GRAPHENE SCIENCE HANDBOOK

Size-Dependent Properties



EDITED BY Mahmood Aliofkhazraei • Nasar Ali William I. Milne • Cengiz S. Ozkan Stanislaw Mitura • Juana L. Gervasoni

CRC Press

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Preface

The theory behind "graphene" was first explored by the physicist Philip Wallace in 1947. However, the name "graphene" was not actually coined until 40 years later, where it was used to describe single sheets of graphite. Ultimately, Professor Geim's group in Manchester (UK) was able to manufacture and see individual atomic layers of graphene in 2004. Since then, much more research has been carried out on the material, and scientists have found that graphene has unique and extraordinary properties. Some say that it will literally change our lives in the twenty-first century. Not only is graphene the thinnest possible material, but it is also about 200 times stronger than steel and conducts electricity better than any other material at room temperature. This material has created huge interest in the electronics industry, and Konstantin Novoselov and Andre Geim were awarded the 2010 Nobel Prize in Physics for their groundbreaking experiments on graphene.

Graphene and its derivatives (such as graphene oxide) have the potential to be produced and used on a commercial scale, and research has shown that corporate interest in the discovery and exploitation of graphene has grown dramatically in the leading countries in recent decades. In order to understand how this activity is unfolding in the graphene domain, publication counts have been plotted in Figure P.1. Research and commercialization of graphene are both still at early stages, but policy in the United States as well as in other key countries is trying to foster the concurrent processes of research and commercialization in the nanotechnology domain.

Graphene can be produced in a multitude of ways. Initially, Novoselov and Geim employed mechanical exfoliation by using a Scotch tape technique to produce monolayers of the material. Liquid-phase exfoliation has also been utilized. Several bottom-up or synthesis techniques developed for graphene include chemical vapor deposition, molecular beam epitaxy, arc discharge, sublimation of silicon carbide, and epitaxy on silicon carbide.

The *first volume* of this handbook concerns the fabrication methods of graphene. It is divided into four sections: (1) fabrication methods and strategies, (2) chemical-based methods, (3) nonchemical methods, and (4) advances of fabrication methods.

Carbon is the sixth most abundant element in nature and is an essential element of human life. It has different structures called carbon allotropes. The most common crystalline forms of carbon are graphite and diamond. Graphite is a three-dimensional allotrope of carbon with a layered structure in which tetravalent atoms of carbon are connected to three other carbon atoms by three covalent bonds and form a hexagonal network structure. Each one of these aforementioned layers is called a graphene layer or sheet. Each sheet is placed in parallel on other sheets. Hence, the fourth valence electron connects the sheets to each other via van der Waals bonding. The covalent bond length is 0.142 nm. The bonds that are formed by carbon atoms between layers are weak; therefore, the sheets can slide easily over each other. The distance between the layers is 0.335 nm. Due to its unique structure and geometry, graphene possesses remarkable physical-chemical properties, including a high Young's modulus, high fracture strength, excellent electrical and thermal conductivity, high charge carrier mobility, large specific surface area, and biocompatibility.

These properties enable graphene to be considered as an ideal material for a broad range of applications, ranging from quantum physics, nanoelectronics, energy research, catalysis, and engineering of nanocomposites and biomaterials. In this context, graphene and its composites have emerged as a new biomaterial, which provides exciting opportunities for the development of a broad range of applications, such as nano-carriers for drug delivery. The building block of graphene is completely different from other graphite materials and three-dimensional geometric shapes of carbon, such as zero-dimensional spherical fullerenes and one-dimensional carbon nanotubes.

The *second volume* of this handbook is predominantly about the nanostructure and atomic arrangement of graphene. The chapters in this volume focus on atomic arrangement and defects, modified graphene, characterization of graphene and its nanostructure, and also recent advances in graphene nanostructures. The planar structure of graphene provides an excellent opportunity to immobilize a large number of substances, including biomolecules and metals. Therefore, it is not surprising that graphene has generated great interest for its nanosheets, which nowadays can serve as an excellent platform for antibacterial applications, cell culture, tissue engineering, and drug delivery.

It is possible to produce composites reinforced with graphene on a commercial scale and low cost. In these composites, the existence of graphene leads to an increase in conductivity and strength of various three-dimensional materials. In addition, it is possible to use cheaply manufactured graphene in these composites. For example, exfoliation of graphite is one of the cheapest graphene production techniques. The behavior of many two-dimensional materials and their equivalent threedimensional forms are completely different. The origin of the aforementioned differences in the behavior of these materials is associated with the weak forces that hold a large number of single layers together to create a bulk material. Graphene can be used in nanocomposites. Currently, researchers have been able to produce several tough and light materials by adding small amounts of graphene to metals, polymers, and ceramics. The composite materials usually show better electrical conductivity characteristics compared with pure bulk materials, and they are also more resistant against heat.

The *third volume* describes graphene's electrical and optical properties and also focuses on nanocomposites and their applications. The *fourth volume* relates to the mechanical and chemical properties of graphene and cites recent



FIGURE P.1 Number of documents published around graphene during recent years, extracted from Scopus search engine by searching "graphene" in title + keywords + abstract.

developments. The *fifth volume* presents other topics, such as size effects in graphene, characterization, and applications based on size-affected properties. In recent years, scientists have produced advanced composites using graphene, which are excellent from the point of view of mechanical and thermal properties. However, in some of these composites, high electrical conductivity only is desirable. For example, the Chinese Academy of Sciences (IMR, CAS) has created a polymer matrix composite reinforced with graphene, which has a high electrical conductivity. In this composite, a flexible network of graphene has been added to a polydimethylsiloxane matrix (of the silicon family).

Investigation of early corporate trajectories for graphene has led to three major observations. First, the discovery-toapplication cycle for graphene seems to be accelerated, for example, compared to fullerene. Even though the discovery of graphene is relatively new, large and small firms have contributed to an upsurge in early corporate activities. Second, a rapid globalization has occurred by companies in the United States, Europe, Japan, South Korea, and other developed economies, which were involved in early graphene activities. Chinese companies are currently starting to enter the graphene domain, resulting in the expansion of research capability of nanotechnology. Nevertheless, science alone does not guarantee commercial exploitation. To clarify the issue, the level of corporate patenting in the United Kingdom, which is a pioneer in graphene research, is slightly ahead of Canada and Germany; however, it is dramatically lower than in the United States, Japan, and South Korea. Third, the potential applications of graphene are rapidly expanding. Corporate patenting trends are indicative of their enthusiasm to utilize the features of graphene in various areas, including transistors, electronic memory and circuits, capacitors, displays, solar cells, batteries, coatings, advanced materials, sensors, and biomedical devices. Although graphene was initially proposed as an alternative to silicon, its initial applications have been in electronic inks and additives to resins and coatings. We have identified six areas of emerging applications for graphene, including displays/screens, memory chips, biomedical devices, batteries/fuel cells, coatings and inks, and materials. In the investigation of the corporate engagement in graphene, we sought to understand early corporate activity patterns related to broader research and invention trends. In traditional innovation models, a lag between research publication and patenting is consistent with the linear model. However, more recent innovation models are stressing concurrent launch, open innovation, and strategic property management.

The *sixth volume* of this handbook is about the application and industrialization of graphene, starting with chapters about biomaterials and continues onto nanocomposites, electrical/sensor devices, and also new and novel applications.

The editorial team would like to thank all contributors for their excellent chapters contributed to the creation of this handbook and for their hard work and patience during its preparation and production. We sincerely hope that the publication of this handbook will help people, especially those working with graphene, and benefit them from the knowledge contained in the published chapters.

