielectric over the course of the sweep. In the absence of light, the $i_d(v_g)$ hysteresis collapses and only a negligible leakage current $\leq 1\,\mu\text{A}$ is observed. Most importantly, the $i_d(v_g)$ measurements show that carrier injection from the gate metal into the oxide does not contribute to the properties of the $i_d(v_g)$ hysteresis curves.

B. Further observations

Gate current measurements indicate that $\sigma_d$ likely originates at the graphene/dielectric interface. The sign of $\sigma_d$ may be inferred by examining the orientation of the hysteresis. On sweeping $v_g$ positive bias to negative bias and back to positive bias, the $i_d$ of the return sweep is to the right of the initial sweep thus describing a hysteresis of clockwise orientation. This implies that negative charge accumulates at the interface when sweeping toward negative bias. Similarly, $\sigma_d$ is positive when the orientation of the sweep is reversed. It is significant that the sign of $\sigma_d$ follows $v_g$ as this is what is expected from space charge effects and opposite to what is expected when carriers from the graphene layer are trapped at interface states. Additionally, all of the measured hysteresis curves shown in Figures 5 and 8 all consist of multiple sweeps and demonstrate very consistent closure. It is significant that the hysteresis demonstrates closure upon completing each sweep. This reversibility property is closely related to weak rate dependence, and supports a space charge/polarization hypothesis. The Fermi level pinning is approximately symmetric about $\epsilon_f = 0$ in both modeled devices indicating that $\sigma_d(\epsilon_f) \approx -\sigma_d(-\epsilon_f)$ such that $D_{id}(\epsilon_f) \approx D_{id}(-\epsilon_f)$. This approximate symmetry in $\sigma_d$ observed in the modeled devices further supports a polarization related effect as $\sigma_d$ should be symmetric around $v_d$. Fermi level pinning then occurs symmetrically about $v_d$ when $\sigma_d$ becomes comparable to the charge due carriers in the channel.

The Lorentz-$\delta$ model implies that the hysteretic component of the polarization is due to some resonant process occurring at the graphene/dielectric interface or entirely within the dielectric. Although crystalline $\text{Al}_2\text{O}_3$ is not ferroelectric, CV measurements of evaporated $\text{Al}_2\text{O}_3$ films embedded with metal nanoparticles (nps) reveal a strong hysteresis of clockwise orientation, while complementary measurements on evaporated $\text{Al}_2\text{O}_3$ films grown without metal-nps reveal no hysteresis. Similar results have been observed in $\text{SiO}_2$ films with embedded Si-nps. A similar process may be responsible for the ferroelectric-like hysteresis observed in the GFET devices presented in this work. In this case, Al-nps may be introduced unintentionally at the graphene/dielectric interface via incomplete oxidation of the Al nucleation layer thus generating a space charge hysteresis similar to what is observed in Refs. 39 and 40. Furthermore, the $\text{Al}_2\text{O}_3$ ALD layers grown on graphene are also highly amorphous such that they may also contribute to the hysteretic effect. Under this hypothesis, it is not surprising that the space charge effect generates a weakly rate dependent hysteresis described by a time constant of large dispersion. A validation of this hypothesis, as well as effects arising from trapping the graphene/substrate interface, requires further

**FIG. 9.** $i_d(v_g)$ hysteresis measurements for a GFET device with (black) and without (red) illumination. (Inset) $i_d(v_g)$ hysteresis measurements taken for $v_d = 50\,\text{mV}$ taken concurrently with the $i_d(v_g)$ curves with (black) and without (red) illumination.
investigation via low temperature CV measurements of Al$_2$O$_3$ films grown on various types of graphene layers.

VIII. CONCLUSION

The current hysteresis curves in GFETs with Al$_2$O$_3$ gate insulator may be modeled by an weakly rate dependent Preisach kernel with functional relays. The properties of the hysteresis are examined, and the hysteresis is attributed to space charge generation in the dielectric layer which occurs during the polarization of the gate oxide. This assumption is supported by the consistent closure of the hysteresis for repeating sweeps of the gate voltage, weak rate dependence of the hysteretic effect up to 1 kHz, and approximate symmetry in $D_p(\varepsilon)$. The current hysteresis curves in GFETs with Al$_2$O$_3$ films grown on various types of graphene layers.

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ARTICLE D

ASSESSMENT OF H-INTERCALATED GRAPHENE FOR MICROWAVE FETs THROUGH MATERIAL CHARACTERIZATION AND ELECTRON TRANSPORT STUDIES

M. Winters, O. Habibpour, I. G. Ivanov, J. Hassan, E. Janzén, H. Zirath and N. Rorsman

Assessment of H-intercalated graphene for microwave FETs through material characterization and electron transport studies

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ABSTRACT

Epitaxial graphene is grown on semi-insulating (SI) 4H-SiC in a hot wall CVD reactor by graphitization and in-situ intercalation with (H)ydrogen. A holistic material characterization is performed in order to ascertain the number of layers, layer uniformity, and electron transport properties of the epi-layers via electronic test structures and Raman spectroscopy. Bilayer graphene field effect transistors (GFETs) are fabricated using a full electron beam lithography (EBL) process which is optimized for low contact resistances of \( r_c < 0.2 \, \Omega \, \text{mm} \). Mobilities of order 2500 cm\(^2\)/V s are achieved on bilayer samples after fabrication. The devices demonstrate high transconductance \( \gamma_m = 400 \, \text{mS/mm} \) and high current density \( \gamma_{ds} = 1.8 \, \text{A/mm} \). The output conductance at the bias of maximum transconductance is \( \gamma_{ds} = 300 \, \text{mS/mm} \). The GFETs demonstrate an extrinsic \( f_{\text{ext}} \) and \( f_{\text{ext}} \text{max} \) of 20 and 13 GHz, respectively and show 6 dB power gain at 1 GHz in a 50 \( \Omega \) system, which is the highest reported to date.

1. Introduction

Epitaxial graphene on SiC has attracted interest from the fields of physics and solid state electronics [1]. Recently, a significant amount of attention has been directed towards the application of graphene bilayers in high frequency devices. This is motivated by a demonstration of a tunable bandgap in graphene bilayers via the application of a vertical electric field [2]. Band gaps of up to 250 meV have been reported in the literature on exfoliated bilayers on SiO\(_2\) [3], and theory predicts a maximum opening of 300 meV [4–6]. Such work is a boon to graphene electronics, as the lack of a bandgap in graphene monolayers has been seen as a fundamental impediment to the realization of high performance devices. For this reason it is of particular interest to investigate transistors in H-intercalated graphene bilayers, which have not widely been reported in the literature. With advances in growth technology, the investigation of electron devices and integrated circuits on large area graphene is now feasible [7].

Transistors on non-intercalated epitaxial graphene grown by thermal decomposition have been reported. An intrinsic transit frequency \( f_{\text{tr}} \) of 100 GHz and intrinsic unity power gain frequency \( f_{\text{ug}} \text{max} \) of 10 GHz is reported for a gate length of 240 nm [8]. Proof of concept high-frequency mixers [9], and amplifiers [10,11] have also been demonstrated in non-intercalated epitaxial graphene. H-intercalated epitaxial
Graphene demonstrates higher low-field mobility $\mu$ and better material uniformity compared to as-grown graphene making it a candidate for high frequency applications [12]. An increase of $f_1$ from 2.3 to 7.3 GHz was demonstrated for GFETs with a gate length of 1 $\mu$m on as-grown and H-intercalated monolayers, respectively. Further improvement of $f_1$ to 23 GHz was achieved via scaling of the gate length to 250 nm in H-intercalated monolayers [13].

The performance of a given GFET depends directly on the surface morphology and electron transport properties of the epitaxial graphene layers. In Section 2, the growth process is described in detail. The surface morphology of epitaxial graphene layers exhibits terrace structures which form during the growth process [14]. Knowledge of the number of graphene layers ($n_l$) is of fundamental importance as different transport properties can be expected from monolayer, bilayer, and multilayer material. In Section 3, Raman spectroscopy is used in conjunction with reflectivity mapping to determine the number of layers over the surface of a large area bilayer sample. Section 4 describes electron transport measurements taken on bilayer samples. Data from an H-intercalated monolayer sample is also included to serve as a metric of comparison to other studies. By collecting material characterization results, electron transport measurements, and a knowledge of the velocity field characteristic in epitaxial graphene, it is possible to outline a limitation on the expected performance of GFETs on H-intercalated epitaxial graphene on SiC.

In Sections 5 and 6, $2 \times 50 \mu$m GFETs with a gate length of 1 $\mu$m are realized on epitaxial graphene bilayers using an EBL process optimized for the formation of high quality Ohmic contacts. The device is then DC and RF characterized. The high frequency performance of the GFET is compared with the fundamental limitations derived from physical principles of electron transport in graphene layers.

### 2. Material growth

Graphene was grown on the Si-face of nominally on-axis high purity semi-insulating (SI) 4H-SiC. In these experiments, $16 \times 16 \text{mm}^2$ substrates obtained from a 3-inch wafer were used. An unintentional off-cut of 0.08° was measured at the center of the wafer. The off-cut may vary over the surface of a wafer, which should be accounted for in a detailed analysis [15]. Graphene growth is carried out in a three phase process consisting of in-situ etching of the SiC substrate, graphitization, and subsequent hydrogen intercalation. All three steps were performed in one sequence in a horizontal hot wall CVD reactor without exposing the samples to air. The growth of graphene is achieved by the thermal evaporation of Si from the surface layers of the SiC substrate (graphitization) [16–20].

The surface preparation (in-situ etching) step removes surface damage and native oxides from the substrate. Since the surface morphology of the substrate strongly influences the thickness uniformity of graphene, an optimized low temperature (1300–1400 °C) and low pressure (5 mbar) in-situ etching step is performed in pure hydrogen ambient. The advantage of the low temperature and low pressure method is that it minimizes surface step-bunching during graphene growth and completely eliminates the formation of micro-pits around threading screw dislocations (TSDs) [21]. After the low temperature in-situ etching process, the surface morphology consists of a fine step structure.

After the in-situ etching step, graphene growth was carried out in vacuum. The number of graphene layers ($n_l$) obtained in growth is determined by the growth temperature for a given Si background pressure [22]. The Si background pressure during graphene growth is due strictly to the thermal sublimation of Si from the substrate, and is controlled using a turbopump. Graphene growth on the Si-face of SiC through thermal sublimation of Si always leads to the formation of a graphene like carbon buffer layer (CBL) at the interface of the SiC and first graphene layer. In order to obtain monolayer and bilayer graphene after H-intercalation, only the CBL is grown and CBL and a graphene monolayer are grown respectively. The temperatures (pressures) of these two processes are 1350 °C (1·10⁻⁵ mbar) and 1400 °C (1·10⁻⁶ mbar). All growth runs are carried out for 60 min. After graphene growth, the fine step structure reorders into a surface defined by smooth terraces and large step edges due to surface step-bunching.

The CBL is chemically bound to the substrate and does not show graphene like properties. This bonding can be removed through a subsequent hydrogen intercalation step thus transforming the buffer layer into an additional graphene layer [23]. The final hydrogen intercalation step is performed at a temperature (pressure) of 800 °C (5·10⁻² mbar) for 60 min. After this step, quasi-free-standing monolayer and bilayer graphene is obtained.

An example scanning electron microscope (SEM) image of bilayer graphene obtained after hydrogen intercalation is shown in Fig. 1. The SEM image indicates a terrace width of order 3–5 $\mu$m. The step height is about 3–5 nm as measured by atomic force microscopy (AFM). An example of an AFM scan is shown in the inset of Fig. 1.

