Advances in the scientific understanding of carbon based structures have opened a wide variety of potential applications that utilize the unique electronic properties of graphene. In this article, the fundamental device physics behind graphene electronics is outlined with a special emphasis on lower dimensional structures. Specifically, the unique semiconducting graphene nanoribbon sheets are shown to be promising candidates for high-speed field-effect transistors (FETs). Material requirements for nanoribbon based FET devices are outlined, and particular attention is given to challenges associated with fabrication of these novel devices.

Introduction

Over the past couple decades, graphene has become known to the world for the extraordinary electronic, thermal, and mechanical properties it exhibits. Graphene is a single layer sheet of carbon that exhibits very high electronic and thermal conductivity, incredible mechanical strength for its size, optical transparency, and interesting spin transport behavior. Though the theoretical understanding of graphene has been mostly established in decades past, recent advances in fabricating high-quality graphene and increased interest from a variety of different fields has resulted in a huge increase in research and a Nobel Prize in 2010.

One exciting application of graphene has been for new, high speed field effect transistors, see Figure 1. Though graphene is typically metallic and conductive, when the sheet is confined to a narrow nanoribbon, the band structure changes such that the material becomes semiconducting. By applying a strong electric field to the graphene nanoribbon through a gate-contact, the relative position of the material’s Fermi energy may be manipulated, allowing for high on/off current ratios on the order of $\sim 10^6 - 10^7$ at room temperature [1] [2]. In particular, high operational speeds are possible due to the high carrier mobility in these structures and the possibility of using conductive patterned graphene as interconnects.

Compared to the large scalability of modern CMOS fabrication, the production of graphene nanoribbons is relatively slow, difficult, and prone to defects. Current fabrication techniques for nanoribbon graphene sheets include mechanical cleavage/exfoliation followed by electron beam lithography, separation of carbon sheets in graphite in an aqueous solution, unzipping or etching of carbon nanotubes, and patterning of graphene sheets using helium ion lasers. From a theoretical standpoint, graphene nanoribbons show great promise as functional components and seem likely to be readily integrated into CMOS processing. However, the fabrication of high performance nanoribbons requires atomic level precision that is currently difficult to achieve. Chem-
Graphene is a fascinating material with unique electronic properties that arise from a unique band structure. The structure of graphene is a two dimensional sheet of carbon atoms that are oriented in a hexagonal lattice pattern. This pattern arises from the $sp^2$ hybridization of $2s$, $2p_x$, and $2p_y$ orbitals, causing strong in-plane $\sigma$-bonds to form. Meanwhile, the third $2p_z$ is left to form weak $\pi$-bonds out-of-plane with neighboring $2p_z$ orbitals. Ultimately, the electronic properties of graphene are dictated by these $2p_z$ electrons [3].

Traditionally, the hexagonal lattice is decomposed into two triangular Bravais lattices (sublattices A and B) with lattice vectors

$$\vec{a}_1 = \frac{a}{2}(\sqrt{3}, 1)$$  \hspace{1cm} (1a)$$
$$\vec{a}_2 = \frac{a}{2}(\sqrt{3}, -1)$$  \hspace{1cm} (1b)

where $a$ is the interatomic spacing ($|a| = 0.246$ nm). The reciprocal vectors $\vec{b}_1$ and $\vec{b}_2$ for each sublattice form a hexagonal reciprocal lattice, as shown in Figure 2.

**Tight-binding Approximation**

In the tight-binding approximation of an atomic structure, the wavefunction of individual electrons is assumed to be confined to its constituent atom and relatively non-interacting with neighboring wavefunctions. In such a case, where a wavefunction $\psi$ may be related to neighboring electron connected by the vector $\vec{R}$ through the Bloch theorem by

$$\psi(\vec{r}) = e^{i\vec{k}\vec{R}}\psi(\vec{r} - \vec{R})$$  \hspace{1cm} (2)
the total wavefunction for each sublattice ($\phi_A$ and $\phi_B$) under the tight-binding approximation is the sum of all constituent wavefunctions

$$\phi_{A,B} = \frac{1}{\sqrt{N}} \sum_{\vec{R}_{A,B}} e^{i \vec{k}_{A,B} \cdot \vec{r}} \psi(\vec{r} - \vec{R}_{A,B}) \quad (3)$$