> Mahmood Aliofkhazraei Nasar Ali William I. Milne Cengiz S. Ozkan Stanislaw Mitura Juana L. Gervasoni Summer 2015

Editors

Mahmood Aliofkhazraei is an assistant professor in the Materials Engineering Department at Tarbiat Modares University. Dr. Aliofkhazraei's research interests include nanotechnology and its use in surface and corrosion science. One of his main interests is plasma electrolysis, and he has published more than 40 papers and a book in this area. Overall he has published more than 12 books and 90 journal articles. He has delivered invited talks, including keynote addresses in several countries. Aliofkhazraei has received numerous awards, including the Khwarizmi award, IMES medal, INIC award, best-thesis award (multiple times), best-book award (multiple times), and the best young nanotechnologist award of Iran (twice). He is on the advisory editorial board of several materials science and nanotechnology journals.

Nasar Ali is a visiting professor at Meliksah University in Turkey. Earlier he held the post of chief scientific officer at CNC Coatings Company based in Rochdale, UK. Prior to this Dr. Ali was a faculty member (assistant professor) at the University of Aveiro in Portugal where he founded and led the Surface Engineering and Nanotechnology group. Dr. Ali has extensive research experience in hard carbon-coating materials, including nanosized diamond coatings and CNTs deposited using CVD methods. He has over 120 international refereed research publications, including a number of book chapters. Dr. Ali serves on a number of committees for international conferences based on nanomaterials, thin films, and emerging technologies (nanotechnology), and he chairs the highly successful NANOSMAT congress. He served as the fellow of the Institute of Nanotechnology for 2 years on invitation. Dr. Ali has authored and edited several books on surface coatings, thin films, and nanotechnology for leading publishers, and he was also the founder of the Journal of Nano Research. Dr. Ali was the recipient of the Bunshah prize for presenting his work on time-modulated CVD at the ICMCTF-2002 Conference in San Diego, California.

William I. Milne, FREng, FIET, FIMMM, was the head of electrical engineering at Cambridge University from 1999 until 2014 and has been director of the Centre for Advanced Photonics and Electronics (CAPE), since 2004. He earned a BSc at St. Andrews University in Scotland in 1970 and later earned a PhD in electronic materials at the Imperial College London. In 2003 he was awarded a DEng (honoris causa) by the University of Waterloo, Canada, and he was elected as Fellow of the Royal Academy of Engineering in 2006. He received the JJ Thomson medal from the Institution of Engineering and Technology in 2008 for achievement in electronics and the NANOSMAT prize in 2010. He is a distinguished visiting professor at Tokyo Institute of Technology, Japan, and a distinguished visiting professor at Southeast University in Nanjing, China, and at Shizuoka University, Japan. He is also a distinguished visiting scholar at KyungHee University, Seoul and

a high-end foreign expert for the Changchun University of Science and Technology in China. In 2015, he was elected to an Erskine Fellowship to visit the University of Canterbury, New Zealand. His research interests include large area silicon- and carbon-based electronics, thin film materials, and, most recently, MEMS and carbon nanotubes, graphene, and other 1D and 2D structures for electronic applications, especially for field emission. He has published/presented approximately 800 papers, of which around 200 were invited/keynote/ plenary talks—his "h" index is currently 57 (Web of Science).

Cengiz S. Ozkan has been a professor of mechanical engineering and materials science at the University of California, Riverside, since 2009. He was an associate professor from 2006 to 2009 and an assistant professor from 2001 to 2006. Between 2000 and 2001 he was a consulting professor at Stanford University. He earned a PhD in materials science and engineering at Stanford University in 1997. Dr. Ozkan's areas of expertise include nanomaterials for energy storage; synthesis/processing including graphene, III-V, and II-VI materials; novel battery and supercapacitor architectures; nanoelectronics; biochemical sensors; and nanopatterning for beyond CMOS (complementary metal-oxide semiconductor). He organized and chaired 20 scientific and international conferences. He has written more than 200 technical publications, including journal papers, conference proceedings, and book chapters. He holds over 50 patent disclosures, has given more than 100 presentations worldwide, and is the recipient of more than 30 honors and awards. His important contributions include growth of hierarchical three-dimensional graphene nanostructures; development of a unique high-throughput metrology method for large-area CVD-grown graphene sheets; doping and functionalization of CVD-grown and pristine graphene layers; study of digital data transmission in graphene and InSb materials; memory devices based on inorganic/organic nanocomposites, novel lithium-ion batteries based on nano-silicon from beach sand and silicon dioxide nanotubes; fast-charging lithium-ion batteries based on silicon-decorated three-dimensional nano-carbon architectures; and high-performance supercapacitors based on threedimensional graphene foam architectures.

Stanislaw Mitura has been a professor in biomedical engineering at Koszalin University of Technology from 2011. He is a visiting professor at the Technical University (TU) of Liberec and was awarded a doctor honoris causa from TU Liberec. He was a professor of materials science at the Lodz University of Technology from 2001 to 2014. He earned an MSc in physics at the University of Lodz in 1974; a PhD in mechanical engineering at the Lodz University of Technology (1985); and a DSc in materials science at the Warsaw University of Technology in 1993. Professor Mitura's most prominent cognitive achievements comprise the following: from the concept

of nucleation of diamond powder particles to the synthesis of nanocrystalline diamond coatings (NDC); discovery of diamond bioactivity; a concept of the gradient transition from carbide forming metal to diamond film; and technology development of nanocrystalline diamond coatings for medical purposes. Professor Mitura has published over 200 peerreviewed articles, communications, and proceedings, over 50 invited talks, and contributed to 7 books and proceedings, including Nanotechnology for Materials Science (Pergamon, Elsevier, 2000) and Nanodiam (PWN, 2006). He organized and coorganized several conferences focused on materials science and engineering, especially diamond synthesis under reduced pressure. He is an elected member of the Academy of Engineering in Poland, guest editor in few international journals, including Journal of Nanoscience and Nanotechnology, Journal of Superhards Materials and also a member of the editorial boards of several journals and an elected Fellow of various foreign scientific societies.

Juana L. Gervasoni earned her doctorate in physics at the Instituto Balseiro, Bariloche, Argentina, in 1992. She has been head of the Department of Metal Materials and Nanostructures, Applied Research of Centro Atomico Bariloche (CAB), National Atomic Energy Commission (CNEA), since 2012. She has been a member of the Coordinating Committee of the CNEA Controlled Fusion Program since 2013. Her area of scientific research involves the interactions of atomic particles of matter, electronic excitations in solids, surfaces, and nano-systems, the absorption of hydrogen in metals, and study of new materials under irradiation. Gervasoni is a researcher at the National Atomic Energy Commission of Argentina and the National Council of Scientific and Technological Research (CONICET, Argentina). She teaches at the Instituto Balseiro and is involved in directing graduate students and postdoctorates. She has published over 100 articles in international journals, some of which have a high impact factor, and she has attended many international conferences. Gervasoni has been a member of the Executive Committee and/or the International Scientific Advisory Board of the International Conference on Surfaces Coatings and Nanostructured Materials (Nanosmat) since 2010, Latin American Conference on Hydrogen and Sustainable Energy Sources (Hyfusen), and the International Conference on Clean Energy (International Conference on Clean Energy, ICCE-2010) and guest editor of the International Journal of Hydrogen Energy (Elsevier). Recently she has focused her research on the study of hydrogen storage in carbon nanotubes. Along with her academic and research work, Dr. Gervasoni is heavily involved in gender issues in the scientific community, especially in Argentina and Latin America. She is a member of the Third World Organization for Women in Science (TWOWS), branch of the Third World Academy of Science (TWAS), Trieste, Italy, since 2010, as well as of Women in Nuclear (WiN), since 2013.