![Fig. 1 – A SEM image of bilayer graphene obtained after H-intercalation. The surface exhibits terracing which is typical to the Si-face of 4H-SiC after graphene growth. (inset) A 5 × 5 $\mu$m² AFM scan on a region of narrow terraces. (A color version of this figure can be viewed online.)](image-url)
Graphene layers with a CBL present at the interface usually show n-type conductivity. After hydrogen intercalation, the conductivity converts to p-type [24,25]. Microwave reflectivity (Lehighton) measurements show a significant enhancement of charge carrier mobility after the hydrogen intercalation process. Mobility measurements on a monolayer and three bilayer samples (A,B,C) indicate mobilities of 2000, 1200, 1200, and 3000 cm²/Vs, respectively. A maximum mobility 3750 cm²/Vs was obtained for hydrogen intercalated bilayers in this growth run. This data should be compared with mobility values obtained from electron transport measurements after device fabrication (Fig. 3).

3. Material characterization

The epitaxial graphene layers are characterized by reflection mapping in order to obtain the number of layers (n). Surface uniformity and a knowledge of the number of graphene layers is important because the electron transport properties of graphene vary with n. Measurements of n via reflection mapping are also used to study the morphology of the substrate after graphene growth. Raman mapping is performed in order to assess material uniformity and determine the presence of lattice defects. The G line and 2D lines are connected with n, while the D line is connected with the defect density. Reflection and Raman mapping are performed in a custom built micro-Raman setup using a diode pumped semiconductor laser with an excitation energy of 2.33 eV (532 nm) [26]. The spatial resolution of the map is determined by the size of the laser spot on the sample. In these maps a spot size of ±0.6 mm is achieved with a 100X objective lens.

The G peak is due to first order zone center optical phonons in the graphene, and the 2D peak is due to double resonant phonon scattering from K/K' intervalley transitions [27,28]. The D peak indicates K/K' intervalley transitions in which one phonon and one defect participate in scattering events. The D peak correlates to the breathing modes of sp2 bonded rings which are forbidden in defect free graphene. Its presence is therefore indicative of disorder in the real space lattice. Additionally, the D peak is dispersive, and its measured value on this sample correlates well with reported values given the laser excitation energy used in the experiment [29–31].

The reflection map measurement is calibrated by measuring the reflected power from a Si 4H-SiC substrate without graphene. The calibration value is then subtracted from reflectivity measurements made on identical substrates with H-intercalated epitaxial graphene. The number of layers is calculated assuming that each graphene layer will contribute an additional 1.7–2% in reflected power [26]. By measuring many points arranged in a grid, a map of the number of layers is obtained. The results of reflectivity mapping for a region with large terraces are shown in Fig. 2a. Terraces show predominately bilayer graphene with occasionalclusions of monolayer graphene, and step edges show trilayer or multilayer material. The step and terrace morphology observed in Fig. 2a correlates with Fig. 1.

The three Raman spectra shown in Fig. 2b are representative of what is observed in epitaxial graphene on SiC. The Raman G, 2D and D lines appear at 1590, 2700 and 1350 cm⁻¹, respectively. On this sample the D line is intermittent and weak. In the trilayer spectrum the G 2D lines are shifted to 1597 and 2720 cm⁻¹, respectively and the D line amplitude is very low. For all lines, a single Lorentzian lineshape is used to calculate the linewidths and peak positions. Although a single Lorentzian does not take into account the full details of the Raman lines [29,27,32], it is sufficient for a basic quantitative analysis [26].

The experimental setup is designed such that reflectance mapping can be performed simultaneously with Raman mapping. Raman spectra are collected from each point in the framed region of shown in Fig. 2a. This region is selected because it shows homogeneous bilayer coverage on a large terrace, and trilayer graphene on a step edge. These spectra are then processed into maps describing the spatial variation of several attributes of the G, 2D, and D lines. A composite of several Raman maps is shown in Fig. 2c. The morphology of the framed region obtained via reflectance mapping correlates with what is observed in the Raman maps.

It is also of interest to observe the ratio of intensities I_D/I_G between the G and D peaks as this provides a qualitative estimate of the defect density in graphene [30]. A low ratio indicates defect-free graphene layers. I_D/I_G is shown in the bottom right subplot of Fig. 2c. I_D/I_G averages at approximately 0.06 and has a maximum at 0.18. The low I_D/I_G ratio in conjunction with the G peak position at ~1590 cm⁻¹ indicates lowly defected graphene as interpreted by the amorphization trajectory available in [31]. There is also a weak correlation between the G peak FWHM map and the I_D/I_G map in the bilayer region. Generally, the presence of the D peak is accompanied by a broadening of the G peak or a splitting of the G peak into two peaks. Both cases yield a larger FWHM when fitted to a single Lorentzian. This behavior in the G peak is associated with uniaxial strain in the lattice [32].

The low I_D/I_G ratio and uniformity in n on terraces is positive from the perspective of the realization of GFETs on graphene. With an accurate knowledge of material properties, it is possible to connect good frequency performance to material quality.

4. Electron transport

The frequency performance of a FET structure is fundamentally limited by the electron transport properties of the active layer. From density of states calculations [33], the sheet carrier densities in monolayers (n_{sh,m}) and bilayers (n_{sh,b}) are calculated via the following integrals:

\[
n_{sh,m} = \frac{g_v}{2\pi} \frac{1}{(\hbar\nu_f)^2} \int_0^{\infty} \frac{d\epsilon}{\epsilon} \left( \epsilon - \epsilon_f, T \right) \right) d\epsilon
\]

\[
n_{sh,b} = \frac{g_v}{2\pi} \frac{1}{(\hbar\nu_f)^2} \int_0^{\infty} \left[ \epsilon + \frac{\gamma_v}{2} \right] \frac{d\epsilon}{\epsilon} \left( \epsilon - \epsilon_f, T \right) \right) d\epsilon
\]

Here g_v and g_e represent the spin and valley degeneracies, and \nu_f \approx 1 \cdot 10^8 cm/s is the Fermi velocity. The term \gamma_v describes the interlayer coupling in bilayer material, \epsilon_f is the Fermi energy, and f(\epsilon - \epsilon_f, T) is the Fermi–Dirac distribution. The prefactors in these relations follow from the band structure
in monolayers and bilayers. At high carrier density, the zero temperature approximations to (Eq. (1) and (2)) apply:

\[ n_{sh} = \frac{g_s g_v}{4\pi} \left( \frac{\epsilon_f}{\hbar v_f} \right)^2 \]  

\[ n_{sh,b} = \frac{g_s g_v}{4\pi} \left( \frac{\epsilon_f + \gamma_{1b}}{\hbar v_f} \right)^2 \]  

The interlayer coupling energy \( \gamma_{1b} \) is approximately 400 meV. At low energy, \( n_{sh,b} \) is approximately linear and is analogous to the case of a two-dimensional electron gas. In the high energy limit \( n_{sh,b} \) behaves analogously to monolayer graphene reflecting the hyperbolic nature of the density of states. The appearance of \( \gamma_{1b} \) in (Eq. (4)) indicates that carrier densities are higher in bilayer material for a given \( \epsilon_f \) [2].

In order to characterize electron transport in H-intercalated samples, several 100 \( \mu \)m\(^2\) Van der Pauw structures were fabricated on several samples. The mobility (\( \mu \)), sheet carrier density (\( n_{sh} \)), and sheet resistance (\( r_{sh} \)) are measured at 300 K with a Hall system (Biorad HIL5500PC). The measured values of the carrier density indicate that the samples are far from those of intrinsic graphene monolayers (1 \( \cdot \) 10\(^10\) cm\(^{-2}\)) and bilayers (1 \( \cdot \) 10\(^12\) cm\(^{-2}\)) at room temperature as calculated from (Eq. (1) and (2)). The H-intercalated monolayer and bilayer samples typically exhibit carrier densities (Fermi energies) on the order of 1 \( \cdot \) 10\(^10\) cm\(^{-2}\) (\( \sim \) 370 meV) and 1.3 \( \cdot \) 10\(^13\) cm\(^{-2}\) (\( \sim \) 265 meV), respectively.

Fig. 3 shows \( \mu \), \( n_{sh} \), and \( r_{sh} \) at several locations on one monolayer sample and three bilayer samples. The measurements shown in Fig. 3 were taken from test structures on
large area samples (1.5 cm²). All of the test structures on H-intercalated material are highly doped and p-type as expected. The Hall data shows a significant amount of variation reflecting non-uniformity in all samples. Within a given Hall structure, there may be a variation in \( n_1 \) as shown by the Raman and reflectivity mapping. It is conceivable that higher mobilities may be observed on smaller area structures in which the active area is devoid of step edges. Low temperature Hall data indicates that the low field mobility in H-intercalated graphene is largely a result of charged and neutral impurity scattering [34,35]. These impurities may be introduced during growth, H-intercalation, and device fabrication. The highest mobilities observed in the H-intercalated epitaxial graphene samples are surpassed by their exfoliated and transferred counterparts on SiO₂/Si in which mobilities \( >10000 \text{ cm}^2/\text{V} \cdot \text{s} \) have been reported [36].

In the case of a graphene layer in which the low temperature mobility is impurity scattering limited, the high field behavior will be determined by the emission of surface optical phonons in the SiC by hot carriers in the graphene layer [37-39]. The energy of these surface optical phonons is \( \epsilon_{SO} \approx 115 \text{ meV} \). From \( \epsilon_{SO} \) it is possible to estimate the saturated electron velocity \( v_{sat} \) via emission of surface optical phonons [34,40,41].

\[
v_{sat} = \frac{2}{\hbar} \pi \sqrt{m_{nsh}} \left[ 1 - \epsilon_{SO}^2 \left( \hbar v_f \right)^2 N_{OP} + 1 \right]^{-\frac{1}{2}}
\]

(5)

Here \( N_{OP} = \left[ \epsilon v_{th} k_F - 1 \right]^{-1} \) is the phonon occupation number. In the high carrier density limit the above relation may be reduced to:

\[
v_{sat} = \frac{2 \epsilon_{SO}}{\hbar \pi \sqrt{m_{nsh}}}
\]

(6)

From Eq. (6), one can expect a saturated electron velocity of \( \approx 1.7 \cdot 10^7 \text{ cm/s} \) in the H-intercalated graphene bilayer samples. This value has been confirmed experimentally in [12]. These results facilitate an assessment of frequency performance of H-intercalated epitaxial graphene layers. The intrinsic transit frequency \( f_t \) in an FET device is related to \( v_{sat} \) by:

\[
f_t = \frac{v_{sat}}{2 \pi l_g}
\]

(7)

Since the electron transport observations translate directly into a limit on the frequency performance, Eqs. 6 and 7 describe a speed limit for H-intercalated epitaxial graphene FETs. For a gate length \( l_g \) of 1 \( \mu \text{m} \) one finds a fundamental limit on the transit frequency of \( f_t = 27.7 \text{ GHz} \) for an \( n_{sh} \) of \( 1.3 \cdot 10^{13} \text{ cm}^{-2} \). The measured performance of any device will be worse then the theoretical limit due to resistive and capacitive parasitics. Generally, \( f_t \propto n_{sh}^{\frac{1}{2}} \) such that lower carrier densities are desirable for high frequency performance.

5. GFET fabrication

2 \( \times \) 50 \( \mu \text{m} \) coplanar graphene FETs with a gate length \( l_g \) of 1 \( \mu \text{m} \) were fabricated on bilayer sample C. The process begins with the evaporation of 3 nm of Aluminum. This seed layer is then thermally oxidized at 170 °C in order to function as a passivation layer. This is necessary to protect the graphene from atmospheric degradation and minimize effects from processing steps.

The GFETs are fabricated by an all electron beam lithography (EBL) process to minimize the contact resistance. First alignment marks and Ohmic contacts are defined using a bilayer of PMMA/MMA resist stack. After development, the passivation oxide is etched and a metal stack of Ti/Pt/Au is deposited via e-beam evaporation. The intermediate Pt layer is used to create a graded work function across the contact [42]. The mesa isolation is defined by patterning using negative resist (ma-N 2401), and etching in an O₂ plasma. Next, more Al₂O₃ is added via the evaporation/oxidation method to form a field oxide with a total thickness of 10 nm. The thickness of
the field oxide is chosen to achieve step coverage of the SiC terraces (Fig. 1). A bi-layer of ZEP/UV5 resist stack is used to define T-shaped gate electrodes. Finally, a thick contact Ti/Au metallization is deposited in the same manner as the Ohmic contact. Fig. 4 shows a transistor with a gate length of 1 μm. The contact resistance \( r_c \) of several transistors is measured using TLM structures before and after a final annealing step at 300 °C in Argon ambient. Due to the non-uniformity of the epitaxial layer, the sheet resistance generally varies from structure to structure making an accurate determination of the contact resistance difficult. Contact resistivities of order 1000 and <200 \( \Omega \)μm are consistently observed before and after annealing, respectively. The low contact resistances are partly due to the high carrier densities observed in H-intercalated graphene. Values of below 100 \( \Omega \)μm have been measured for the EBL process, which is comparable to the lowest reported [43].