where N is the total number of 2p$_z$ electrons. From this model, where each atom located on sublattice A is neighboring three atoms on sublattice B, the energy eigenvalues have been shown to have the closed form of

$$E(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}} \quad (4)$$

where $\gamma_0$ is the transfer integral between neighboring wavefunctions [4][5]. The higher energy term corresponds to the anti-bonding $\pi^*$ band and the lower energy term is the $\pi$ band. This expression for energy in relation to wavevector, or dispersion relation, is unique in that at the K and K’ points in reciprocal space, the energy expression is degenerate and equal to zero, see Figure 4a. To further explore the behavior of electrons at these points, we can look at a point $\vec{k}_0$ slightly displaced from a K-point such that $\vec{k}_0 = \vec{k}_{\text{small}} + \vec{K}$. Plugging this back into equation [4] and approximating the result to a first-order Taylor series expansion, we have

$$E_{\pm}(\vec{k}_{\text{small}}) = \frac{\sqrt{3}}{2} \gamma_0 a k_{\text{small}} \quad (5)$$

Thus, since $E_F = v_F \hbar k$, the fermi velocity, $v_F$, is given by $\sqrt{3} \gamma_0 a / (2 \hbar) \approx 10^6$ meters per second [3]. In addition, due to the linearity of the dispersion relation near the K-points, the density of states and energy are directly proportional to one another. The conical dispersion relation of these particles near the K-points, or sometimes called Dirac points, leads to fast moving electrons that when treated relativistically provide insight to other rich, interesting physical phenomena.

**Graphene with Edges**

The treatment of graphene must be reconsidered when dealing with lower-dimensional systems (ie. sheets of graphene with finite boundaries and edges). Specifically, for graphene nanoribbons there are two types of edge-configurations that are possible: armchair edges (Figure 3a) and zigzag edges (Figure 3b). To account for these edge states, it is possible to define new rectangular lattice vectors shown in Figure 4b. The band structure of a sheet with armchair edge defects may be theoretically calculated by projecting the band structure of a 2D graphene sheet onto the a vector using the zone-folding technique demonstrated by Samsonidze, et al. [6]. In the zone-folding scheme, the energy eigenstates of a low-dimensional structure (such as a graphene nanoribbon) are described as a subset of the energy eigenstates of a bulk structure with the same periodicity (such as a graphene sheet). In essence, by cutting the graphene sheet along one of the a or z edges to form edge defects, we impose a set of boundary conditions that, similar to a particle in a box, discretize one-dimension of the reciprocal lattice vector k. The number of allowed states, or lines in k-space, is then related to the width of the ribbon. For graphene ribbons of sufficiently small width, the dispersion relation, as shown in Figure 4b, will be “cut” such that the regions near the K-points are not included and a band-gap emerges.

Exact, quantitative calculations of the band structure for graphene nanoribbons with armchair edges show that the electrically properties are highly sensitive to the width of the ribbon, N. For armchair edges, N is the number of two-atom horizontal pairs, as shown schematically in Figure 3a. In fact, the tight-binding model calculation with zone-folding technique predicts that the graphene nanoribbon has a state(s) near
Figure 4: Image borrowed from Nakada M., et al [7]. Dispersion relation in (a) of an edge-less graphene sheet. In (b), real-space lattice vectors \( \mathbf{a} \) correspond to armchair edges and \( \mathbf{z} \) to zigzag edges. Reciprocal lattice vectors of \( \mathbf{a} \) and \( \mathbf{z} \) shown in (c) by \( \mathbf{a}^* \) and \( \mathbf{z}^* \).

The fermi level (i.e. is metallic) when \( N = 3M - 1 \), with \( M \) an integer [7]. When this condition is not satisfied, a bandgap is present and the material is semiconducting. In general for armchair nanoribbons, the smaller the width is, the larger the energy bandgap. This intuitively makes sense because in the limit of large \( N \), the dispersion relation should approach the result for intrinsic graphene sheets.

Graphene nanoribbons with zigzag edges exhibit quite different electronic properties. In these structures, there is always a degeneracy of an energy state in the valence band and an energy state in the conduction band at \( k = \pi \). What is interesting is that these degeneracies do not occur at the K-points, where \( |k| = \frac{2\pi}{3} \). In fact, these wavefunctions are degenerate from \( \frac{2\pi}{3} \leq |k| \leq \pi \), see Figure 5 are highly localized at the edges of the graphene sheet, and do not physically arise from the band structure of intrinsic graphene [7].