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Section I

Size Effect in Graphene

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1 Graphene as a Spin-Polarized Tunnel Barrier

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ABSTRACT

This chapter describes a novel use of graphene as a tunnel barrier for both charge and spin transport. Graphene is typically studied for its extraordinary in-plane conductance properties, while its out-of-plane transport properties are largely ignored. Graphene is metallic in-plane due the large availability of conduction channels. In contrast, there are substantially fewer out-of-plane conduction channels, resulting in a low resistivity in that configuration. A tunnel barrier comprises of two electrodes separated by a thin insulator where current flows between the electrodes entirely by quantum mechanical tunneling. Graphene exhibits many of the characteristics expected for an ideal tunnel barrier. The strong in-plane sp² bonding of carbon atoms results in a strong tendency to form complete, defect-free monolayers, enabling tunnel barriers with discrete thicknesses. Graphene is chemically inert and thus prevents the electrodes from intermixing with the tunnel barrier material and/or getting chemically altered. It is also impervious to diffusion, forming a natural diffusion barrier between the two electrodes. It is thermally robust, which allows for an increased thermal budget of the overall structure. As theory predicts, graphene can also be an excellent spin filter in combination with a few selected ferromagnetic contacts. This chapter summarizes the tunnel barrier properties of graphene and its potential use in spintronic devices.

1.1 SPINTRONICS: POTENTIAL APPLICATIONS FOR GRAPHENE TUNNEL BARRIERS

Typical commercial electronic devices ignore the spin state of electrons and only use the charge state. For example, the charging or discharging of a capacitor is used as a memory element in computer random access memory (RAM). As another example, consider field effect transistors (FETs), which are switched on and off by the charge on their gates and combined into logic gates, of which millions in combination can make complex versatile devices, such as a state-of-the-art central processing unit (CPU).

However, the electron charge is just one of the fundamental properties of an electron—it also has a mass, momentum, and a spin state. Here, we are interested in the spin state to give additional degrees of freedom to electronic devices. Indeed, the spin state is recognized by the international roadmap for semiconductors as a viable alternative to charge for operation beyond Moore's law.¹

One of the first successful commercial transitions in spintronics was based on the giant magnetoresistance (GMR) effect²⁻⁴ discovered in 1988 (see *timeline* in Figure 1.1a). Here, a nonmagnetic metal layer separates two magnetic layers. Electrons are naturally spin polarized in a FM due to its spinpolarized density of states. Majority spin electrons have their



FIGURE 1.1 (a) Timeline, magnetoresistance devices. 1975: Anisotropic magnetoresistance (AMR), 1988: Giant magnetoresistance (GMR), 1995: Tunnel magnetoresistance (TMR) based on Al_2O_3 , 2004: TMR based on MgO tunnel barriers. (b) GMR device from Fe/Cr/Fe multilayers; Fe layers are parallel, one spin species experiences weak scattering only in both magnetic layers, and an overall low resistance is measured. (c) Both spin species experience strong scattering and a high resistance is measured.

moment aligned parallel and spin aligned antiparallel to the magnetization of the FM,⁵ and majority spin electrons have more states available at the Fermi level $(E_{\rm F})$. These electrons experience weak scattering during transport within the FM and at the FM/normal metal interface. Minority spin electrons have their moment (spin) aligned antiparallel (parallel) to the magnetization, have fewer states available at $E_{\rm F}$, and thus experience stronger scattering in the FM and at the interface. If the magnetizations of the two magnetic layers are parallel, as depicted in Figure 1.1b, then the majority spin electrons of the top layer will enter the bottom layer as majority spin and the overall resistance will be low. When the two layer magnetizations are aligned antiparallel, as depicted in Figure 1.1c, the majority spins of the top layer will be minority spins in the bottom layer, and the overall stack resistance will be higher. Resistance changes on the order of 15% can be obtained with these structures, which were far better than the best anisotropic magnetoresistance⁶ (AMR) devices that were used as the read heads to detect the small changes in magnetic field lines on the magnetic platter of a hard disk at the time. Within the time span of 5 years this discovery went from lab experiment to commercial product, making this the first commercially available spintronic technology. This discovery of GMR led to the 2007 Nobel Prize for A. Fert and P. Gründberg⁷ and the 2014 Millennium Technology Prize for S. Parkin.

Later work replaced the metallic interlayer of the GMR stack by a thin insulator.^{8,9} Transport across this thin insulator is possible by quantum mechanical tunneling. Tunneling across a thin insulator depends critically on the density of states (DOS) available on both sides of the tunnel barrier. As the DOS at the FM/insulator interface is spin dependent, the tunnel process also becomes spin dependent.¹⁰ When the magnetic layers are aligned with their magnetizations parallel, majority electrons that have a large DOS in the left



FIGURE 1.2 Simplified diagram of tunneling from ferromagnet to ferromagnet. (a) Magnetization is parallel. One spin species tunnels from a large density of states to a large density of states, and a low tunnel resistance is measured. (b) Both spin species tunnel from a large (low) density of states to a low (large) density of states, and a high tunnel resistance is measured.

electrode (Figure 1.2a) can readily tunnel to the large DOS of the majority state of the right electrode. However, when the magnetic electrodes have their magnetizations antiparallel, the majority electrons with a large DOS can only tunnel to the minority states of the right electrode, which has a much smaller DOS. Thus, the tunnel resistance is increased by this spin-dependent effect. Tunnel magnetoresistance effects of over 800% have been observed in Fe/MgO/Fe tunnel barriers.^{11,12} These barriers are now the workhorses in read heads for hard disks and they are the memory elements of choice in magnetic RAM.

It can be easily seen that a magnetic tunnel junction (MTJ) has two states, parallel and antiparallel, with two significantly different resistances. These states can be used to build a magnetic random access memory (MRAM). As the parallel and the antiparallel states are stable states, this memory is nonvolatile. MRAM is another major success story of spin-tronics.¹³ There are two types of commercially available MRAM: toggle MRAM¹⁴ and spin-torque transfer MRAM.¹⁵

Toggle MRAM uses an array of MTJs, like those described previously, with the bottom electrode layer typically magnetically fixed in one direction and the top electrode layer set as the magnetically free layer. Write wires, which are conductors that run on top of the MTJs, are arranged in a grid (see Figure 1.3). Where two wires cross, the combined magnetic field is strong enough to switch the magnetic free layer of that individual MTJ. All the other MTJs in the array either experience only the magnetic field of a single wire or no magnetic field at all. Besides, the obvious benefit of this memory being nonvolatile, it also has short access time, large number of read/write cycles, and is radiation hardened. Nowadays, this type of memory is being used for applications in satellites and airplanes. The relatively high power needed to switch a memory element using write wires and scalability issues has prevented this type of memory from seeing more widespread usage in electronic products.

Spin-torque transfer switching is an alternative to toggle MRAM that solves the high switching power and scalability issues. This transfer switching is a low-power technique to change the magnetic state without the need for write wires,



FIGURE 1.3 Conceptual MRAM device with both graphene interconnects and graphene tunnel barriers.

making it a scalable technology.¹⁶ In short, spin–torque switching occurs when the spin-polarized current from one magnetic contact is used to switch the magnetization of a second magnetic contact, thereby eliminating the need of the power-hungry write wires. However, to make spin–torque transfer devices function properly, it is essential to fabricate MTJs with a low-enough resistance–area product, which is determined in large part by the thickness of the tunnel barrier. The thinnest possible tunnel barrier is a pinhole-free insulating monolayer. Later in this chapter, we will discuss how graphene, an inherent single layer, can be used to fabricate spin-polarized MTJs.