6. GFET characterization

DC and RF characterization was performed on a GFET with a gate length of \( l_g = 1 \) μm, and a gate width of \( w_g = 2 \times 50 \) μm. The DC characterization of the H-intercalated GFET devices show p-channel conductivity in agreement with the Hall measurements above.

The device transfer characteristic is shown in Fig. 5. The device exhibits a maximum transconductance of 400 mS/mm at \( V_{ds} = -3 \) V and \( V_{gs} = 3.5 \) V as shown in the inset of Fig. 5. At the bias point of maximum transconductance, the corresponding output conductance is \( \approx 300 \) mS/mm. Furthermore, the device exhibits a minimum output conductance of 160 mS/mm at \( V_{ds} = -1.4 \) V. At this drain bias the maximum transconductance is \( \approx 280 \) mS/mm. The device exhibits a maximum current density of 1.8 A/mm which is typical for GFET devices [43]. This high current density is the reason for achieving high transconductance despite the low on-off ratio of 2.4 at \( V_{ds} = -3 \) V.

RF characterization is performed by bias-dependent S-parameter measurement from 100 MHz to 20 GHz with a network analyzer (Agilent E8361A). Measurements are taken at the bias point corresponding to maximum transconductance. (\( V_{ds} = -3 \) V, \( V_{gs} = 3.5 \) V). The device provides an \( |S_{21}| > 1 \) up to 7 GHz. Various quantities describing the gain of the GFET calculated from the S-parameter data are shown in Fig. 6. An \( f_t \) of 20GHz is calculated from the zero crossing of \( h_{21} \). The transistor is potentially unstable up to 5 GHz. A maximum frequency of oscillation (\( f_{max} \)) of 13 GHz is calculated from the zero crossing of the maximum available gain. The GFET demonstrates 6 dB power gain at 1 GHz in a 50 Ω system, which is the highest reported to date.

The values achieved for \( f_t \) and \( f_{max} \) are realistic given the limitation on \( v_{sat} \) from remote phonon scattering via the
substrate discussed above. Additionally, these figures indicate that it is possible realize a working MMIC amplifier in epitaxial graphene bilayers up to 5 GHz using a 1 μm technology. Table 1 compares the 1 μm GFET to other semiconductor technologies. The $f_t \cdot l_g$ product in the bilayer GFET compares with that of InAs/InP HEMTs indicating its potential as a competitive technology for high frequency applications. Despite being considerably lower than $v_t$, the $v_{sat}$ in epitaxial graphene is comparable to those of other semiconductor materials. Narrow gate devices have been attempted, but preliminary results indicate that GFETs with short gate lengths (<200 nm) show poor modulation due to the lack of a band gap. With the prospect of a tunable bandgap via backgating in bilayers a competitive high frequency device is within reach. Another opportunity for improvement lies in the alignment of devices on or parallel to terraces to maximize carrier mobility.

7. Conclusion

H-intercalated graphene layers were grown in a horizontal hot wall CVD reactor, and characterized from the perspective of surface morphology, uniformity in the number of layers, and electron transport properties. Hall measurements show that H-intercalated graphene layers are heavily and uniformly p-doped. The high carrier densities observed translate directly into lower mobilities and saturated electron velocities $v_{sat}$, which in turn sets an upper limit on the frequency performance. The high sheet carrier density also results in low sheet resistance, which translates into low access resistances and aiding in the formation of good Ohmic contacts. However, a high carrier density is a disadvantage regarding transconductance (gate modulation) and output conductance, which tends to deteriorate both $f_t$ and $f_{max}$. The maximum $f_t$, as calculated from the theoretically calculated and measured [12] saturation velocity for H-intercalated bilayer epitaxial graphene on SiC is 27.7 GHz for a gate length of 1 μm.

Graphene FETs were fabricated on bilayer H-intercalated epitaxial graphene layers and the DC characteristics and frequency performance were measured. From the DC data, a maximum extrinsic transconductance of 400 mS/mm is observed. The device exhibits a high output conductance of 1.8 A/mm partly due to the lack of a bandgap in bilayer graphene.

From the RF measurements, an $f_t$ of 20 GHz and an $f_{max}$ of 13 GHz are calculated. The GFET is found to have 6 dB of power gain at 1 GHz thus demonstrating the feasibility of high frequency amplifiers in graphene. The $f_t \cdot l_g$ product of this device is 20 GHz·μm, which compares well with other high frequency technologies. However, downscaling the gate length further deteriorates both the output conductance and the gate modulation, affecting both $f_t$ and $f_{max}$. The high frequency performance of GFETs based on bilayer H-intercalated graphene on SiC would benefit from developments in material growth enabling control of carrier density and larger terraces.

Acknowledgment

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## References


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Article E

Graphene self-switching diodes as zero-bias microwave detectors


Graphene self-switching diodes as zero-bias microwave detectors

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Self-switching diodes (SSDs) were fabricated on as-grown and hydrogen-intercalated epitaxial graphene on SiC. The SSDs were characterized as zero-bias detectors with on-wafer measurements from 1 to 67 GHz. The lowest noise-equivalent power (NEP) was observed in SSDs on the hydrogen-intercalated sample, where a flat NEP of 2.2 nW/Hz¹/² and responsivity of 3.9 V/W were measured across the band. The measured NEP demonstrates the potential of graphene SSDs as zero-bias microwave detectors. © 2015 AIP Publishing LLC, [http://dx.doi.org/10.1063/1.4914356]

Graphene exhibits electronic properties which are relevant for high-frequency applications¹ such as zero-bias detection in passive imaging arrays.² Detectors drawing zero bias current offer reduced 1/f-noise compared to biased detectors. Zero-bias detectors are today normally based on heterojunctions or Schottky diodes, reaching noise-equivalent power (NEP) below 20 pW/Hz¹/² beyond 100 GHz.³,⁴ Zero-bias detection has been demonstrated in graphene field-effect transistors (FETs) with an NEP of 515 pW/Hz¹/² at 600 GHz.⁵

Self-switching diodes (SSDs) offer a fundamentally different approach to zero-bias detection in which rectification and detection is achieved by a lateral field-effect.⁶ Simulations have shown the feasibility of achieving rectification in graphene using SSD structures.⁷,⁸ SSD detectors have previously been realized in other materials⁹–¹² with the most promising results for GaAs SSDs in which an NEP of 330 pW/Hz¹/² was observed.¹³ In this work, detection with rectifying graphene SSDs at frequencies up to 67 GHz is demonstrated. The SSDs are realized in both as-grown (n-type) and hydrogen-intercalated (p-type) epitaxial graphene on SiC.

Figure 1 shows a scanning electron micrograph of a single SSD channel fabricated in epitaxial graphene. The narrow graphene channel behaves as a lateral nanowire transistor.⁶ The surrounding flanges act as lateral gates which are directly connected to the drain such that the drain voltage is simultaneously applied to the gates. This has the effect of modulating the carrier density in the nanowire channel generating a non-linear current-voltage characteristic.¹⁴ The inset shows an SSD design implemented for RF detection with nine nanowire channels acting in parallel to reduce resistance and NEP.¹⁵ The SSDs were fabricated at the end of a 70 μm coplanar transmission line, in order to provide a partial RF match.

Graphene was grown on the Si-face of two 20 × 20 mm² nominally on-axis semi-insulating (SI) 4H-SiC substrates in a horizontal hot wall chemical vapor deposition (CVD) reactor.¹⁶ Graphene growth was carried out at 1300 °C to 1400 °C in vacuum after an initial in-situ surface preparation of the substrates in a hydrogen/silane background. One of the samples was then intercalated in hydrogen at a temperature (pressure) of 800 °C (500 mbar) in order to obtain quasi-free standing graphene. SSDs and supplementary test structures were fabricated on the graphene layers with and without H-intercalation. As-grown samples then consisted of a monolayer plus carbon buffer layer (CBL), and samples which were intercalated with hydrogen consisted of quasi-free standing graphene bilayers.¹⁷–¹⁹

Processing began by patterning the SSD flange structures via electron beam lithography (EBL). The flanges were then etched in O₂ plasma. Ti/Au ohmic contacts were deposited and mesas etched via O₂ plasma followed by the definition of Ti/Au contact pads.²⁰ In order to prevent long term sample degradation, an encapsulation using benzosicylobutene (BCB) diluted in (1,3,5) trimethylbenzene (1:4) was done.²⁰ Hall measurements yielded an average mobility (carrier density) of 1392 cm²/Vs (−6.91·10¹¹ cm⁻²) for the as-grown material and 1130 cm²/Vs (±1.95·10¹³ cm⁻²) for H-intercalated material. This corresponds to mean Fermi energies of ε_F = 88 meV (−366 meV) for the as-grown (H-intercalated) samples, respectively.²¹ The measured mobilities and sign of the majority carriers for as grown and H-intercalated material are consistent with previous results.²⁰

FIG. 1. Scanning electron micrograph (SEM) of a single SSD channel etched in as-grown monolayer graphene on SiC. The narrowest width of the depicted channel is 15 nm. The inset shows the SSD design used in the RF detection experiments, with nine parallel channels fabricated at the end of a 70 μm coplanar transmission line.

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The as-grown and H-intercalated samples were characterized using micro-Raman spectroscopy. The Raman spectra were obtained after device fabrication using a setup with a 2.33 eV (532 nm) diode pumped semiconductor laser. Due to the BCB passivation layer, the Raman spectra were obtained by measuring through the SiC substrate resulting in reduced spatial resolution (2 μm) and spectral intensity.

The Raman spectra of the as-grown and H-intercalated samples after background subtraction of the second-order Raman scattering from the substrate are shown in Fig. 2. The as-grown and H-intercalated materials have G (2D) peaks centered on 1589 (2724) cm⁻¹ and 1595 (2717) cm⁻¹, respectively. The spectrum of the as-grown sample contains a significant contribution from the CBL in the range of 1340–1640 cm⁻¹, which is absent in the H-intercalated sample, demonstrating the effect of intercalation. The observed upshift (downshift) in the G (2D) peaks upon intercalation reflects a reduction of the stress in the graphene as well as a change in carrier density. Additionally, the H-intercalated sample demonstrates a very weak D-peak at 1364 cm⁻¹. Since the D-peak in defect free graphene is forbidden in Raman scattering by momentum conservation, its presence indicates defects in the lattice. The intensity ratio I_D/I_G of the D-peak (I_D) and the G-peak (I_G) therefore defines a figure of merit regarding material quality. The intercalated layer demonstrates I_D/I_G = 0.023 indicating low defect density. Such a comparison is intratable in the as-grown sample because the D-peak is obscured by the CBL spectrum. The increase in linewidth from the as-grown sample because the D-peak is obscured by the CBL spectrum.27 The increase in linewidth from the as-grown sample because the D-peak is obscured by the CBL spectrum.27 The increase in linewidth from the as-grown sample because the D-peak is obscured by the CBL spectrum.27 Such a comparison is intratable in the as-grown sample because the D-peak is obscured by the CBL spectrum.27

A nonlinear current-voltage (IV) relationship enables RF detection with SSDs. For an RF detector based on nonlinear IV characteristic, the voltage responsivity with an RF source of impedance Z_0 is \( \beta_{Z_0} = \frac{1}{2} R_D \Gamma (1 - |\Gamma|^2) \). where \( R_D = \frac{dV_D}{dI_D} \) is the differential resistance, \( \gamma = \frac{(d^2I_D/dV_D^2)}{(dI_D/dV_D)} \), and \( \Gamma \) is the reflection coefficient between source and detector. At low frequencies and for \( R_D \gg \text{Re}(Z_0) \), the responsivity is \( \beta_{Z_0} \approx -\frac{1}{2} \text{Re}(Z_0) \). At zero-bias, the dominating noise process is Johnson noise. The noise-equivalent power is thus \( \text{NEP} = \frac{1}{4} \omega R_D \sqrt{B} \), where \( k \) is Boltzmann’s constant, \( T \) is the temperature, and \( R_0 = R_D (V_D = 0 \text{ V}) \).