Thus, in a zigzag edged graphene nanoribbon, the states lying within the nanoribbon exhibit a modest bandgap, but the degenerate states near the fermi energy at the edges of the bands result in the nanoribbon behaving as a metal.

In general, it is difficult to experimentally realize perfect armchair or perfect zigzag edged nanoribbons. Typically, nanometer sized sheets of graphene will have a mix of both kinds of edges. It is possible to define a quantity, sometimes referred to as a “zigzag ratio”, or the ratio of zigzag edge states to total edge states. In materials with relatively low zigzag ratios, it is still possible for noticeable edge states to exist.

Additional interest in graphene nanoribbons from the spintronics community has resulted from calculating the electronic properties of the weakly bound \( \pi \)-electrons in graphene structures with edges. Through a first-order perturbation of the tight-binding Hamiltonian, it is found that edge states in zigzag edges are stable, despite the very high density of states near the fermi energy. In addition, accounting for coulomb interactions has confirmed the stability of these edge states and also shown that there is a spontaneous ordering of spins at the edge of graphene sheets due to electron-electron interactions. Since the corresponding edge state on the opposite side of the graphene nanoribbon typically belongs to the other sublattice, the opposite edge is typically spin-polarized in the opposite direction and preserves the neutral magnetization of the graphene sheet, see Figure 6 [8]. These stable ferromagnetic edge-states have attracted interest from the...
spintronics community due to the high degree of spin-ordering and other unique properties of graphene.

Thus, accounting for the edges of thin strips of graphene demonstrates that decreasing nanoribbon widths result in an increased bandgap and semiconductor behavior. The specific states present at the edges must also be carefully taken into account, as they can possess different charge distributions, spin-states, and overall electronic properties.

Graphene Nanoribbon FET

The graphene nanoribbon field-effect transistor (FET) is a device utilizing the semiconducting nature of nanometer sized nanoribbons. Shown in Figure 1, a graphene nanoribbon FET might consist of a thin layer of SiO\(_2\) or other high dielectric, thin insulator grown onto of a gate contact such as highly p-doped Si. On this, the graphene nanoribbon directly connects a source and drain which may be made of Pd, a larger sheet of graphene, or any conductive, patternable material. In this example, a Schottky barrier type FET is considered since the thin, semiconducting graphene layer is in direct contact with the source and drain contacts.

The gate-contact applies an electric field to the graphene nanoribbon, bending the graphene bands either to a higher or lower potential (depending on the sign of the electric field) until the graphene fermi-energy lies within the conduction or valence bands. From here, the current flowing across the device is described by the tunneling probability of electrons through Schottky barriers on the source and drain side. In experimentally fabricated graphene nanoribbon FETs by X. Wang et al., Pd was used as the source drain and contacts because it lowered the Schottky barrier height for holes in p-type operation (Pd is a high-work function metal), resulting in lower threshold gate voltages. These novel transistors, typically of width less than 10nm, have demonstrated on/off current ratios as high as \(10^6\) and large current densities on the order of \(\sim 2000\mu\text{A}/\mu\text{m}\) [1].

In order to gain some theoretical insight into the transport properties of electrons in graphene nanoribbons, it is possible to use a Green’s function method to solve for the conductance of a graphene nanoribbon. Green’s function methods are often implemented for calculating the properties of low-dimensional systems due to their efficiency of solving inhomogeneous differential equations with various boundary conditions. The scattering matrix of a single particle moving longitudinally across a graphene nanoribbon is typically given in terms of the longitudinal velocity, the transverse wavefunction in the channel, and the energy-dependent retarded Green’s function [9]. Recursive computation techniques are typically used to calculate the retarded Green’s function for noninteracting particles that are described by the tight-binding Hamiltonian

\[
H = \sum_n s_n |n\rangle \langle n| + \sum_{n,m} \gamma_{n,m} |n\rangle \langle m| \tag{6}
\]

where \(s_n\) is the energy density of each site determined by the voltage of the gate, and \(\gamma_{n,m} = -0.266\) eV is a carrier hopping parameter describing the magnitude of hopping along with the overlap between wavefunctions \(n\) and \(m\) [10].