The MRAM devices in the previous example use MTJs as the memory elements and rely on conventional charge-based electronics to do the addressing and signal amplification of these memory elements. The next step in replacing chargestate operation electronics with spintronics is to build the magnetic elements directly into the transistor itself and create a "spin-FET"¹⁷ (see Figure 1.4). This allows one to build the magnetic memory directly into the switching transistor, thus greatly simplifying the memory structure. These spin-FETs also conceptually allow for future fabrication of reconfigurable electronics.^{18–21}

Modern CPUs are versatile devices and can perform many functions described in software, but at a cost of adding a lot of overhead to make a general-purpose device. Dedicated hardware, called application-specific integrated circuits (ASICs), can perform a logic function far more efficiently, thus at lower power, because they are hardwired to do just one function. Reconfigurable logic can combine these two worlds to make a versatile general-purpose device, like a CPU, with the efficiency of dedicated ASICs. One could program this circuitry on the fly to perform a single task by changing the function of the spin-FET with the magnetic state of the source and drain. The circuit would then perform this task as if it were dedicated hard-wired logic. One can then use a second programming step to fully reprogram the logic function to perform an entirely different task. In order for this type of electronics to function as theoretically designed, one would need to inject, manipulate, and detect spin-polarized current in the transistor channel. Later in this chapter, we will address why graphene is an important and necessary ingredient toward spin-FETs



FIGURE 1.4 Conceptual spin-FET, with FM/graphene as the spin-injecting contact.

and spin-logic by using an example of the injection of spins into silicon from a FM metal across a graphene tunnel barrier.

1.2 SPIN TRANSPORT ACROSS GRAPHENE

Several groups have studied the in-plane spin transport properties of graphene (see Table 1.1).^{22–25} The high in-plane mobility, low intrinsic spin–orbit interaction, and low (zero theoretically expected) hyperfine interaction of electron spins with the carbon nuclei lead one to expect very long spin lifetimes in graphene. Using nonlocal measurements,^{26,27} spin lifetimes on the order of 50–500 ps have been observed. These experimentally measured spin lifetimes lead to long spin diffusion lengths, up to several microns, even at room temperature. Lateral spin transport in graphene will not be discussed in this chapter—for more information, see, for example, References 28–32.

In contrast to the large number of reports in the literature on the lateral charge transport (the subject of other chapters of this publication) and lateral spin transport through graphene, the out-of-plane properties have largely been ignored.³³ Although highly conductive in plane, graphene exhibits poor conductivity out of plane.34 Spin transport of hot electrons through 7-17 nm thick graphite flakes perpendicular to the layer plane was recently demonstrated using scanning tunneling microscopy-based techniques.35 Perpendicular transport through multilayers of FM/graphene/FM has been studied in the conductive regime, although early results were complicated by space-charge effects or oxidation.^{27,36} Measuring graphene's out-of-plane conductivity is quite complicated due to the presence of highly conductive edge states,³⁷ which also manifest near grain boundaries, that can effectively short out any intrinsic out-of-plane transport. Here, by carefully avoiding graphene's conductive edge states, we examine the spinpolarized tunnel transport across a layer of graphene in an MTJ structure.38-41

1.2.1 FABRICATION

Standard microfabrication techniques were used to produce an array of NiFe bottom electrodes on a SiO₂/silicon wafer. A single sheet of graphene, grown by chemical vapor deposition (CVD),⁴² was transferred from its original copper foil substrate **Graphene Science Handbook**



FIGURE 1.5 Schematic cross-sectional diagram of a graphene MTJ and optical photo of a junction prior to top contact deposition.

to the electrode array and patterned using polymethyl methacrylate (PMMA) resist and deep-UV photolithography. The graphene's conductive edge states were buried in a layer of Si_2N_3 and a Co top electrode was deposited.³² A schematic of a device is shown in Figure 1.5.

1.2.2 RESULTS

Initial room-temperature *I–V* characterization shows a nonohmic junction with the increased low-bias resistivity typical of tunnel junctions (Figure 1.6). The temperature dependence of the junctions' zero bias resistance (ZBR), a characteristic measure of tunnel barrier quality,⁴³ shows the weak decrease with temperature characteristic of tunneling transport rather than the weak increase or dramatic decrease in resistance characteristic of metal and semiconductor transport, respectively.⁴⁴ Normalizing the individual junction resistances to their room-temperature values shows that the junction resistances fall by a factor of about 3.5 in the temperature range 10–300 K (Figure 1.6 *inset*), comparable to factors of 2.5 reported for high-quality tunnel junctions.⁴³

In canonical MTJs, the resistance depends on the ability of electrons from the emitter to tunnel into available states of matching polarization in the collector (see Figure 1.2).

TABLE 1.1 Lateral Spin Transport in Graphene Measured with Nonlocal Spin Valves					
Author	Tunnel Barrier	Graphene	$\Delta \boldsymbol{R}$ (Nonlocal)	λ_{sf}	τ
Tombros	Al_2O_3	Exfoliated	2 Ω	1.3 µm	100-1

Author	Tunnel Barrier	Graphene	ΔR (Nonlocal)	λ_{sf}	τ_{s}	References
Tombros	Al_2O_3	Exfoliated	2 Ω	1.3 μm	100–170 ps	[21]
Ohishi		Exfoliated	$2 \text{ m}\Omega$	~100 nm		[22]
Han	MgO	Exfoliated	130 Ω	2.5–3.0 μm	450–500 ps	[23]
Friedman	F-Graphene	CVD	2.5 Ω	1.5 μm	200 ps	[24]
Popinciuc	Al_2O_3	Exfoliated	50 Ω		100–180 ps	[29]
Avsar	MgO	CVD	4 Ω	1.2 μm	~150 ps	[30]
Guimaraes	Al_2O_3	Suspended	4 Ω	4.7 μm	150 ps	[31]



FIGURE 1.6 Typical nonlinear current–voltage character of a graphene tunnel junction at various temperatures. Inset: Zero bias resistance of several graphene MTJs normalized to their room temperature resistances, showing weak temperature dependence.

When the electrodes are oppositely magnetized, the majority spin DOS in the emitter corresponds to the smaller minority spin DOS in the collector, and vice versa. Consequently, resistance is higher in the antiparallel configuration than in the parallel case where majority spin states in the electrodes have the same polarization.

When an in-plane magnetic field is applied, the magnetizations of the NiFe and Co electrodes reverse at fields corresponding to their respective coercivities, with the NiFe switching at a much lower field than the Co. Their magnetizations can thus be aligned either parallel or antiparallel, and two distinct resistance states are observed in the data, as seen in Figure 1.7. The junction resistance can be controllably and reversibly switched from a low-resistance parallel state to a higher-resistance antiparallel state with the applied field. At low temperatures and low biases, where the physics of tunneling are simplest and most evident, the TMR reaches a value of 2%.^{38,39}

The traditional Julliere model gives the magnitude of the TMR as TMR = $2P_1P_2(1 - P_1P_2)^{-1}$, where P_1 and P_2 are the interface polarizations of the collector and emitter metal surfaces.⁴⁵ Using this model, we obtain an average interface spin polarization of 10% for the two interfaces in our junctions at the lowest temperatures. For comparison, a NiFe/Al₂O₃ interface fabricated under high vacuum conditions typically has a surface polarization of about 30%. The reduced spin polarization in the graphene junctions can be attributed to interface contamination. The bottom NiFe/graphene interface was exposed to air prior to graphene transfer, resulting in some ambient oxidation of the metal surface. The resulting anti-FM NiO is a strong spin scatterer expected to reduce the spin polarization and associated TMR.