DC characteristics of SSDs from the as-grown and H-intercalated sample are shown in Fig. 3. At zero bias, the as-grown sample exhibits \( \gamma = 0.024 \text{ V}^{-1} \) and \( R_0 = 67.1 \text{ kΩ} \). At zero-bias, a low-frequency responsivity of \( \beta_{\text{SSD}} \approx -2.4 \text{ V/W} \) is expected with a \( Z_s = 50 \text{ Ω} \) source. The corresponding figures for the H-intercalated sample are \( \gamma = -0.022 \text{ V}^{-1} \), \( R_0 = 4.21 \text{ kΩ} \), and \( \beta_{\text{SSD}} \approx 2.2 \text{ V/W} \). The non-zero \( \gamma \) at zero-bias in both SSDs enables zero-bias RF detection.

SSDs fabricated on as-grown and H-intercalated graphene are expected to exhibit opposite signs for \( \beta_{\text{SSD}} \). In the as-grown sample, which is n-type, the lateral gates at forward bias \( (V_D > 0 \text{ V}) \) act to increase carrier density and reduce \( R_D \) as shown in Fig. 3(a). In weak reverse bias \( (V_D < 0 \text{ V}) \), carrier density is decreased and \( R_D \) increased. In the p-type H-intercalated sample, the holes are the majority carriers and the operation reversed.

The SSD on the as-grown sample exhibits a local maximum of \( R_D \) when biased at the Dirac voltage \( V_{\text{Dirac}} = -70 \text{ mV} \), see Fig. 3(a). A maximum \( R_D \) is expected for the \( V_D \) which brings the Fermi energy \( \epsilon_f \) to the Dirac point in the material (i.e., \( V_{\text{Dirac}} \)). This corresponds to a minimum in the carrier density. The sign and value of \( V_{\text{Dirac}} \) in the as-grown sample indicate that the channel is n-type and lowly doped in qualitative agreement with the mean Fermi energy extracted from Hall measurements. For the H-intercalated sample, \( V_{\text{Dirac}} \) occurs at positive bias and is not visible within the measured range, indicating a highly p-doped graphene channel, which is also consistent with Hall data (Fig. 3(b)).

Responsivity was measured on wafer in the band 1–67 GHz using the setup shown in the inset of Fig. 4. The signal source was an Agilent 8275D. A 10 dB attenuator provided the nominal source impedance \( Z_s = 50 \text{ Ω} \). RF power was applied to the detector with a 75 μm pitch coplanar probe. The available power at the SSD input \( (P_{SSD}) \) was

![FIG. 2. Raman spectra for the as-grown and H-intercalated samples after fabrication of SSD devices. The G, 2D and D peak positions are shown. The as-grown material is monolayer graphene plus CBL, whereas the H-intercalated sample is bilayer graphene. In the as-grown material, the D-peak overlaps with the CBL spectrum; the thin solid line underneath the G peak is an estimate of the contribution of the CBL in the region of overlap. The observed intensity ratios of the G- and 2D-peaks suggest monolayer graphene in the as-grown sample and bilayer in the H-intercalated one. The peaks marked with asterisks are likely due to contribution from the BCB top film. Note the horizontal-axis break.](image)

![FIG. 3. Differential diode resistance \( (R_D) \) and \( \gamma = (d^2I_D/dV_D^2)/(dI_D/dV_D) \) for nine-channel SSDs on the (a) as-grown sample and the (b) H-intercalated sample.](image)
The average NEP is 2.2 and 8.2 nW/Hz for the as-grown and H-intercalated samples, respectively. The SSDs exhibit an average voltage responsivity $R_{\text{th}} = 4.2 \, \text{V/W}$ from 1 to 67 GHz for the H-intercalated and as-grown samples. The SSD detectors operate in the intended way as indicated in Fig. 3.

The estimated NEP up to 67 GHz is plotted in Fig. 5. The average NEP is 2.2 and 8.2 nW/Hz for the H-intercalated and as-grown samples, respectively. While both SSDs demonstrate similar $\beta_{50\Omega}$, the estimated NEP is considerably lower in the H-intercalated sample due to the lower $R_{\text{th}}$ and $R_0$ compared to the as-grown sample.

The graphene SSD presented in this study can be improved for zero-bias microwave detection. First, the SSD channel fabrication can be developed for better edge acuity (Fig. 1). The varying channel width causes a non-uniform electric field across the channel leading to reduced responsivity. On the H-intercalated sample, a single-channel SSD exhibited $\gamma = -0.1 \, \text{V}^{-1}$, $R_0 = 9.2 \, \Omega$, and thus an expected $\beta_{50\Omega} = 10 \, \text{V/W}$. With the same $\gamma$, nine parallel channels and an SSD driven by a source with the free-space impedance $Z_t = 377 \, \Omega$, a low-frequency responsivity $\beta_{50\Omega} = -2\gamma Z_t = 75 \, \text{V/W}$ and NEP = 54 pW/Hz can be expected. Second, the width of the isolating trenches can be reduced to enhance gate-to-channel coupling thus increasing $\gamma$. The non-optimized graphene SSDs exhibit similar performance compared to more optimized InAs SSDs with $\gamma = 0.35 \, \text{V}^{-1}$ and $R_0 = 15 \, \Omega$ per channel. Even though the graphene SSDs in this study were only characterized up to 67 GHz, the results point to the graphene SSD as a potential candidate for millimeter wave or even terahertz detection. Graphene SSDs are potentially of interest for transparent electronics. Furthermore, the use of epitaxial growth of graphene on commercially available 4H-SiC wafers makes the SSD detectors viable for volume production of detector arrays.

In conclusion, self-switching diodes (SSDs) using epitaxial graphene on 4H-SiC have been demonstrated. Zero-bias graphene SSD detectors showed promising results using on-wafer measurements up to 67 GHz. Graphene SSDs on H-intercalated graphene exhibited a flat voltage responsivity of 3.9 V/W and an NEP of 2.2 nW/Hz. This work was supported by the Swedish Research Council (VR 621-2012-4633) and European Science Foundation (ESF) under the EUROCORES Program EuroGRAPHENE (EPiGRAT). We also acknowledge support from the Swedish Foundation for Strategic Research (SSF), project “Graphene based high-frequency electronics” (RE10-0077), and the Knut and Alice Wallenberg Foundation (KAW), project “Swedish Graphene Initiative.”

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ARTICLE F

HIGH FREQUENCY ELECTROMAGNETIC DETECTION BY NONLINEAR CONDUCTION MODULATION IN GRAPHENE NANOWIRE DIODES

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High frequency electromagnetic detection by nonlinear conduction modulation in graphene nanowire diodes

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We present graphene nanowires implemented as dispersion free self switched microwave diode detectors. The microwave properties of the detectors are investigated using vector corrected large signal measurements in order to determine the detector responsivity and noise equivalent power (NEP) as a function of frequency, input power, and device geometry. We identify two distinct conductance nonlinearities which generate detector responsivity: an edge effect nonlinearity near zero bias due to lateral gating of the nanowire structures, and a velocity saturation nonlinearity which generates current compression at high power levels. The scaling study shows that detector responsivity obeys an exponential scaling law with respect to nanowire width, and a peak responsivity (NEP) of 250 V/W (50 pW/√Hz) is observed in detectors of the smallest width. The results are promising as the devices exhibit responsivities which are comparable to state of the art self switched detectors in semiconductor technologies. © 2015 AIP Publishing LLC.

The detection of high frequency microwave and THz radiation is of integral importance to a diverse range of disciplines in the physical sciences, and efficient detectors realized in graphene may prove to be of relevance owing to the unique electronic properties of the material.1,12 Self switched devices (SSDs) offer a unique alternative to high frequency detection as broken conduction symmetry is achieved via lateral gating.3,4 Several studies have been presented in which laterally gated nanowires patterned in semiconducting heterostructures demonstrate asymmetric current/voltage (IV) characteristics thereby enabling high frequency detection at zero bias.5–8 The choice of material in these experiments is motivated by the high mobility two dimensional electron gas which forms at the heterostructure interface. This suggests that efficient high frequency detection in graphene nanowire diodes (GNDs) is feasible to similar effect.9–11 As monolayer and bilayer graphene are semi-metallic materials exhibiting ambipolar transport, the nonlinearity which facilitates detection is of a different character than that seen in semiconducting nanowire diodes.

Nanowire structures are formed by etching narrow trenches into an electrically isolated graphene mesa. The high frequency GND detector consists of a linear array of GNDs etched into a single mesa which is bridged by a coplanar waveguide (see Fig. 1(a)). The operation of the GND is attributed to a geometric effect, whereby the outlying mesa laterally gates the nanowire when a drain bias (v_d) is applied across the junction (Figs. 1(b) and 1(c)). The responsivity in GNDs is strongly controlled by the channel width (w), channel length (l), and the width of the isolating trenches (wo) indicated in Fig. 1(c). In particular, the scaling of w is of relevance as it lends insight into the physics of electron transport within the graphene channel. As w decreases, lateral gating becomes more effective, resulting in a stronger nonlinearity and enhanced responsivity. In this work, the nonlinear IV characteristic in GND detectors of various nanowire widths (100, 70, 50, and 30 nm) is connected to trends in responsivity and noise equivalent power (NEP). The GNDs are fabricated via electron beam lithography (EBL) in epitaxial graphene grown by chemical vapor deposition (CVD) on semi-insulating 4H-SiC substrates.12 After growth, the monolayer graphene is intercalated with Hydrogen resulting in quasi-free standing bilayer graphene with enhanced carrier mobility.13–16 Monolayer and bilayer graphene nanowires transition to a semiconducting state with decreasing width due to the lateral confinement of carriers and edge disorder induced Anderson localization.17–21 The resulting energy gap (ε_F) becomes relevant on the smallest width scales probed in this study and may contribute to enhanced responsivity in the 30 nm devices.

DC measurements are performed using a semiconductor parameter analyzer and the results are summarized in Fig. 2(a). In narrow structures, a charge neutrality feature is observed in the conductance near ν_d = 0, which is consistent with the lateral gating effect depicted in Fig. 1(b). The charge neutrality feature is gradually occluded with increasing w. In order to understand the effect of lateral gating on the zero bias nonlinearity, a one dimensional transport model may be applied to the nanowire. When biased, the electric field couples capacitively from the outlying mesa to the nanowire via the substrate. The GND structure may be modeled as a capacitive divider as shown in Fig. 1(c). C_s = ε_0κ_s/w_0 represents the substrate capacitance, where ε_0 is the vacuum permittivity, and κ_s is the relative static permittivity. κ may be estimated as the mean of the substrate permittivity and the vacuum permittivity κ = (κ_s + 1)/2. C_q = ε^2ρ(ε) is the quantum capacitance in graphene. The quantity ρ(ε) in C_q represents the density of states in graphene as a function of chemical potential (ε).22–24 The quasi-Fermi potential (v) along the length of the nanowire may be
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The conductance minimum observed at the charge neutrality point is expected to be strongly enhanced when the energy gap in the graphene nanowires is of order $k_B T$. In Ref. 18, the energy gap is shown to scale inversely with nanowire width $w/C_{15} g(w) = a(w/C_{0}w/C_{3})/C_{0}$, where $a = 200$ meV nm and $w/C_{3} = 16$ nm are empirical constants. For the width scales considered in this study, the energy gap is expected to range from 2 meV for the 100 nm devices to 14 meV for the 30 nm devices. The energy gap is especially relevant in the case of narrow devices as it introduces a strong temperature dependence into the conductance minimum at zero bias.18,21 In this work, $k_B T > \epsilon_g$, such that the energy gap effect is sufficiently suppressed due to thermalisation of carriers for all devices with the possible exception of the 30 nm devices in which an enhanced zero bias nonlinearity is observed.