From the transmission element of the scattering matrix, the Landauer formula can be used to calculate the conductance \(G(E)\) of the graphene nanoribbon:

\[
G(E) = \frac{2e^2}{\hbar} T(E) \tag{7}
\]

Using this model, numerical simulations of the electrical performance of graphene nanoribbon FETs are readily accessible. Work done by S.
Thornhill et al. has simulated graphene nanoribbon FETs with source and drain contacts of semi-infinite sheets of graphene, as shown in Figure 8. Employing an iterative Green’s function approach, they demonstrated the decreasing overall conductivity of graphene (especially away from the fermi energy) for both armchair and zigzag type nanoribbons with the increase in applied gate voltage (Figure 7). This has been suggested for FET applications and is predicted to have on/off current ratios of $10^3 - 10^4$. This device is fundamentally different from the sub-10 nm graphene nanoribbon FETs experimentally realized by X. Wang et al., since this scheme does not utilize a Shottky barrier.

Materials Requirements

As stated before, the critical material in graphene nanoribbon FETs is the $sp^2$ hybridized constituent carbon atoms. The electronic properties of these graphene nanoribbons are highly sensitive to the structure of these nanoribbons, where edge patterns and nanoribbon width can alter the bandstructure and transport properties of edge states. Critical to the theoretical derivations described previously have been the assumption that edges of the graphene nanoribbon (dangling $\sigma$-bonds) are terminated by hydrogen atoms. In reality, a variety of chemicals may bond to the edges of these graphene sheets and significantly alter the edge states. As a result of this, there has been a significant discrepancy between theoretical modeling and predictions and experimental results. Though general graphene nanoribbon trends have been experimentally confirmed (such as the presence of a bandgap at sufficiently narrow nanoribbon widths), the exact behavior of states near the edge require more realistic theoretical modeling to account for defects and the presence of chemicals at the edge of the sheets. There is a need for more accurate methods of observing the behavior of edge states, but an even larger need for the ability to experimentally fabricate nanoribbons that have sufficiently smooth edges.

Additional special considerations with respect to field effect transistor operation include gate materials involved in applying the electric field to the graphene, materials for the source and drain contacts, and other materials involved with the stability of the graphene layer. Typically, source and drain contacts are a heavy metal acting as a Shottky barrier or a graphene nanoribbon that is wide and serves as a conducting channel to other parts of the device. In addition, for research purposes the backside of the substrate (usually highly doped Si under a SiO$_2$ insulating layer) is used as the gate oxide.

Various materials are required for fabrication of the nanoribbon graphene sheets, but this largely depends on the fabrication method being considered. For example, many solution-based methods of forming thin sheets of graphene have been developed, but these depend on the oxidizing/reducing conditions, specific chemicals in solution, and the host material that graphene will be produced from (ie. graphite, carbon nanotubes, etc.). In these cases, it is also very important to consider the byproducts of such reactions, as unknown functional groups can create various interactions and electronic states that alter carrier transport behavior.

Bilayer Graphene

The predominant method of opening the graphene band gap for use as a field effect tran-

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**Figure 7:** Image borrowed from Thornhill S., et al. Figures (a)-(d) show the numerically calculated conductance curves for monolayer and bilayer graphene nanoribbons with armchair and zigzag type edges.
sistor relies on quantum confinement in a narrow ribbon. However, several other methods have been proposed to break graphene’s crystal symmetry, which is the source of the sharp Dirac peaks and metallic conductive behavior. Such approaches tend to be scientifically interesting and relevant to the understanding of fundamental condensed matter, but the direct applications following from these tend not to be immediately clear. For example, McCann et al. performed theoretical work that predicted a broken symmetry and band gap opening when an electric field is applied to bilayer graphene stacks [12]. From this work, several groups have performed experimental confirmation of emerging band gaps in two-layer systems grown on SiC [13]. The bandgap tends to be small (on the order of 10-100 meV) and experiments measuring the electrical properties require cooling to low-temperatures around 4 K. Thus, devices leveraging symmetry-breaking properties are possible, but larger band gaps are required for practical room-temperature applications.