A monotonic decrease in the observed TMR occurs with increasing temperature, as shown in Figure 1.8a from 50 to 400 K. It is worth noting that the signal remains evident well above room temperature, albeit with reduced magnitude. Higher temperatures lower the spin polarization of the metal surfaces through various mechanisms such as spin-wave excitation. This was previously modeled by Shang et al.⁴⁶ as a power law dependence of the metal surface spin polarization *P* as a function of temperature *T*, $P(T) = P_0(1 - \alpha T^{3/2})$, where the parameter α is material specific. By inserting this temperature dependence in the traditional Julliere model, we obtain the expected temperature dependence for TMR. We compared our measurements with this model and observed good agreement (Figure 1.8b) using accepted parameters for the metals used.³⁸

The TMR signal is also expected to decrease with higher junction bias. Higher bias raises the Fermi level of the emitter electrode and imparts more energy to the emitted electrons, enabling them to access more empty states in the collector electrode even in the antiparallel case, thereby lowering the



FIGURE 1.7 Graphene junction TMR curves at low temperature (T = 4 K), showing the typical MTJ switching behavior at low bias of (a) 0.125 and 0.250 mV and (b) 0.42–1.15 mV. The arrows indicate the relative orientation of the NiFe (lower arrow) and Co contacts.

(b) 1.2 (a) 1.2 Device 1 Device 2 -100 K 1 • Device 3 - 150 K Normalized TMR (arb. units) Device 4 200 K . Device 5 0.8 250 K $\alpha = 9.5 \times 10$ 0.8 TMR (percent) 300 K $\alpha = 5.0 \times 10^{-1}$ 350 K 0.6 $\alpha = 1.1 \times 10^{-1}$ 400 K 0.6 0.4 0.4 0.2 0.2 0 0∟ 0 -0.2-1000 100 100 200 300 400 -200200 Magnetic field (Oe) Temperature (K)

FIGURE 1.8 Temperature dependence of the TMR displayed by (a) TMR curves for selected temperatures up to 400 K and (b) observed TMR for various junctions studied compared with a temperature-dependent TMR model derived from Jullier⁴⁵ and Shang et al.⁴⁶

resistance. This behavior is reflected in the graphene MTJ devices, as displayed in Figure 1.9a, which shows the observed TMR falling from over 1% at 12 mV of bias to under 0.5% at 86 mV of bias. The exact behavior depends on the DOS of the collector electrode, and thus on which metal the collector comprises of, producing an asymmetry in the forward versus reverse bias dependence, also observed in the graphene MTJs (Figure 1.9b). The asymmetry could also be attributed to different interface contaminations created during sample processing.

The four-point junction resistance measurement avoids convolution of the TMR signal with anisotropic magnetoresistance (AMR) of the FM leads. This distinction is evident when looking at simultaneously acquired two-probe resistance measurements (Figure 1.10) that display a clear AMR peak at very low field values. The AMR signal, although superficially similar to TMR, occurs in a much narrower range of field values and does not display the temperature or bias dependence characteristic of TMR. Several authors have predicted a large spin-filtering effect at the interface between graphene and various FM metals, including nickel, cobalt, and iron.^{47,48} The theoretical prediction rests on the peculiar band structure of graphene at the Fermi level and its interaction with the spin-polarized band structure of the metals. This prediction is similar to that of spin filtering at Fe/MgO interfaces,^{49,50} which was quickly verified experimentally⁵¹ and has since led to room temperature TMR in excess of 800%.^{11,12} The mechanisms leading to spin filtering are quite different, however. In Fe/MgO, it derives from band symmetry effects, while in FM/graphene, it derives from band alignments, that is, the positions of the majority/minority spin bands relative to $E_{\rm F}$.

Briefly, nickel (111) and cobalt (0002) close-packed surfaces share the hexagonal lattice of graphene and are closely lattice matched. The spin-resolved band structure of both of these metals contains only minority spin bands at the K points in the Brillouin zone. Graphene has states only at these



FIGURE 1.9 TMR as a function of bias. (a) Evolution of TMR curves at increasing junction bias and (b) TMR magnitude versus applied field for higher biases at T = 20 K. The TMR decreases with bias and is asymmetric, reflecting the asymmetry in the junction materials and interfaces.



FIGURE 1.10 Two-probe MR measurement displaying a convolution of TMR and AMR features at various temperatures. The AMR component is clearly distinguishable from the broader and more temperature-sensitive TMR effect.

K points in its band structure. Therefore, transport across these epitaxial metal–graphene interfaces is provided by minority spin carrier states in the graphene while majority spin states can only tunnel through the graphene. The expected magnetoresistance for a single layer of graphene between two FM metal surfaces with some degree of interface disorder is about 10%, and qualitatively in agreement with the two percent observed for single-layer graphene MTJs.^{32,33} Additional layers of graphene are predicted to produce dramatically higher magnetoresistance. Extrapolating the conductance difference between majority and minority spin carriers with five layers of graphene at the interface yields nearly 100% spin-polarized transport and TMR values in excess of 2000%. The effect has been predicted to be fairly robust to interface disorder and nonmagnetic impurity atoms at the interface.⁵²

Direct experimental measurements of this spin filtering effect have not yet been reported. Experimental results published to date have utilized only one or two layers of graphene in the MTJ structure,^{38–41} where the spin filtering is expected to be weak (Table 1.2). In addition, while the theory postulates epitaxial single crystal structures with clean interfaces,^{43,44} the experimental structures typically are noncrystalline with at least one air-exposed interface. Cobas et al. fabricated FM/ graphene/FM heterostructures by transfer of a single layers of CVD-grown graphene onto prefabricated NiFe electrodes,

TABLE 1.2Vertical Spin Transport across Graphene

		Tunnel	MR	
Author	Structure	Barrier	(%)	References
Cobas et al.	NiFe/Gr/Co	Single layer	2	[38]
Iqbal et al.	NiFe/Gr/NiFe	Bilayer	0.65	[40]
Chen et al.	Co/gr/Co	Bilayer	1	[41]
Dlubak et al.	Ni/Gr/Al ₂ O ₃ /Co	Gr/Al ₂ O ₃	-10	[53]

and reported TMR values of 2% at low temperature, as described previously.³⁸ Iqbal et al. fabricated similar structures and compared the TMR of single and bilayer graphene junctions from room temperature to 10 K, observing values as high as 0.65% for two (nonepitaxial) graphene layers and 0.15% for single-layer graphene.³⁹ Shortly thereafter, Chen et al. applied a similar fabrication technique to Co/graphene/ Co junctions, obtaining an MR of 1% at 1.5 K for a two-layer graphene junction.⁴¹ In a related experiment, Dlubak et al.⁵³ measured MR in a nickel/graphene/Al₂O₃/Co heterostructure, using the known majority-spin Al₂O₃/Co interface as the spin analyzer for the nickel/graphene interface. Their results confirmed the prediction of minority spin filtering by showing a lower resistance in the antiparallel state than in the parallel state. Assuming a literature value of 32% spin polarization at the Al₂O₃/Co interface, they extracted a spin polarization of 16% at the nickel-graphene interface.

1.3 SILICON SPINTRONICS

In this section, we focus on silicon spintronics⁵⁴ and show how graphene tunnel barriers can make a significant improvement in this field by reducing resistance area products and eliminating interdiffusion between the FM metal contact and the silicon. There are many examples of semiconductor spintronic devices.^{15,16,18} We focus here on silicon (Si) because of its technological importance as the backbone of modern electronics and because its low atomic mass and crystal inversion symmetry result in very small spin–orbit interactions and long spin lifetimes.