When $w$ is more than a few $w_c$, lateral gating only produces an edge effect and the core of the nanowire behaves as a normal linear conductor ($g_0$). This interpretation of device operation is supported by the work of Panchal et al. in which carrier transport in laterally gated graphene devices is investigated using scanning probe techniques.28 In Ref. 28, p-type edge conduction is observed in n-type bulk graphene as a consequence of lateral gating. Additionally, the width of the edge conduction channels is estimated at 60–125 nm which is of the order of a few $w_c$ in their material. Thus, at low bias, the GND IV characteristics observed in Fig. 2 may be modeled by a linear bulk conductance and a nonlinear edge conductance in parallel such that $i_d = \frac{1}{2} g(v_d) + g_0$. The nonlinear component $i_d = g(v_d) v_d$ is approximated via Eq. (1).

As $v_d$ increases, the conductivity begins to decrease as a consequence of velocity saturation. As the nanowires are highly resistive relative to the ohmic contacts and access resistances, the majority of the voltage drop due to an applied $v_d$ occurs over the length of the wire ($l = 1.1 \mu m$). The onset of velocity saturation in H-intercalated graphene occurs at an electric field of $E_c \approx 20$ kV/cm.29 In the fabricated devices, $E_c$ is reached at approximately 2.2 V and coincides with the observed current compression and decrease in conductivity at high bias. In graphene, velocity saturation occurs when carriers have sufficient energy to scatter via emission of polar optical phonons in the substrate.29–31

Low-frequency bias dependent S-parameter measurements are performed in order to investigate trapping effects in the GNDs (Fig. 2(b)). The small signal conductance $\text{Re}(y_{11})$ is observed to be nearly constant with frequency dispersion free operation. Similarly, the small signal susceptance $\text{Im}(y_{11})$ reflects a pure capacitance and is attributed to
the capacitance of the contact pads ($C_{pad}$). The behavior of $v_{DC}$ in addition to the absence of DC hysteresis suggests an overall absence of trapping effects in the device which would otherwise generate $1/f$ noise. Thus, the dominant noise contribution in GND devices is Johnson-Nyquist noise. The NEP is defined via the ratio of RMS noise voltage and responsivity $\sqrt{\langle i^2 \rangle}/\beta$ and is thus approximated by

$$NEP = \sqrt{4k_BT}\frac{r_d}{\beta}.$$ (2)

Here, $k_BT$ is the thermal energy, $r_d$ is the zero-bias differential resistance of the entire device. For a given responsivity, the NEP may be reduced by simply increasing the number of parallel GND channels. Increasing $\beta_{DC}$ has a similar effect of reducing $r_d$ such that NEP also improves with material quality. The lack of dispersion may be attributed to the fact that the devices as fabricated are passivated, thus precluding interface traps and associated material degradation resulting from dielectric deposition.

Responsivity in GND detectors may be interpreted as a consequence of two interacting nonlinearities: the charge neutrality nonlinearity near zero bias and the saturation nonlinearity at high bias (Fig. 2(a)). Responsivity measurements are carried out using a large signal network analyzer (LSNA). The high impedance of the GND detectors needs to be accounted for, hence vector corrected power measurements are used in order to correctly determine the detector responsivity ($\beta = v_{DC}/P_{in}$). The LSNA enables vector corrected measurements with amplitude and phase information at the fundamental frequency as well as at higher order harmonics. The delivered RF power ($P_{in}$) to the GND is measured at 1 GHz by the LSNA, and a voltage meter is used to measure the DC voltage across the diode generated by the nonlinearity ($v_{DC}$). The resulting vector corrected responsivity for various input powers is shown in Fig. 3(b). The nonlinear IV waveforms at the GND terminal are then directly reconstructed via inverse Fourier Transform of the amplitude and phase data obtained from the LSNA measurements such that details about device operation can be observed. The IV waveforms versus input RF power are shown in Fig. 3(a), illustrating the approximately symmetrical characteristics of the GND. Current compression is observed in the waveforms as a consequence of velocity saturation, in line with the DC measurements in Fig. 2(a). The agreement between the 1 GHz waveforms of (Fig. 3(a)) and the DC measurements (Fig. 2(a)) is confirmation of the non-dispersive operation observed in small signal measurements (Fig. 2(b)).

The behavior of $\beta$ scales accordingly with observations of the nonlinearity in conductance shown in Fig. 2(a). At low input power, the dependence of $\beta$ on nanowire width is observed to obey a simple exponential scaling law

$$\beta(w) = \beta_0 e^{\eta w_c / w}.$$ (3)

Here, $\eta$ is a scaling constant, $\beta_0$ is an amplitude constant, and $w_c = 2r_d$ is the critical width. For the 1 GHz data in Fig. 3(c), an exponential fit yields $\eta = 6.15$ and $\beta_0 = 1.1$ V/W (see the inset of Fig. 3(c)).

For the 100 nm and 70 nm GNDs, the responsivity is low near zero bias. As $w$ is larger than a few $w_c$ in these structures, the charge neutrality feature is suppressed due to a lack of effective self gating. In the case of the 50 nm and 30 nm structures, $w$ approaches $w_c$, and an appreciable $\beta$ is observed. As the input power is increased $\beta$ gradually increases as the waveform encounters a gradually decreasing conductance due to velocity saturation in the nanowire. This additional nonlinearity generates a steady rise in $\beta$ at high input power. LSNA measurements are also performed in order to obtain $\beta$ as a function of frequency from 1 GHz to 49 GHz at an input power of 0 dBm (Fig. 3(c)). The associated NEP is calculated by extracting $r_d$ from the low-frequency S-parameter measurements (Fig. 3(d)). A low-frequency responsivity (NEP) of 250 V/W (50 pW/√Hz) is observed in the 30 nm GND detector. The GND responsivity is observed to be relatively constant as a function of frequency with the exception of a gradual drop which may be attributed to $C_{pad}$ and resistive losses in the substrate. Despite the parasitic effect, a flat responsivity (NEP) of 80 V/W (170 pW/√Hz) is observed in the 30 nm GND detectors at high frequency.

In conclusion, high frequency detection graphene nanowire diodes have been demonstrated. DC, small signal, and large signal measurements are performed in order to investigate the nonlinearities in the device which enable detection. Two sources of nonlinearity are described: lateral gating at low bias and velocity saturation at high bias. A small energy gap may enhance the low bias nonlinearity in narrow graphene nanowires at finite temperature. High frequency measurements are consistent and reveal that the GND detectors obey a simple scaling law. In this work, we establish the feasibility of graphene nanowire diode detectors as a competitive platform for high frequency power detection.

**Methods:** The GNDs are fabricated in several steps using the JEOL 9300FS EBL system. First, Ohmic contacts are patterned using a liftoff compatible bilayer MMA/PMMA resist stack. The contact is then formed by deposition of a Ti/Pt/Au (10 nm/10 nm/70 nm) metal stack. Next, the GND trenches are patterned in PMMA via EBL. Several dose tests were performed in order to determine the optimum dose for achieving the designed nanowire width. The nanowire width was observed to vary within ±3 nm depending on the dose used in the EBL exposure. As PMMA is positive tone resist, higher doses resulted in channels and wider isolation trenches. A dose of 485 μC/cm² was found to yield device geometry maximally close to the design values. The isolating trenches are then etched using a low pressure (3 mTorr/50 W) O₂ plasma for 10 s. This low pressure etch is maximally directional, which is essential for achieving the high edge acuity required for device operation. Following this step, a mesa isolation is achieved via EBL patterning of ma-N 2403 negative tone resist and etching in (50 mTorr/50 W) O₂ plasma for 20 s. Finally, Ti/Au (100 nm/100 nm) contact pads are patterned and deposited via EBL patterning of MMA/PMMA and subsequent liftoff. The nanowire width ($w$) is varied, while the isolation width ($w_i = 100$ nm) and channel length ($l = 1.1\mu m$) are held constant. All devices presented in this work consist of nine parallel GND channels etched into a single mesa. Ancillary structures for characterization included transfer length method (TLM) structures for assessment of the contact resistance and large area sheet
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ARTICLE G

QUASI-FREE-STANDING MONOLAYER AND BILAYER GRAPHENE GROWTH ON HOMOEPIAXIAL ON-AXIS 4H-SiC(0001) LAYERS


Quasi-free-standing monolayer and bilayer graphene growth on homoepitaxial on-axis 4H-SiC(0001) layers

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ABSTRACT

Quasi-free-standing monolayer and bilayer graphene is grown on homoepitaxial layers of 4H-SiC. The SiC epilayers themselves are grown on the Si-face of nominally on-axis semi-insulating substrates using a conventional SiC hot-wall chemical vapor deposition reactor. The epilayers were confirmed to consist entirely of the 4H polytype by low temperature photoluminescence. The doping of the SiC epilayers may be modified allowing for graphene to be grown on a conducting substrate. Graphene growth was performed via thermal decomposition of the surface of the SiC epilayers under Si background pressure in order to achieve control on thickness uniformity over large area. Monolayer and bilayer samples were prepared through the conversion of a carbon buffer layer and monolayer graphene respectively using hydrogen intercalation process. Micro-Raman and reflectance mappings confirmed predominantly quasi-free-standing monolayer and bilayer graphene on samples grown under optimized growth conditions. Measurements of the Hall properties of Van der Pauw structures fabricated on these layers show high charge carrier mobility (>2000 cm²/Vs) and low carrier density (<0.9 × 10¹³ cm⁻²) in quasi-free-standing bilayer samples relative to monolayer samples. Also, bilayers on homoepitaxial layers are found to be superior in quality compared to bilayers grown directly on SI substrates.

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1. Introduction

Epitaxial growth of graphene on semi-insulating (SI) SiC has the potential to enable next generation ultra high frequency and low power electronic devices [1–6]. The main advantage is the possibility to obtain large area graphene directly on SI substrates which is one of the main requirements for high frequency devices. A lot of efforts have been made during the last decade on the growth of graphene on SiC using different techniques and growth mechanisms [7–11]. The growth process is mainly based on the thermal decomposition of the substrate surface at high temperature under ultra high vacuum or under argon background pressure. Silicon sublimes from the surface layers while the carbon atoms left behind on the surface form a carbon buffer (C-buffer) layer and graphene layer(s).
graphene on SiC has also shown to be possible through chemical vapor deposition of carbon on the surface using propane as a source gas under optimized growth conditions [12,13]. Other methods to obtain large area graphene include chemical vapor deposition (CVD) growth on metals [14–16]. However, the CVD on metal process is less suitable for device fabrication as the graphene layers must be transferred onto a semiconducting or Si substrate [17]. These transferred graphene layers tend to be both defected and contaminated as a result of the transfer process, thus resulting in graphene which is not suitable for device oriented applications [18].

High frequency electronic devices require electrical isolation which is achieved through the growth of active layer structure on Si substrates. The Si-face of nominally on-axis 4H-SiC substrates is preferred over the C-face for the growth of graphene. This is mainly due to the fact that graphene growth is easier to control on the Si-face and under optimized growth conditions the thickness of the graphene can be limited to just a few layers over large areas. On-axis substrates are used in order to avoid a high surface step density thereby facilitating the growth of very uniform graphene monolayers and bilayers over large areas of the substrate.