Impact of Material Defects

As described before, a graphene nanoribbon under the tight-binding approximation is given by equation [6]. To replicate the effect of vacancies in the graphene lattice, it is possible to set specific \( s_n \) values (the on-site energy density) to infinity to suppress electron occupation at that site [11].

Fabrication of graphene nanoribbons using methods such as electron beam lithography will result in graphene nanoribbons with edges that are not perfectly smooth. Though this form of lithography is relatively accurate, it still results in roughness on the order of nanometers at the edges of the nanoribbons. Reminding ourselves that the lattice constant of graphene’s hexagonal structure \( |a| = 0.246 \) nm, it is clear that this degree of roughness will result in irregular and highly disordered edge configuration. Though states corresponding to armchairs and zigzag type edges have been theoretically discussed and calculated, the nature of complex combinations of armchairs and zigzags in edges that are more rough and curved has yet to be determined.

Fabrication Constraints

Perhaps the largest, most difficult obstacle standing before graphene nanoribbon FETs is the difficulty in realizing high quality, scalable fabrication. In general, there are typically two critical steps for graphene nanoribbon production. The first is creating large area, high quality sheets of graphene with a known atomic thickness (i.e., single-/bi-/multi-layer sheets), and the second is finding methods of patterning the sheets and possibly moving them to a more suitable substrate. Other methods exist that are capable of directly fabricating graphene nanoribbons, but they all tend to have different and unique shortcomings.

This section will present three methods of graphene production and four methods of pat-
tnering graphene nanoribbons that have been experimentally demonstrated. For creating large sheets of graphene, mechanical exfoliation, epitaxial growth on SiC, and chemical vapor deposition has been developed over the course of the last decade. The first patterning method, electron beam lithography, is a technique common to researchers in academia due to its high level of accuracy. The second, generating graphene nanoribbons from an aqueous solution via intercalating chemicals promises high scalability, but is difficult to directly control and relies on fabricating large quantities of graphene particles then selecting the best ones. High quality ribbons have also been formed from carbon nanotubes by unzipping, which promises both scalability and nanoribbon uniformity. Lastly, helium ion beam etching is a technique that promises a much larger degree of accuracy, control, and versatility in a research setting than current electron-beam and reactive ion etching techniques. It has been demonstrated to produce high quality graphene nanoribbon FETs, but is unscalable due to the price and scarcity of helium.

**Graphene Sheet Production**

Currently, there are three available means of creating large sheets of graphene. The first, and most common in academic research, is mechanical exfoliation. Epitaxial graphene growth on SiC substrates and chemical vapor deposition are the two other schemes, which tend to produce lower quality single/multilayer sheets but are much more readily scalable.

In essence, mechanical exfoliation is the process of using strips of adhesive tape to mechanically remove sheets of carbon from a solid piece of graphite. Typically this process leaves multilayer thick sheets of carbon adhered to the tape. Adhering this tape to a clean substrate, typically SiO$_2$ or Si, results in a few sheets of graphene getting transferred to the substrate. Surprisingly, it is possible to view these graphene sheets using optical microscopy. Light traveling through the graphene and SiO$_2$ has a slightly larger optical path length than light traveling solely through the SiO$_2$ layer, as visualized by numerical simulations in Figure 9a [14]. The contrast is large enough to noticeably distinguish between single layer, multilayer, and graphitic sheets, as confirmed by Raman spectroscopy and shown in Figures 9, 10.

Epitaxial growth of graphene sheets was originally pioneered by Berger and de Heer through the growth of high quality, thin graphene sheets on the (0001) surface of SiC substrate. These films were grown via thermal decomposition of the SiC and desorption of Si at 1250°C to 1400°C [15]. This technique has attracted much interest due to its increased scalability over mechanical exfoliation. However, the temperatures required for decomposition prohibit the device from being integrated with CMOS processing. In addition, the high cost of SiC substrates has cast doubt on this method’s practicality.

Lastly, chemical vapor deposition of graphene has been developed as a third means of fabrication. Advantages of this approach include the ability to cover a wider surface area and grow films at lower temperatures. Typically this approach involves forcing carbon to dissolve into a material and then cooling. As the substrate cools, the carbon precipitates out and forms graphene structures on the surface. According to M. Lemme, graphene films have been grown directly on nickel, ruthenium, iridium, copper, and other substrates. Since these substrates are typically metallic and conductive, removing the graphene layers and transporting them to a separate insulating substrate is required for nanoelectronics integration.