In 2007, several studies showed the first proof of spinpolarized injection into silicon using vertical transport structures. Applebaum et al. used a hot electron transistor to inject spin-polarized electrons into a silicon base layer and showed multiple precessions of this electron spin by applying an external magnetic field.55 Jonker et al. used a Si spinlight emitting diode (LED) to confirm electrical spin injection from a Fe/Al₂O₃ tunnel barrier into Si.⁵⁶ In that experiment, the magnetic tunnel contact was fabricated on top of an epitaxially grown Si n-i-p LED. The circular polarization of the light emitted from this type of LED can be used as a measure of the electrical spin polarization.⁵⁷ Spin-polarized electrons injected into the LED will recombine with unpolarized holes, and the circular polarization of the emitted light is directly related to the spin polarization of the injected electrons, thus providing unambiguous evidence of spin-polarized electron injection and transport in Si. From the magnitude of circular polarization, an initial electron polarization of 30% was calculated at low temperature.

Van 't Erve et al. were the first to demonstrate lateral transport of pure spin current in Si in 2007 using a fully electrical scheme of injecting and detecting spin polarization in the diffusive transport regime.^{58,59} In that work, Fe/Al₂O₃ tunnel contacts were employed in a four-terminal (4T) nonlocal spin valve geometry to generate and detect the flow of pure spin current. Here two sets of contacts are used: one set is used to inject spin-polarized electrons into Si by applying a DC bias current. The other set of electrodes, used to detect the electron spin accumulation, is placed outside of the charge current path. Electron spins will diffuse from an area with high spin polarization to an area with low spin polarization without the need for an electric field, generating a *pure* diffusive spin current. If the second set of electrodes is placed within a few spin diffusion lengths of the injecting contact, a voltage will appear on these electrodes caused by the splitting in electrochemical potential for spin up and spin down electrons. The authors showed both nonlocal spin valve and nonlocal Hanle precession using Fe/Al₂O₃ tunnel barriers on molecular beam epitaxially grown Si channels, thereby using a fully electrical scheme to inject and detect electron spin in Si.

In 2009, Dash et al. used a technique where a single FM tunnel barrier contact was used to simultaneously inject and detect electron spin polarization in Si up to room temperature, using the contact geometry of Figure 1.11a and b.⁶⁰ This geometry employs two reference contacts with the FM tunnel barrier and is referred to as the "three terminal" (3T) geometry.



FIGURE 1.11 (a) Conceptual diagram of three-terminal (3T) measurement, magnetic field is applied in the *z*-direction. (b) Schematic diagram of 3T measurement, current is applied from nonmagnetic contact 1 to magnetic contact 2. The 3T voltage is measured across the magnetic contact 2 and the nonmagnetic reference contact 3. (c) Discrete component equivalent, indicating the tunnel resistance, the substrate resistance, and the ohmic contact resistance.

In contrast with 4T nonlocal measurements, 3T measurements enable one to focus on and probe the characteristics of the spin system in the semiconductor directly beneath the spin-injecting contact. The magnetic contact interface is likely to introduce additional scattering and spin relaxation mechanisms not present in the bulk. Understanding the physics underneath the spin injecting contact is important. The region of the semiconductor directly beneath the contact is a necessary part of spin devices and is expected to be a critical factor in any future spin device performance. Also, the geometry of a 3T measurement makes these devices much easier to fabricate.

1.3.1 Measuring Spin Accumulation

We begin with a more detailed description of the 3T geometry used in measuring spin accumulation. Spin accumulation and precession directly under the magnetic tunnel barrier contact interface can be observed using a single contact for both spin injection and detection with the 3T Hanle measurement.⁶¹ This measurement uses three contacts as shown in Figure 1.11a and b. Contacts 1 and 3 are nonmagnetic ohmic contacts, typically Ti/Au, and contact 2 is a magnetic tunnel contact and can be anything from FM/Al₂O₃, FM/MgO, FM/SiO₂ to, as we will show here, FM/graphene. Spin injection occurs when a bias current is applied from contact 2 to contact 1 and a spin accumulation develops underneath contact 2. This spin accumulation results in a spin splitting of the chemical potential, which is manifested as a voltage at the FM tunnel barrier contact 2 relative to reference contact 3. As can be seen from the resistor equivalent circuit (Figure 1.11c), no current is flowing from the tunnel contact to the reference contact 3. This geometry has an advantage over a two-probe measurement in that it eliminates the magnetotransport effects of the substrate. The dominant voltage drop is across the barrier and this voltage depends on the spin accumulation on the semiconductor side.62

The spin accumulation in the Si caused by injection of spinpolarized electrons can be described by the splitting of the spin-dependent electrochemical potential, $\Delta \mu = \mu_{up} - \mu_{down}$ The measured 3T voltage is a function of this spin-dependent electrochemical potential. When a magnetic field B_{z} is applied perpendicular to the electron spin direction (along the surface normal, Figure 1.11a), the spins start to precess at the Larmor frequency $\omega_{\rm L} = g\mu_{\rm B} B_z/\hbar$, resulting in a reduction of the net spin accumulation to zero due to precessional dephasing (Hanle effect).⁶³ Here, g is the Lande g-factor (g = 2 for Si), μ_B is the Bohr magneton, and \hbar is the reduced Planck's constant. $\Delta V_{3T} = \gamma \Delta \mu / 2e$, where $\gamma \sim 0.4$ is the tunneling spin polarization of the FM tunnel contact (i.e., the tunnel current has a spin polarization of 40%) and *e* is the electron charge. The magnitude of the voltage $\Delta V_{3T}(B_z)$ decreases with B_z with an approximately Lorentzian lineshape given by

$$\Delta V_{3\rm T}(B_{\rm z}) = \frac{\Delta V_{3\rm T}(0)}{[1 + (\omega_{\rm L} \tau_{\rm s})^2]},\tag{1.1}$$

and the spin lifetime, τ_s , is obtained from fits to this line shape.

1.3.2 CONDUCTIVITY MISMATCH

Injecting spin-polarized electrons into Si is not trivial. Owing to what is known as the "conductivity mismatch" problem,64 one cannot simply create spin polarization in the semiconductor using an FM contact in the ohmic regime. Because the conductance of the Si is much less than that of the metal, the Si limits the current flow. Thus, equal amounts of majority and minority spin current flow into the Si from the FM, and no spin accumulation will be created on the semiconductor side. By separating the high conductivity of the metal from the semiconductor using a spin-dependent interface resistance, such as a tunnel barrier, one can overcome this problem. A tunnel barrier that is used extensively for MTJ devices is aluminum oxide. This barrier has been well studied and Al₂O₃ tunnel barriers are routinely used in research-grade and commercially available MTJs and are thus a good test system for spin-dependent measurements.

1.3.3 SPIN INJECTION REFERENCE EXAMPLE: AL₂O₃ TUNNEL BARRIER

Here, a 1.5-nm-thick Al₂O₃ layer is grown *in situ* on Si by a two-step natural oxidation process. A uniformly doped n-type Si wafer (n-doping 3×10^{19}) was first etched in HF acid and rinsed in deionized water to remove the thin native oxide and create a hydrogen-passivated surface. The sample was placed in a vacuum chamber and briefly exposed to dry O_2 to ensure that a layer of 0.5 nm of polycrystalline Al would wet this surface. This layer was oxidized at 100 mTorr partial pressure of O₂ for 15 min, and a second 0.5 nm layer of Al was deposited and oxidized to get a total Al₂O₃ thickness of ~1.5 nm. A 100 Å layer of NiFe was subsequently grown and then capped with 1000 Å of gold. The Al₂O₃ layer provides the necessary interface resistance to overcome the conductance mismatch. Previous work has demonstrated that electron spin polarizations of at least 30%, corresponding to NiFe majority spin, can be expected by electrical carrier injection from such contacts.65

1.3.4 IV CHARACTERIZATION

Figure 1.12a shows the typical nonlinear I-V curve of the same NiFe/Al₂O₃ tunnel contact on a highly doped Si substrate $(n = 3 \times 10^{19} \text{ cm}^{-3})$. The high doping level minimizes the influence of the depletion region that exists at the Si interface, and the conductivity of the Si is metallic in character. Simmons⁶⁶ and Brinkman⁶⁷ showed that, at intermediate voltages, the current across a metal-insulator-metal contact is proportional to $\alpha V + \beta V^3$. The derivative of the contact *I*–*V* curve is typically fit to this parabolic model, and the barrier parameters, such as barrier height (here 1.3 eV) and barrier thickness (here 17 Å) can be calculated. At low bias voltage, a zero bias anomaly (ZBA) is seen which is typical for highquality tunnel barriers.⁶⁸ A more rigorous test to show that the transport across the contact comes from tunneling rather than from parasitic effects, such as pinholes in the tunnel barrier film, is to measure the temperature dependence of the ZBR.