Monolayer and bilayer graphene are of particular importance due to their unique physical properties. Monolayer and bilayer graphene exhibits a high carrier mobility which is suitable for high frequency electronics. Pristine monolayer graphene is a semi-metal with zero bandgap and does not allow high on/off ratio (a basic requirement for switching devices). On the other hand, bilayer graphene has shown to open up a narrow bandgap of 100–250 meV in the presence of potential gradient across the two adjacent layers [19–23]. The potential can be created either through different doping levels in the adjacent layers or by applying external electrical potential across the structure. The latter method is more practical and also allows tuning of the bandgap during device operation. An external potential can be applied through dual gating of the device via top- and back-gating. This idea has so far been only tested on exfoliated graphene flakes on SiO2 which are not suitable for large scale production.

In order to be able to apply potential gradient across adjacent layers of graphene on Si substrates, a conductive layer with controlled doping is needed underneath the graphene layers. Such a conductive layer can be obtained through homoepitaxial growth on the Si-face of nominally on-axis 4H-SiC substrate using CVD; a wide range of conductivity can be obtained in the epitaxial SiC through controlled doping. In this work we report the details of our approach of the growth of graphene on homoepitaxial layers of 4H-SiC – grown on nominally on-axis Si substrates – as well as the structural and electronic properties obtained. The structure can be used for back-gated electronic devices such as graphene-based high-frequency field-effect transistors (GFETs).

The Si face of the substrates are chemo-mechanically polished providing a smooth surface prior to epitaxial growth. Large 16 × 16 mm² pieces diced from a single wafer were used in this study. All of the growth processes and substrate surface preparations were performed in a conventional horizontal hot-wall CVD reactor, mainly used for the growth of SiC layers. The heating zone of the reactor is equipped with SiC-coated high purity graphite susceptor while the heating is implemented using RF-induction. The temperature is measured using a pyrometer facing to the ceiling of the susceptor directly above the substrate and can be controlled up to 1900 K. The reactor is also equipped with high-throughput turbomolecular pump which can maintain high vacuum level down to 1 × 10⁻⁵ Pa.

2. Homoeptaxial growth of 4H-SiC

Epitaxial growth on the Si-face of nominally on-axis 4H-SiC substrates under standard growth conditions leads to the formation of 3C-inclusions and other defects in the epilayer. In this study we have used our unique growth process developed for on-axis homoepitaxy, which allows us to obtain pure 4H polytype in the epilayer without inclusions of foreign polytypes [24].

In the case of standard homoepitaxial growth on off-cut substrates (4° off-cut), in-situ surface preparation of substrate is performed in a background pressure of hydrogen at high temperature in order to remove subsurface damages. The epitaxial growth is then performed at the C/Si ratio of 1. In the case of on-axis epitaxy, we have observed that in-situ surface preparation of the substrate and growth in slightly Si-rich environment together with slightly higher growth temperature plays a key role in the replication of the substrate polytype into the epilayer. Surface preparation under such conditions reveals more uniform surface step structure mainly composed of large steps that are usually about 10–40 nm and small steps that are 0.5–1 nm [25]. The small steps originate from threading screw dislocations intersecting the surface while the large steps are related to small unintentional off-cut in the substrate and surface step-bunching on the Si-face. In-situ etching conditions were optimized to minimize the formation of large steps and preferential etching around dislocations. Homoeptaxial growth was performed at a growth temperature of about 1870 K and a pressure of 1 × 10⁴ Pa. The epitaxial layers were grown at growth rate of 7 µm/h to a total thickness of 2–3 µm using silane and propane as silicon and carbon sources. Since surface roughness is known to increase drastically with thickness, thin layers were grown in order to avoid large surface inhomogeneities [26]. The layers were grown with a controlled n-type doping of 1 × 10¹⁶ cm⁻³ using nitrogen gas as dopant. The doping level in the reference epilayers was confirmed via capacitance–voltage (CV) measurements using a mercury probe.

The surface morphology of on-axis homoepitaxial layers observed using optical microscope with Nomarski contrast, displays a relatively inhomogeneous surface. These inhomogeneities are due to different growth mechanisms active in different regions of the epilayer and to heavy surface step-bunching native to the Si-face of SiC [Fig. 1]. In the case of off-cut substrates (e.g., 4° or 8° off-cut) the epitaxial growth
is driven by step-flow growth which results in very smooth surface whereas in the case of on-axis substrates the growth can be a mixture of step-flow (Fig. 1a) and spiral growth (Fig. 1b) which together with step-bunching leads to rougher surface. However, very large areas completely free of large steps are also observed, as illustrated in Fig. 1c.

The surface of the homoepitaxial layers was also characterized with tapping mode atomic force microscopy (AFM). Regions which are dominated with step flow growth (Fig. 1a) demonstrate large steps with heights on the order of 20–200 nm separated by >100 μm wide regions which are relatively smooth (Fig. 1d). These relatively smooth regions are covered with a fine structure of 0.5–1 nm steps while the edges of large steps are covered with larger 1–4 nm steps (Fig. 1d). Spiral growth regions (Fig. 1b) appears to be relatively flat with arm-like features pointing towards [11\(\overline{2}0\)] directions (Fig. 1e). The regions which appear very smooth under the optical microscope (Fig. 1c) are also found to be dominated by the spiral growth mode interlaced with fine 0.5–1.0 nm steps (Fig. 1f).

The epilayers were confirmed to be 100% of the 4H polytype by measuring the low temperature photoluminescence (PL) spectrum on random areas. The spectra did not show any PL emission related to foreign polytype inclusions. The near band gap emission spectrum is dominant with sharp nitrogen-bound exciton lines. The free-exciton lines are also visible at this doping level reflecting the high purity and quality of epilayers.

2.2. Growth of monolayer and bilayer graphene under Si ambient

After homoepitaxial growth, the samples were loaded in the reactor along with reference pieces (bare substrate pieces from the same wafer used for the homoepitaxial growth) and surface preparation was made in hydrogen in the temperature range of 1670–1770 K and pressure of \(1 \times 10^3\) Pa for a few minutes to remove the native oxide. The reference samples were used to compare the surface morphology, graphene thickness and uniformity with those on homoepitaxial layers. We introduce a new approach of graphene growth under Si background pressure to have better control on the number of layers and thickness uniformity over large area whereas the growth process is still based on thermal decomposition of the surface through sublimation of Si. The growth was performed under Si background pressure of \((0.6–1) \times 10^{-3}\) Pa in the temperature range of 1670–1770 K for 60 min.

When graphene is grown under vacuum, the thickness and uniformity are controlled exclusively by the growth temperature \([11,27]\). This is due to high preferential removal rate of Si at step edges \([28,29]\) and around threading screw dislocations intersecting the surface. This removal rate can be controlled to some extent via a combination of a relatively low growth temperature and a high background pressure of Si.

The excess Si over SiC substrate efficiently suppresses the decomposition rate of the surface by reducing the removal rate of Si from the surface. Additionally, high background
pressure also allows for high temperature growth through shifting the surface phase transitions towards higher temperatures. Higher pressures lead to the formation of relatively high quality graphene with large domains. The process is compatible with the growth system and is easy to control. The Si background pressure during the growth of graphene was achieved through the evaporation of excess Si from the inner side of the susceptor that was deposited intentionally during a separate preceding growth run. The deposition process of excess Si was also optimized in order to achieve constant silicon background pressure during the whole graphene run. The Si ambient pressure as well as the growth temperature is found to be the main factors which control the thickness of graphene and its uniformity over large areas.

The growth processes were optimized to obtain quasi-free-standing monolayer and bilayer graphene under Si background pressure. In order to obtain quasi-free-standing monolayer graphene, only the C-buffer layer was grown, whereas when bilayer graphene was desired, the growth conditions were optimized to obtain monolayer graphene on the surface of homoepitaxial 4H-SiC layers (Fig. 2). Subsequent hydrogen intercalation transformed the C-buffer layer into quasi-free-standing monolayer, and the monolayer graphene into quasi-free standing bilayer graphene (Fig. 2). The whole growth process including substrate surface preparation, on-axis homoepitaxial growth, graphene growth and hydrogen intercalation can also be performed in a single sequence without exposing the samples to air. However, in this study, the samples were removed from the reactor after homoepitaxial growth in order to study the properties of the 4H-SiC layers. The subsequent graphene growth and hydrogen intercalation was performed in a single growth process without exposing the samples to air.

As mentioned in the previous section, the surface morphology of the homoepitaxial layer is mainly dominated by large steps and the regions between them are covered with small steps of 0.5–1 nm height. Graphene growth on such surfaces does not seem to alter the structure of the large steps (Fig. 3a) formed through either surface step-bunching or spiral-growth related arm-like features. However, the 0.5–1 nm steps covering the wide regions between large steps on as-grown epilayer surface coalesce to form 2–4 nm steps leaving relatively wide atomically flat terraces during graphene growth (Fig. 3d). This is more clearly demonstrated in Fig. 4, where Fig. 4a is AFM image taken after the growth of homoepitaxial layer whereas Fig. 4b is taken after the growth of graphene. By comparing these two images one observes that the 0.5–1 nm steps on the homoepitaxial layer transform into 2–4 nm steps and consequently the width of atomically flat terraces is also increased. Similar behavior of the rearrangement of surface step-structure was also observed in monolayer and bilayer graphene samples. Featureless and very smooth regions of the as-grown epitaxial layers (Fig. 4c) also seem to degrade through the coalescence of 0.5–1 nm steps into 2–4 nm steps as a result of surface step-bunching during graphene growth. Furthermore, features related to step-bunching in smooth regions also appear under optical microscope (Fig. 3b) after graphene growth.

The reference sample on the other hand does not show any large steps on the surface although the surface is still step-bunched with step height of 2–4 nm (Fig. 3c and e). The absence of large steps is mainly due to substrate surface preparation at relatively low temperature and pressure and the subsequent growth under background pressure of Si. Similar reconstruction of 0.5–1 nm steps into 2–4 nm steps has been reported during graphene growth in vacuum on bare substrates that were etched in hydrogen prior to the growth of

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**Fig. 2** – A schematic illustration of graphene growth processon on homepitaxial layers. For quasi-free-standing monolayer samples, only the C-buffer layer was grown, whereas for quasi-free-standing bilayer samples, C-buffer layer plus monolayer graphene was grown. Hydrogen intercalation transformed the C-buffer layer sample into quasi-free-standing monolayer and C-buffer layer plus monolayer sample into quasi-free-standing bilayer graphene. The step edges in both cases show one additional graphene layer. (A color version of this figure can be viewed online.)
However, in this case, large steps are also observed on the surface due to high temperature surface preparation. Low temperature growth under controlled Si background pressure leads only to the formation of a C-buffer layer on wide terraces and narrow strips of monolayer graphene (about 1 μm width) formed on step edges. Hydrogen intercalation transforms the buffer layer on wide terraces into quasi-free-standing monolayer while at the step-edges, narrow strips of quasi-free-standing bilayers are formed.

A relatively high growth temperature is used for the growth of the C-buffer layers plus monolayer graphene under the same ambient conditions. This leads to the formation of monolayer graphene on wide terraces decorated with narrow stripes of bilayer graphene only along the step edges. Hydrogen intercalation transforms monolayer graphene on the wide terraces into bilayer graphene whereas bilayer graphene along the step edges is transformed into a trilayer. The stripes of trilayer along the step edges in bilayer samples are relatively wider (about 2–3 μm)
compared to the bilayer stripes (~1 μm) along the step edges in monolayer samples. This is likely due to the relatively higher growth temperature used for the growth of bilayer graphene.