**Electron Beam Lithography**

Electron beam lithography is a method of using focused electrons to expose a photoresist and develop high resolution features typically unattainable by traditional photolithography. Since electron beam lithography is a direct writing method, it has a very low throughput and is typically used in research and development. Nonetheless, its ability to pattern sub-10nm features has enabled researchers to use it for graphene nanoribbon fabrication.

M. Han, et al., fabricated 10-20 nm wide sheets of graphene using electron beam lithography and was among the first to experimentally demonstrate the existence of a bandgap in sufficiently narrow nanoribbons [16]. First, single
sheets of graphene are mechanically cleaved from a bulk graphite crystal and deposited onto a substrate (SiO$_2$/Si was used by M. Han). Graphene sheets of a width on the order of $\sim 20\mu$m are then located and then manually aligned with Cr or Au contacts. Next, hydrogen silsesquioxane, a specific negative photoresist for electron beam applications, is spun over the surface and the resist is exposed to the device pattern using electron beam lithography. After the unexposed regions are removed with an appropriate developer solution, oxygen plasma is used to etch away certain parts of the graphene. This seminal work provided strong evidence for the opening of a bandgap at sufficiently narrow widths, but was unable to determine any electrical differences between graphene crystallographic orientations (i.e. the effects of zigzag, armchair, or a mix of both types of edge states).

Published around the same time as M. Han’s paper was additional experimental evidence from Z. Chen et al. [17]. This work, done at IBM, showed the same increase in resistivity with lowering ribbon width trend but also performed measurements of the electrical current noise. This noise is important as it has a direct impact on the device’s signal to noise ratio and helps to determine the viability of nanoscale graphene electronics. In fabrication, Z. Chen also used a micromechanical cleavage method to separate sheets of graphene from pyrolytic graphite (HOPG). These were then placed on top of a 200 nm SiO$_2$ layer which was grown on a p-type Si substrate (to be used as the gate contact later). Atomic force microscopy was used to locate sheets of graphene and determine the corresponding number of graphene layers via thickness measurements. From here, hydrogen silsesquioxane was used as a photoresist, the sample was exposed via electron beam lithography, and oxygen plasma etched the structure. After this, palladium metal was deposited on both ends of the graphene ribbons for source/drain contacts. This method of fabrication was successful in achieving 20-500 nm thick graphene nanoribbon FETs.

Nanoribbons from Solution

Work done by Xiaolin Li et al. has pioneered a new approach for making graphene nanoribbons [2]. The group developed a means by chemically forming graphene nanoribbons with sizes below 10 nm in solution. This approach opened a new path towards inexpensive, scalable sheets of
graphene. The sheets were shown to have ultra smooth edges, possibly exhibiting armchair and zigzag edge states, though further work and more advanced characterization methods are required to confirm this.

To form these graphene nanoribbons, graphite flakes with widths on the order of 100 µm were turned into expandable graphite, a form of graphene with chemicals lying between and shearing apart the individual sheets of carbon. This was done via intercalation with nitric acid and sulfuric acid. Important to note is that the sulfuric acid likely oxidized edges and defects. Next, the graphite was rapidly heated to 1000°C, which formed volatile gases near the intercalants. This process exfoliated the graphite into loose stacks of graphene sheets. This process not only leads to a 100-200 times volume increase in the material, but can defunctionalize the graphite through desorbing chemicals bonded to edges, defects, or steps. Lastly, the exfoliated graphite is immersed in 1,2-dichloroethane solution of poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene), or PmPV, which functionalizes the graphene after it adsorbs to the walls via π stacking. While immersed, the solution is sonicated (agitated via application of ultrasonic sound waves) for 30 minutes. The sonification process has been reported to be a critical parameter for determining the size, yield, and shape of the resulting solution of graphene nanoribbons. Following sonification, centrifugation removed larger sheets and pieces of graphene.