FIGURE 1.12 (a) Parabolic dependence of the conductance of an Al_2O_3 barrier. (b) Normalized zero bias resistance versus temperature.

Previous work has shown that a weak temperature dependence is the definitive test for a pinhole-free tunnel barrier.⁴³ Figure 1.12b shows the weakly insulating behavior for the NiFe/Al₂O₃, demonstrating high-quality tunneling contacts.

3T devices (Figure 1.11a) are fabricated with these tunnel barriers and placed in a cryogen-free closed-cycle cryostat equipped with an electromagnet. An out-of-plane magnetic field is applied and the 3T resistance is recorded. Figure 1.13 shows a typical measurement at T = 10 K for a NiFe/Al₂O₃/ n-Si (3 × 10¹⁹) contact. A small parabolic background signal with positive magnetoresistance has been removed. The result is a curve showing a negative magnetoresistance with a Lorentzian lineshape caused by the dephasing of the spin accumulation in Si. This is the electrical equivalent of the familiar Hanle curve we know from optical measurements.⁶¹ This curve can be fit using Equation 1.1, and from this fit we obtain a spin lifetime of 130 ps, commensurate with values reported in the literature on similar devices.^{69–72}

1.3.5 GRAPHENE AS A TUNNEL BARRIER ON SILICON

These measurements using Al₂O₃ tunnel barriers with known spin injecting properties illustrate the great potential of injecting spin-polarized carrier into Si. However, Al₂O₃ and other metal-oxide-based tunnel barriers have a serious drawback.



FIGURE 1.13 3T Hanle measurement for NiFe/Al₂O₃/n-Si (3×10^{19}) at 10 K.

By the time they are thick enough (~1 nm) to be pinhole free, they are also too resistive to yield useful spintronic devices. To overcome this problem, we need to look elsewhere and understand exactly what we need in a tunnel barrier. An ideal tunnel barrier should exhibit several key material characteristics: a uniform and planar habit with well-controlled thickness, minimal defect/trapped charge density, a low resistance–area product for minimal power consumption, and compatibility with both the FM metal and semiconductor of choice, ensuring minimal diffusion to/from the surrounding materials at temperatures required for device processing.

Metal Schottky barriers and oxide layers are susceptible to interdiffusion, interface defects, and trapped charge, which have been shown to compromise spin injection/transport/ detection. FM metals readily form silicides even at room temperature,⁷³ and diffusion of the FM species into the Si creates magnetic scattering sites, limiting spin diffusion lengths and spin lifetimes in the Si. Even a well-developed and widely utilized oxide such as SiO₂ is known to have defects and trapped or mobile charge that limit both charge and spin-based performance. Such approaches also result in contacts with high resistance–area products (*RA*).

Graphene offers a compelling alternative. Although it is very conductive in plane, it exhibits poor conductivity perpendicular to the plane. Its sp² bonding results in a highly uniform, defect-free layer, which is chemically inert, thermally robust, and essentially impervious to diffusion. These qualities ensure minimal diffusion to/and from the surrounding materials at temperatures required for device processing. A single monolayer provides a much lower RA product than a film of any oxide thick enough to prevent pinholes, while successfully circumventing the conductivity mismatch between a metal and a semiconductor.

1.3.6 GRAPHENE SAMPLES

Graphene was synthesized via low-pressure CVD on a copper foil substrate using methane gas.⁴² The typical grain size of the graphene films is several hundred microns. The graphene/ Cu samples were coated in PMMA⁷⁴ and the Cu was etched in an ammonium persulfate-based solution.⁷⁵ The remaining graphene/PMMA films were transferred in a deionized water bath onto hydrogen-passivated n-type silicon (001) substrates ($n = 6 \times 10^{19}$ and 1×10^{19} cm⁻³). The PMMA was removed with acetone. The quality of the graphene was assessed using Raman spectroscopy⁷⁶—the absence of the "D" line (~1350 cm⁻¹) associated with defects and the widths and ratios of the "G" (~1580 cm⁻¹) and "2D" (~2700 cm⁻¹) lines confirm that the graphene is of high quality with minimal defects.

The graphene was patterned using PMMA (50 nm) deep-UV photolithography⁷⁷ to minimize residues left by conventional processing with Shipley photoresist and etched with oxygen plasma. The PMMA was exposed in a mask aligner to a 193 nm ArF excimer laser source at a dose of 900-1000 mJ/cm². Subsequent developing was 60 s in 100% MIBK at room temperature. A brief oxygen reactive ion etch was used to remove all graphene not located within the desired tunnel barrier mesa. The conducting edges of the graphene mesa were buried in a layer of sputter-deposited Si₃N₄. Ni₈₀Fe₂₀ was then deposited by e-beam evaporation or sputtering onto the graphene through vias in the Si_3N_4 , defining the spin-polarized contacts, followed by another layer of Si₃N₄, and the device was finished with the electron-beam evaporation of ohmic Ti/Au contacts and bond pads (see Figure 1.14). The dimensions of the contacts are typically $40 \times 40 \,\mu m^2$.

Figure 1.15 shows the I-V curve of a contact with and without graphene on n-type Si (6 × 10¹⁹). This highly doped



FIGURE 1.14 Schematic and cross section of the samples. (a) Monolayer graphene serves as a tunnel barrier between the FM metal contact and the Si substrate. Contacts 1 and 3 are ohmic Ti/Au contacts. (b) The contact is designed so that the edges of the graphene are embedded in the SiN insulator, preventing conduction through the graphene edge states which would short out the tunnel barrier.



FIGURE 1.15 (a) A nonlinear *I*–*V* curve of a NiFe/graphene/n-Si (6×10^{19}) contact at room temperature. The inset shows the *dI/dV* curve measured with standard lock-in techniques. (b) *I*–*V* of similar contact without graphene. (c) Temperature dependence of the zero bias resistance is shown to be weakly insulating for the NiFe/graphene/n-Si (6×10^{19}) and metallic for the NiFe/*n*-Si (6×10^{19}) contact.

(metallic) Si substrate is a good test substrate for these graphene contacts. The I-V curve for the contact without graphene, shown in Figure 1.15b, is completely linear, as is expected for this type of ohmic contact. However, the inclusion of a single layer of graphene completely changes the nature of this contact and a nonlinear I-V curve is observed. The inset in Figure 1.15a shows the conductance versus voltage measured directly with a lock-in amplifier. The conductance shows the quadratic behavior associated with tunnel barriers, albeit somewhat asymmetric due to the drastically different contacts

on either side of the tunnel barrier and the effect of the depletion width that exists even in 6×10^{19} -doped Si.

As described earlier, the temperature dependence of the ZBR provides insight into the quality of the tunnel barrier.⁴³ This measurement is shown in Figure 1.15c.