2.3. Hydrogen intercalation

Thermal decomposition of the Si-face of SiC always leads to the formation of graphene-like C-buffer layer at the interface of SiC and first graphene layer. The buffer layer is chemically bound to the substrate and therefore does not show graphene like properties. However, the bonding can be removed through hydrogen intercalation under certain conditions and the buffer layer can be transformed into an additional graphene layer. [31]. Hydrogen intercalation of the samples following the graphene growth process was performed in the temperature range of 1000–1100 K under a hydrogen background pressure of 5–6 × 10^4 Pa for 60 min without exposing the samples to air. Contactless measurements of charge carrier mobility, sheet carrier density and sheet resistance were estimated in as-grown samples using microwave reflectivity at room temperature. After the growth of C-buffer layer, the reference sample did not show any conductivity. However, after hydrogen intercalation, the sample became conductive with sheet resistance of about 200–400 Ω/□, a charge carrier density of about 1 × 10^{13} cm^{-2} and a mobility of about 2000 cm^2/V·s. This confirms the formation of C-buffer layer during the growth and its transformation into quasi-free-standing monolayer through hydrogen intercalation. The reference samples grown together with quasi-free-standing bilayer graphene samples showed relatively high values for mobility and charge carrier density 3000 cm^2/V·s and 1.5 × 10^{13} cm^{-2}, respectively and correspondingly low values of sheet resistance 150–300 Ω/□, as measured by contactless measurements. These are averaged values obtained on large areas of several millimeters. The passivation of the SiC surface through hydrogen intercalation at the interface and conversion of C-buffer layer into monolayer graphene are also confirmed by Raman spectra where much narrower G and 2D peaks are observed compared to as-grown graphene with C-buffer layer present at the interface.

3. Graphene characterization

Several characterization techniques were used to assess the graphene layers. The number of graphene layers was determined on random areas of the samples by reflectance mapping using a micro-Raman spectrometer. In case of graphene grown on semi-insulating substrate, the sheet resistance and the charge-carrier mobility were estimated using a contactless measurement technique. Van der Pauw structures were also fabricated in monolayer and bilayer graphene grown on homoepitaxial layers to access the electronic properties, and a comparison was made with graphene grown on bare substrates.

3.1. Reflectance and Raman mapping

The reflectance mapping as described in [32] is useful for obtaining direct information on the number of graphene layers on the investigated sample. Since the reflectance mapping alone is much faster than Raman mapping, it is used to map the graphene morphology (expressed in number of layers) on a relatively large area on the sample. Subsequent Raman mapping was performed on a chosen area within the larger reflectance map, thus yielding additional information on the stress conditions and the doping of the graphene. Since Raman and reflectance are compatible, another reflectance map is recorded during the Raman measurement in order to confirm that the same area within the larger reflectance map is repeated. Furthermore, each individual Raman spectrum can be labeled with the corresponding number of graphene layers.

Figs. 5 and 6 illustrate examples of reflectance and Raman maps of samples with predominantly monolayer (Fig. 5) and bilayer (Fig. 6) graphene together with typical Raman spectra obtained from the corresponding regions. In processing the Raman spectra of the monolayer, each of the G- and 2D-peaks is fitted with a single Lorentzian allowing for the rapid extraction of the peak positions and full widths at half maximum (FWHM) for each point on the map. In the case of bilayer or thicker graphene a single Lorentzian line is not appropriate for describing the line shape of the 2D-peak due to the changed band structures in these more complicated systems. However, forcing a fit with a single Lorentzian still provides a reasonable estimation of the corresponding peak position and line width. In both figures, part (a) displays the larger reflectance map showing the number of graphene layers, with the region chosen for Raman-reflectance mapping is outlined. Part (b) in Figs. 5b and 6b display the maps built by color-coding the four parameters obtained from the fitting (peak position and FWHM of G- and 2D-peaks) together with the second reflectance map obtained simultaneously with the Raman mapping. Finally, in part (c) of each figure (Figs. 5c and 6c) typical Raman spectra from the corresponding regions are shown.

The reflectance map in Fig. 5 obtained in conjunction with the Raman mapping repeats the outlined area of the larger pure reflectance map of Fig. 5a. This area is chosen in advance for Raman mapping since it mainly contains quasi-free-standing monolayer graphene. Despite the homogeneity of the monolayer region as seen in reflectance, the positions of the G- and 2D-peaks from the Raman map displayed in Fig. 5b exhibit significant dispersion typical for graphene on SiC. This feature is typically interpreted in terms of the variation of mechanical stress conditions in the graphene layer. The assignment of the peak-position variations to stress variations in the graphene layer is also corroborated by the good correlation between the 2D- and G-peak positions (not shown). The G and 2D FWHM maps of the monolayer may qualitatively be divided into two regions which are well correlated. These two regions are seen as darker areas in the upper-left part and lighter in the lower-right part of the monolayer region in the FWHM maps for both 2D and G in Fig. 5b. The line broadening between these two areas is quite distinguished, from about 6 to 7 cm^{-1}.
Fig. 5 – (a) Reflectance map on a sample with predominant monolayer graphene showing the number of graphene layers; (b) reflectance map (left) taken on the outlined area of the larger map in part (a) of the figure together with the maps (right) of the peak positions and FWHM of the G- and 2D-peaks obtained from the Raman spectra; (c) the top spectrum represents the typical Raman spectra taken on the part of monolayer region with smaller line widths of the G- and 2D-peaks (the darker region in the FWHM maps in part (b) of the figure); the bottom spectrum is representative for the monolayer region with larger line widths (lighter region in the FWHM maps in part (b) of the figure). (A color version of this figure can be viewed online.)

Fig. 6 – (a) Reflectance spectrum on a larger (60 μm × 60 μm) area of sample with predominantly bilayer graphene. One-, two- and three-layer regions are observed as marked in the map. (b) The results from the simultaneous Raman-reflectance mapping on the area outlined in part (a), plotted in the same manner as in Fig. 4b. (c) The top three spectra picture the rather large variation of the peak positions of the G- and 2D-peaks on the bilayer region alone. The bottom spectrum is taken on one of the trilayer streaks and is given for comparison. (A color version of this figure can be viewed online.)
in several dilute HF and etching the graphene layer is amorphous due to the deposition (25–26 cm\(^{-1}\)) to approximately 9 cm\(^{-1}\) (29 cm\(^{-1}\)) for the G (2D) peak respectively. The reason for this segregation of the monolayer region is presently not understood. Such a clear segregation has not been observed previously in hydrogen intercalated samples grown directly on semi-insulating substrates. The observed change in the line widths is not likely to be due to change in the doping when moving from the one region to the other, because the G-peak shift associated with change in the doping [33] is not observed (cf. the spectra in Fig. 5c). Also, as seen from the peak-position maps in Fig. 5b, neither the G-nor 2D-peak positions are correlated with the different line widths in the two regions (cf. the peak-position maps in Fig. 5b). The D\(^{-}\) peak at 1618 cm\(^{-1}\) which is associated with defect scattering is also present in the regions demonstrating broad G and 2D lines.

The reflectance map in Fig. 6a shows that although most of the surface is covered with bilayer, the morphology expressed in number of graphene layers is strongly influenced by the morphology of the underlying substrate (i.e. the CVD-grown epitaxial layers discussed previously). The spiral growth mode leads to the formation of relatively large hillocks possessing many larger steps on their slopes. A part of one such hillock is visible in the left part of the map in Fig. 6a. The area for Raman-reflectance mapping (outlined) was chosen away from the hillock in a region of the sample where presumably the step-flow growth mode has been effective. As was the case with the monolayer map, the reflectance map obtained together with the Raman measurement essentially repeat the outlined region in Fig. 6a. However, unlike the case of monolayer graphene, the maps of the four Raman parameters show much more dispersion in both the peak positions and line widths of G- and 2D-peaks. The spectra change quite abruptly between neighboring points on the map despite the fact that the laser spot (~700 nm) is larger than the pitch of the map (300 nm). This indicates an inhomogeneous stress distribution which manifests on a microscopic scale (smaller than the laser spot). Many spectra exhibit split of the G-peak into two components (not shown), which also suggests large stress variations on a microscopic scale. These variations are likely due to the rougher morphology of this bilayer sample. The upper three spectra in Fig. 6c illustrate the large variation of the peak positions on the bilayer region alone (about 7 cm\(^{-1}\) and 15 cm\(^{-1}\) for the G- and 2D-peaks, respectively). The bottom spectrum taken on one of the trilayer inclusions is also displayed for comparison. Monolayer inclusions are also encountered in few points, also confirmed by the corresponding Raman spectra (not shown). These inclusions are visible also in the large reflectance map (cf. Fig. 6a).

### 3.2. Electrical characterization

Several 100 \(\mu\text{m}^2\) Van der Pauw structures are fabricated on graphene grown on both Si SiC substrates and on n-type homoepitaxial layers of SiC [34]. Measurements of the Hall properties of these structures yield valuable information about the uniformity of the electron transport properties in large area epitaxial graphene layers. The fabrication of the Hall structures is performed using an in-house process optimized for epitaxial graphene. The process begins by the deposition of a 10 nm passivation layer of Al\(_2\)O\(_3\) in several steps. In each step 1.5 nm of Aluminum metal is deposited over the graphene layer and subsequently oxidized at 453 K [35]. The purpose of this passivation layer is to protect the native graphene layers from further process environments. Although the Al\(_2\)O\(_3\) layer is amorphous due to the deposition method, it serves quite well as an initial passivation layer.

Following the patterning of alignment marks, Ohmic contacts are patterned using photolithography. The thin passivation layer is then etched in a weak solution of 1:10 HF:DI. Following etching, a metal stack of 10/10/40 nm of Ti/Pt/Au is deposited in order to form Ohmic contacts to the graphene layers. Next, mesa isolation is performed by patterning via photolithography and ICP etching in Cl\(_2\)/Ar plasma at 400 W for 30 s. Alternatively, the mesa isolation can be achieved by wet etching the Al\(_2\)O\(_3\) in dilute HF and etching the graphene in O\(_2\) plasma at 50 W for 30 s. The first method is found to be desirable as the HF solution has a tendency to corrode the Ti layer of the contact metallization thus degrading the contact quality. Finally, the Ohmic contacts are extended onto the SiC substrate via photolithography and evaporation of a 10/100/10 nm stack of Ti/Au/Ti. The first Ti layer serves to glue the contact to the substrate, while the final Ti layer aids in lift-off. This final step is necessary as the adhesion of Ti to graphene is generally found to be quite poor. Electrical characterization of the fabricated Van der Pauw structures is performed in a Biorad HL5500PC Hall system. The carrier mobility and sheet resistance are plotted as a function of carrier density for several samples. For the measurements of graphene grown on the homoepitaxial SiC, the sheet resistance of the epitaxial layer is very high compared with that of the graphene. For this reason, it can be assumed that the measured Hall voltage will be almost entirely due to current carried by the graphene layers. The influence of the conductivity of the homoepitaxial SiC layers on Hall measurements is assumed to be minimal.

Monolayers and bilayers grown on epitaxial SiC layers are compared to a typical monolayer sample grown directly on the Si SiC substrate. The measurements are carried out at 300 K, and each data point represents a measurement of a separate Hall structure. On each 16 \(\times\) 16 \(\text{mm}^2\) chip, 48 structures are measured; only structures with high symmetry in the Hall voltage indicating a reliable measurement are reported. The results are summarized in Fig. 7.

Several Hall structures on three 16 \(\times\) 16 \(\text{mm}^2\) samples are measured: monolayer on Si substrate, monolayer on epitaxial SiC, and bilayer on epitaxial SiC. The epilayers demonstrate several divergences from monolayer on Si substrate. First, it should be noted that the monolayer on Si substrate exhibits a fairly constant carrier density of \(1 \times 10^{13} \text{ cm}^{-2}\). The mobility of this monolayer sample is of order 1500–2500 cm\(^2\)/Vs and its sheet resistance varies on the order of 200–400 \(\Omega\cdot\text{square}\). Such values are typical of epitaxial graphene grown on SiC after processing. Furthermore, the sample is uniformly p-type which is expected from hydrogen intercalation [31,36]. Overall, the Si SiC control sample represents a high quality control by which to gauge the overall electrical characteristics of epitaxial graphene grown on SiC epi-layers.
For the monolayer on epitaxial SiC, the Hall data forms a very tight cluster of points with an average mobility on the order of 800 cm$^2$/Vs. Furthermore, the carrier density observed is very high when compared to the Si control sample however, the origin of this high carrier density is currently unknown. On the other hand, the graphene monolayer on epitaxial SiC demonstrates exemplary uniformity in terms of its electron transport characteristics. This uniformity is thought to be reflective of the underlying uniformity of the SiC epitaxial layers that is observed after monolayer growth (Fig. 4).