Figure 10 shows various sized graphene nanoribbons produced by Xiaolin Li et al. To observe the graphene nanoribbons and utilize them after formation in solution, a highly doped p-type Si substrate with 300 nm SiO₂ was immersed in the final solution for 20 minutes. After drying, the substrate was calcined, or thermally treated in air at 400°C to decompose the remaining PmPV. After successfully fabricating various graphene nanoribbons, field effect transistors were assembled using Pd metallic contacts and p-type Si substrate as the backdate. Current-voltage characteristics were obtained for a wide variety of graphene nanoribbon sizes, and on/off current ratios ranging from $10^5$ to $10^7$ were observed, see Figure 11. Since the FET performance is governed by carrier movement across the Schottky barrier at the Pd contacts, the relationship

$$\frac{I_{on}}{I_{off}} \propto e^{\frac{E_g}{k_BT}}$$

was used to estimate the nanoribbon band gaps. A good correlation between experimentally observed values and theoretical predictions was found for all experimental data. Thus, solution based graphene nanoribbon fabrication has demonstrated itself to be a worthy means of FET nanodevice fabrication, though many issues with scaling for practical applications have yet to be solved.

Unzipping Carbon Nanotubes

A third means of fabricating nanoribbons has been experimentally demonstrated by D. Kosynkin et al., where multi-walled carbon nanotubes were “unzipped” to form thin sheets of graphene [18]. The method is similar to the approach by X. Li et al. in that it is solution-based and a chemical process as opposed to a lithographically defined process, but is fundamentally different in that carbon nanotubes, and not graphene sheets, are the starting material. The first step in this process is creating a suspension of multi-wall carbon nanotubes in sulfuric acid. Following this, the solution is treated with potassium permanganate (KMnO₄) for an hour.

![Figure 11](image.jpg)
at room temperature and another hour at 50-70°C. The result of this treatment is a solution of ‘unzipped’ nanoribbons that is highly soluble in water and polar solvents.

When the carbon nanotubes are initially exposed to the potassium permanganate, a manganese ester can form along nanotube wall, see Figure [12]. As a result, an oxidation step can break a carbon-carbon bond in the graphene sheet and terminated by two ketones (π-bonded oxygen atoms). These ketones create a strain on neighboring carbon-carbon bonds, which making the nearby alkenes more prone to manganese ester formation. In addition, as a hole begins to emerge in the side of a carbon nanotube, the mechanical strain further increases the reactivity of nearby alkenes and initiates a positive feedback cycle for breaking carbon-bonds. The more energetically favorable process of permanganate attacking neighboring carbon-carbon bonds as opposed to randomly located carbon-carbon bonds results in higher quality nanoribbons. As a result of this, the bond-breaking process is directionally dependent such that when a hole forms the gap continues to increase along a single direction.

A major drawback of the unzipped carbon nanotube approach is that the resulting nanoribbons contain carbonyls, carbonyls, and hydroxyls at the surface and edges. The oxygen atoms from these functionals disrupt the π-electron network and negatively impact the materials conductivity. Several methods have been tested to chemically reduce the nanoribbons, such as exposure to hydrazine (N₂H₄) which has had limited success in restoring the conductivity. When methods are implemented to decrease oxygen-containing functionals, the graphene ribbons and remaining graphite particles tend to aggregate. The aggregation may be countered by placing the nanoribbons in a surfactant solution such as sodium dodecyl sulphate. Attenuated-total-reflection infrared (ATR-IR) spectroscopy and X-ray photoe-
mission spectroscopy confirmed that the reduction process successfully removed all functional groups except for carboxylic acid at the edges. This process demonstrates a readily scalable method of producing graphene nanoribbons in solution. At present, the oxygen-containing functional groups prevent the device performance from competing with devices fabricated from exfoliated sheets of graphene. Future work in refining this specific process is necessary for practical utilization.

A more promising approach towards utilizing carbon nanotubes for nanoribbon formation involves plasma etching carbon nanotubes that are halfway set in a polymer. First, carbon nanotubes are deposited onto a Silicon substrate. From here, a polymer such as poly(methyl methacrylate) (PMMA) is spun onto the substrate, baked, and then removed in a KOH solution [19]. The carbon nanotubes were lifted from the substrate with the PMMA, and as a result of conformal coating, a section of the nanotubes was exposed. A 10 watt Ar plasma was used to then etch away at the side of the exposed nanotubes. The resulting long, cylindrical valley left behind is coated with single-, bi-, or multi-layer nanoribbons corresponding to the number of walls in the nanotubes. To utilize these new structures, the PMMA can be contact printed onto a Si substrate and then etched away to leave only the nanoribbons of width much smaller than typically obtained using other solution based techniques. Thus, there are many promising methods by which single walled carbon nanotubes may be used to make sub-10 nm graphene nanoribbons with sufficient bandgap for electronics applications.