The results for bilayers grown on epitaxial SiC are equally interesting. A very wide dispersion in the mobility, sheet resistance and carrier density appears in the Hall measurements. The mobility, sheet resistance and carrier density vary from 700–2300 cm$^2$/Vs, 200–500 Ω/□, and 0.85–1.3 × 10$^{13}$ cm$^{-2}$ respectively. Of these figures, the variation in the carrier density is perhaps the most relevant as it implies a wide variation in the Fermi energy at various points in the bilayer sample. In particular, the measurement of 0.85 × 10$^{13}$ cm$^{-2}$ suggests a Fermi energy of 150 meV. A device fabricated on material of such low doping would likely exhibit a high capability for modulation as the Fermi energy is somewhat near to the point of minimum conduction. It should be noted that this particular structure also exhibits a respectable carrier mobility of about 2000 cm$^2$/Vs and a sheet resistance of 360 Ω/□. The bilayer sample also has many structures which demonstrate very high carrier density which are not suitable for a device oriented application. Perhaps the most striking feature is the lack of uniformity in the electron transport characteristics of the bilayer sample. This reflects the observation that the epitaxial SiC layers become more disordered after bilayer growth than after monolayer growth (i.e. that disorder in the graphene layers is reflective of the substrate surface properties). The average carrier density of the bilayer on epitaxial SiC sample is on the order of 1.1 × 10$^{13}$ cm$^{-2}$, which is very typical of H-intercalated bilayers on Si SiC.

In general, the electron transport characteristics measured on the graphene on homoepitaxial SiC layers are quite positive for this preliminary experiment as the results conform relatively well with what is observed on graphene grown on Si SiC samples [34]. Furthermore, all structures were found to be p-type suggesting that hydrogen intercalation was successful. Also, the transport measurements after fabrication correlate well with microwave reflectivity measurements taken prior to fabrication indicating that the graphene layers are not substantially altered by processing. These results suggest a compatibility between graphene growth and epitaxial n-type SiC which is positive from the perspective of electron devices in graphene.

4. Discussion

The surface morphology of on-axis homoepitaxial layers is highly influenced by the growth mechanism, and the growth mechanism is mainly controlled by the off-cut of the substrate under certain growth conditions. However, on nominally on-axis substrate with an off-cut of less than 0.1, the growth mechanism can be controlled by tuning the C/Si ratio. Spiral growth dominates in carbon rich conditions, while step-flow growth dominates in silicon rich conditions [37]. By tuning to a carbon rich environment, it is possible to limit the growth mode to step-flow growth thereby obtaining well-arranged large steps on the surface with very wide terraces. However, in this work homoepitaxial layers were grown at C/Si ratio of 1 in order to obtain high nitrogen doping at low flow rate of nitrogen.

The epilayer surface appears to be relatively rougher compared to the substrate surface exposed to similar temperature under hydrogen ambient. This is mainly due to heavy step-bunching during homoepitaxial growth on the Si-face along with a mixture of different growth mechanism on the on-axis substrate. However, it is possible to further optimize the growth process to reduce the surface roughness. As-grown epilayer surfaces consist of relatively wide regions covered with small steps of 0.5–1 nm height between large steps of few tens of nm height. The large steps are usually not steep and extend over very large area (several tens of microns) on the surface. This morphology is advantageous in the context of graphene growth when compared to steep steps formed on...
the substrate during surface preparation in hydrogen ambient. Steep edges usually show uncontrolled growth of multilayer graphene which may significantly influence the electrical properties of devices made in such material. Also the atomically flat terraces on epilayer surface are much wider compared to the substrate surface etched in hydrogen under similar temperatures. Under controlled growth conditions, wide terraces lead to the formation of uniform thickness of graphene over large areas only limited by the width of the terraces.

The number of graphene layers and thickness uniformity is found to be extremely sensitive to the growth temperature and ambient conditions. Although the temperature distribution in the region of the susceptor (75 × 75 mm²) used for samples is within ±10 K, a considerable variation has been observed in the thickness uniformity among different samples grown during the same growth run. The measured temperature distribution was observed under heavy hydrogen flow at a pressure of 20 kPa. However, the pressure used for graphene growth is around 1 × 10⁻³ Pa. These low pressures may significantly influence temperature distribution in the susceptor. The graphene thickness variations are generally high among the samples placed along the length of the susceptor which is most probably due to inhomogeneous ambient conditions and temperature gradient along the length of susceptor. A comparison of reflection maps (not shown), taken from the sample placed in the upstream side of the susceptor showed considerably more uniform graphene thickness compared to the samples placed at the downstream side of the susceptor. Considering the monolayer graphene samples, large areas without graphene formation are observed in the samples placed towards the downstream side of the susceptor. This clearly indicates a relatively lower temperature and higher Si background pressure at the downstream side of the susceptor. These observations manifest the importance of both the uniformity of temperature and the Si background pressure on graphene uniformity.

It is well known that under vacuum growth, higher preferential removal rate of Si from larger steps leads to the formation of multiple layer of graphene on step edges. The height of large steps formed on the epilayer surface is much greater compared to the steps formed on the substrate surface during in-situ surface etching. However, the stripes of bilayer/trilayer graphene visible along the edges in the samples containing mainly monolayer/bilayer graphene are very narrow. This shows that a more homogeneous removal rate of Si can be maintained under Si-rich environment and high thickness uniformity of graphene can be obtained over large areas. Similar behavior was observed in the case of monolayer and bilayer graphene growth directly on the substrate under Si background pressure (the reference samples).

When the growth is optimized for only the C-buffer layer, step edges demonstrate both buffer layer and monolayer graphene. This suggests that nucleation of graphene starts at the step edges in the form of a C-buffer layer and then proceeds towards the smoother regions of the substrate. Under precisely controlled temperature and Si background pressure, the nucleation process can be limited to the formation of C-buffer layer. However, this may lead to incomplete coverage of the substrate. Our growth process was optimized to obtain complete coverage of C-buffer layer which also lead to the formation of additional graphene layer at the step edges.

The background pressure during graphene growth plays a critical role at relatively high temperature. The temperature of the phase transition at the surface between Si-rich to C-rich can be increased by at least a few hundred Kelvin by just increasing the background pressure. A relatively high background pressure also widens the window for graphene growth in the context of temperature allowing for the tuning the growth process to avoid preferential evaporation of Si at the step edges. This in turn allows one to overcome the limits on thickness uniformity posed by the preferential high evaporation rate of Si at the step edges.

Successful intercalation of hydrogen is also evident from the narrowing of the G- and 2D-peaks in the case of monolayer graphene compared to as-grown graphene with C-buffer layer present at the interface. As-grown monolayer graphene with C-buffer layer usually displays broader peaks with FWHM larger than 10 cm⁻¹ (34 cm⁻¹) for the G (2D) peak. However, when the monolayer is obtained by conversion of the C-buffer layer in graphene the typical G and 2D peak FWHMs are in the ranges 5–10 cm⁻¹ and 20–30 cm⁻¹, respectively. In this case, the narrowing of the G-peak is associated with the increased doping as discussed before.

The surface morphologies of monolayer and bilayer graphene as observed by optical microscopy are quite similar. AFM characterization revealed a relatively rougher surface on the bilayer sample. This increase in surface roughness was expected due to a relatively high growth temperature. The large steps are relatively higher compared to those in monolayer graphene samples but the structure of smaller steps is similar to the monolayer case. High surface roughness leads to a non-uniform sublimation rate and enhances the possibility of thickness non-uniformities which is confirmed by reflectance and Raman mappings. The Raman maps also provide evidence for inhomogeneous surface morphology of bilayer graphene compared to the case of monolayer graphene, which leads to the scattered stress distribution observed in bilayers. Large area reflectance maps of monolayer and bilayer samples (Figs. 5 and 6) show different distributions of thicknesses of monolayer and bilayer graphene, respectively. In samples grown intentionally as monolayer graphene, only stripes of bilayer graphene on step edges are observed while monolayer graphene is formed on wide terraces. On the other hand, in the case of bilayer graphene, inclusions of monolayer graphene are also formed on some of the wide terraces together with trilayer graphene on step edges. Although, it is possible to eliminate these monolayer inclusions by increasing the growth temperature, an accompanying extension of the trilayer regions onto terraces is also observed. This indicates much narrower growth window for bilayer graphene compared to monolayer graphene, and the presence of steps on the surface makes the bilayer growth much more difficult than monolayer.

The surface morphology of graphene grown on a bare substrate is substantially different from the graphene on epitaxial layers (Fig. 3c and e). A more linear surface step structure with relatively narrow terraces is observed in these samples. Also, no large steps with irregular pattern are observed in samples on bare substrates. The corresponding
reflectance and Raman maps (not shown) also reproduce similar structure in the form of non-uniform distribution of the thickness of graphene. A comparison of reflectance maps and Raman maps of graphene grown on homoepitaxial layers and on bare substrates reveals that the thickness uniformity of graphene is much better on homoepitaxial layers. Also, the growth window for monolayer graphene is wider compared to bilayer grapheme making it easier to obtain large area monolayer graphene.

Measurements of the room temperature electron transport properties of graphene monolayers and bilayers grown on epitaxial SiC conform somewhat well to the properties of graphene layers grown directly on SiC substrates. All of the hydrogen intercalated samples measured were observed to be uniformly p-type. The monolayers on epi-SiC demonstrate a mobility of order 800 cm²/Vs and a high carrier density of $1.5 \times 10^{13}$ cm⁻². Furthermore, the monolayers are highly uniform with regard to their transport characteristics. Bilayers on epi-SiC demonstrate a much wider range of mobilities (700–2300 cm²/Vs) and carrier densities (0.85–1.3 cm⁻³). This suggests that transport properties in graphene bilayers grown on epitaxial SiC inherit the non-uniformity observed in AFM and Ramam measurements of graphene bilayers. Furthermore, the bilayer sample exhibits regions of high mobility (>2000 cm²/Vs) and low carrier density (<0.9 $\times 10^{13}$ cm⁻³). Such regions are not demonstrated by bilayer counterparts grown directly on SiC substrates. The inhomogeneities of graphene transport properties in bilayer graphene on epitaxial reflect, in part, that of the SiC surface morphology. The large surface steps in bilayer graphene on epitaxial are regarded as the sources of the degradation of mobility in epitaxial graphene and leads to large variations in mobility across the sample. This observation is consistent with several other recent investigations showing a correlation between macroscopic electrical measurements and surface morphology [38–40]. If these properties could be uniformly achieved over large areas, then bilayers grown on epitaxial SiC layers could offer a substantial improvement to the current technique of graphene grown directly on SiC substrates in the context of a device oriented application. Further efforts will be directed towards optimizing the growth of hydrogen intercalated graphene bilayers on epitaxial SiC with the aim of achieving uniformly high mobility and low carrier density.

5. Summary

Quasi-free standing monolayer and bilayer graphene is grown on n-type doped ($1 \times 10^{15}$ cm⁻³) on-axis homoepitaxial layers of 4H-SiC. Homoepitaxial layers with 100% 4H polytype were grown using an optimized on-axis growth process. Graphene growth was made in controlled Si background pressure. In order to obtain monolayer graphene only C-buffer layer was grown whereas for bilayer graphene, monolayer graphene was grown on homoepitaxial layers. The hydrogen intercalation process was used to convert C-buffer layer into monolayer and monolayer into bilayer graphene. Micro-Raman and reflectance mappings confirmed predominant quasi-free-standing monolayer and bilayer graphene on samples grown under optimized growth conditions. Van der Pauw structures are fabricated in these layers using photolithography. Bilayer samples show relatively high values of charge carrier mobility (>2000 cm²/Vs) and low carrier density (<0.9 $\times 10^{13}$ cm⁻³) compared to monolayers on homoepitaxial layers with charge carrier mobility of (800 cm²/Vs) and high carrier density (1.5 $\times 10^{13}$ cm⁻³). Furthermore, bilayers on homoepitaxial layers are also superior in quality compared to bilayers grown directly on Si substrates.

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