**Helium Ion Beam Etching**

The last method of fabrication to be discussed is the use of a Helium ion microscopy for nanoscale precision lithography. According to M. Lemme, et al., the motivation for exploring Helium ions has been the result of shortcomings with previously discussed methods [20]. Electron beam lithography is typically accurate from only 5 - 50 nm and requires a sheet of graphene to be suspended on transmission microscope grids which are bulky and a poor platform for electrical testing. Reactive ion etching tends to erode photomasks and cause rough graphene edges. Other methods, such as carbon nanotube unfolding or solution based graphene fabrication have yet to be refined and often result in unwanted defects. Helium ion microscopy is fundamentally a better tool for imaging and lithography than electron-beam lithography due to the factor of 100 difference in the de Broglie wavelength of helium and electrons. As a result the maximum resolution tends to be under 0.5 nm, a significant upgrade from other known lithography methods. Additionally, it has been demonstrated that in situ electrical measurements are possible using Helium ion microscopes [20]. Since Helium ion microscopy operates by directing a focused beam...
of ionized Helium at the substrate, it is a direct-write method and therefore a relatively slow process (yet fast enough for research purposes). This, coupled to the fact that Helium is currently a limited resource and is becoming expensive, makes the technique impossible for scalable fabrication.

In recent experiments by M. Lemme et al., graphene nanoribbon FETs were fabricated using this method. Ontop of a SiO$_2$/Si substrate, a sheet of graphene produced by mechanical exfoliation is deposited. On this, metallic source/drain (chromium/gold) contacts are deposited and the material is etched so that graphene is exposed, see Figure 13. From here, the sample is placed in the Helium ion microscope and certain sections are selectively removed to form a graphene nanoribbon. For some experiments, the SiO$_2$ under-layer was removed from beneath the graphene to create a suspended, substrate-decoupled device. The goal of such decoupling was to study the physics of graphene nanoribbons without needing to account for defects or interactions between substrate and graphene.

![Image borrowed from M. Lemme et al.](image)

**Figure 13:** Image borrowed from M. Lemme et al. [20]. On the left is a schematic of the graphene nanoribbon device. Dashed lines indicate areas where the Helium ion beam will cut through the graphene. To the lower right is a photo of the Helium ion chamber with installed sample and wires for electrical testing during lithography.

**Present Limitations and Future Outlook**

Currently, the feasibility of graphene nanoribbon FETs is severely limited by current methods for fabricating these ultra sensitive devices. As was previously discussed, the electronic transport properties of graphene are highly dependent on the shape of the ribbon and the specific edge configurations. As such, atomic level precision is necessary for repeatable fabrication of sub-10nm, high bandgap, low defect nanoribbons. In addition, control and knowledge of the specific chemicals bonding to the graphene nanoribbons is necessary for appropriately modeling the electrical behavior. As a result, graphene based field effect transistors are not expected to arrive commercially for over another five years.

Assuming these issues are not a concern, the ultimate cost of these FETs will depend on the fabrication method that is implemented. Mechanical exfoliation/cleavage will likely be impossible to scale since it primarily relies upon manual labor. Solution based graphene nanoribbon production and carbon nanotube unzipping would both be less expensive since the relative cost of graphite, carbon nanotubes, and chemicals are low. Graphene epitaxy on SiC has also been proposed, but high temperatures for thermal decomposition and the price of SiC wafers would drive up production costs. Lastly, helium ion beam etching is a promising new technique for patterning sub nanometer features in graphene, but is prohibitively expensive and has low throughput since it is a direct-writing process.

In conclusion, sufficiently thin graphene strips have been theoretically and experimentally proven to exhibit a suitable bandgap for use in field effect transistors. Many theoretical models and simulation techniques have been developed to characterize the behavior of ideal graphene nanoribbons with very optimistic assumptions. However, experimentally fabricated devices suffer from defects, imperfections, and expensive production methods. Presently, the many factors associated with fabricating these sensitive devices are limiting its ultimate realization. Nonetheless, the field is still expanding and pioneering new research is likely to generate more effective means
of creating transistors from graphene.

References