The resistance of the ohmic contact decreases with decreasing temperature reflecting the metallic nature of the 6×10^{19} doped Si substrate and the contact. In contrast, the contact with a single layer of graphene shows a weak insulating-like temperature dependence, the definitive test for a pinhole-free, high-quality tunnel barrier.⁴³

These samples are then placed in a small out-of-plane magnetic field (<0.5 T) and the 3T resistance is recorded, as described earlier. Figure 1.16 shows the room temperature spin resistance of a NiFe/graphene/n-silicon (1×10^{19}) sample after removal of a weak quadratic background. The data exhibit a negative magnetoresistance with the Lorentzian line-shape indicative of Hanle spin precession. Spin accumulation underneath a spin-injecting contact will depolarize in an out-of-plane magnetic field, following a Lorentzian line shape, as in Equation 1.1, just as observed here. Using Equation 1.1 to fit the data in Figure 1.16, we obtain a spin lifetime of 180 ps. This result confirms the spin-injecting properties of the NiFe/graphene contact.

When using 3T measurements, one needs to take extra care in ruling out spurious effects that might be causing this magnetoresistance.⁷⁸ Typical magnetoresistance effects like the ordinary magnetoresistance effect (OMR) and resistance changes caused by Lorentz forces acting on the moving electrons have a positive magnetoresistance and these have been removed with the quadratic background removal. A known source for negative magnetoresistance with a similar lineshape is weak localization (WL). Here, an out-of-plane magnetic field dephases time-reversal paths of weakly localized electrons and these



FIGURE 1.16 Hanle spin precession measurements, graphs are offset for clarity. Room temperature Hanle data for spin injection NiFe/graphene/Si (1×10^{19}) . Also shown are the control samples: nonmagnetic/graphene/Si (1×10^{19}) and NiFe/Si (1×10^{19}) measured at 10 K.

no longer interfere with themselves, thus reducing resistance. WL has been observed in bulk Si, thin Si films, and inversion layers,^{79–81} but is only seen at low temperatures. The data in Figure 1.16 was measured at room temperature, so should be unaffected by WL. To rule out WL completely, however, a control sample was fabricated identical to the one discussed earlier, except the NiFe is replaced by Ti/Au. We measured this contact at low temperatures where the MR effects should be the highest (black curve in Figure 1.16) and saw no observable effects, thus completely ruling out WL as the cause of the observed magnetoresistance.

The geometry of the 3T devices is such that it is, in principle, possible to measure local Hall effects.^{82,83} Here stray fields from the magnetic contacts due to geometry or roughness can exert a Lorentz force on moving electrons, altering the electrons' path and changing the resistance with field. However, the stray fields should follow the out-of-plane magnetics of a thin magnetic film (100 Å) of NiFe, which is a magnetic hard axis with a saturation magnetization of 1.1 T. Even if there were a slight angle to the out-of-plane magnetic field, causing the magnetization to rotate in-plane, a hysteretic behavior would be observed in the local Hall effect. We observe a single peak centered around zero magnetic field that saturates at ~1500 Oe. Nonetheless, a control sample was made. NiFe was deposited directly on Si, and should show all of the same local Hall effects, since the stray fields are identical. Although NiFe/Si (1×10^{19}) forms a Schottky contact and spin-polarized electrons could, in principle, tunnel across this barrier, silicide formation and diffusion of metallic ions from the NiFe occur without the graphene as a diffusion barrier. Spin scattering by these impurities suppresses spin injection for this contact. This measurement is shown at the bottom of Figure 1.16. Even at low temperatures, where the effect should be largest, there is no observable local Hall effect. Similar arguments can be made for AMR effects⁸⁴ and tunnel AMR effects (TAMR).⁸⁵ AMR effects should be manifested in the NiFe/Si control sample and have been actively suppressed by adding a 1000-Å gold layer on top of the 100-Å NiFe layer to shunt any of the spreading currents that might cause AMR. Both AMR and TAMR should follow the out-of-plane magnetization of the NiFe, which is clearly not seen in the measurement.

It has been shown for some combinations of magnetic material and high-resistance tunnel contacts that the spin accumulation actually occurs in the tunnel barrier rather than in the semiconductor due to a two-step tunnel process.⁸⁶ Even though the graphene/Si contact is a low-resistance tunnel barrier and two-step tunneling is unlikely, it is still possible that the spin accumulation occurs in traps at the graphene/Si interface. The best way to prove that spin accumulation occurs in Si and not in states inside the graphene tunnel barrier is to change the properties of the Si, by, for instance, changing the carrier concentration of the Si substrate. From the electron spin resonance (ESR) literature on Si,87-89 we know that spin lifetimes in Si depend strongly on dopant concentration, decreasing with increasing dopant density. We therefore made several 3T devices on Si substrates with doping concentrations that range from 3×10^{18} to 6×10^{19} . For each of these



FIGURE 1.17 Spin lifetimes obtained from 3T Hanle measurements at 10 K as a function of the Si electron density for the tunnel barrier materials indicated and different ferromagnetic metal contacts (Fe, CoFe, and NiFe). The symbol shape distinguishes the tunnel barrier material: triangles—SiO₂, circles—Al₂O₃, squares—MgO, and stars—graphene. Solid symbols correspond to devices with Ni_{0.8}Fe_{0.2} contacts, half-solid symbols to Fe contacts, and open symbols to Co_{0.9}Fe_{0.1} contacts. The spin lifetimes show a pronounced dependence on the Si doping level and little dependence on the choice of tunnel barrier or magnetic metal.

carrier concentrations, we measured the spin lifetime of several devices with different tunnel barriers and different FM contacts. These data are summarized in Figure 1.17, where we plot the spin lifetime at 10 K obtained from 3T Hanle data on n-Si as a function of electron density for four different tunnel barrier materials (graphene, Al_2O_3 , SiO_2 , and MgO) and three different magnetic metal contacts (Fe, CoFe, and NiFe). The spin lifetime measured with the 3T Hanle geometry shows a clear dependence only on dopant density, and the dependence is consistent with literature ESR data on bulk Si. The spin lifetime is completely independent of the tunnel barrier material or magnetic metal used for the contact. The values for the graphene tunnel barriers fall directly on the curve. These data confirm that the spin accumulation occurs in the Si and not in the graphene or possible interface trap states.

1.3.7 IMPORTANCE OF LOW RA PRODUCTS

In addition to good spin properties, a spin contact must also exhibit a low conventional *RA* product. This is important for any future spintronic device, such as a spin-FET (Figure 1.4). A spin-FET has magnetic contacts, one spin injector and one spin detector. In order for the spin-FET to function properly, a significant local magnetoresistance is essential. To observe any local MR, the conventional *RA* product of these contacts has to be within a narrow window. This window depends upon the Si channel conductivity, the spin lifetime, the contact spacing (e.g., the spin transistor gate length), and the contact width.^{62,90,91}

In Figure 1.18, we calculate the local MR as a function of the *RA* product and electron concentration using the model of



FIGURE 1.18 *RA* product window for local magnetoresistance. Calculation of the local (two terminal) magnetoresistance as a function of the contact's conventional *RA* product and the Si electron density for the device geometry shown in the inset, using the theory of Reference 60. The data points are the *RA* products measured for our FM metal/tunnel barrier/Si contacts using 2 nm SiO₂ (triangles), 1.5 nm AlO_x (squares), and monolayer graphene (circles) tunnel barriers prepared from identical Si wafers in our lab. The FM metal/graphene *RA* products fall within the window of useful MR values. W = w = 11 nm.

References 62 and 91 and the contact geometry shown as the inset in Figure 1.18. The geometric parameters are chosen to be consistent with the 11 nm node anticipated for Si device technology within the next 5 years. The maximum obtainable magnetoresistance occurs in the middle of the colored band. Tunnel barrier contacts of FM/AlO_x and FM/SiO₂ fabricated previously in our lab have been shown to produce significant spin accumulation in Si (e.g., Figure 1.13) but have RA products that are too high to generate useable local MR. In contrast, utilizing monolayer graphene as the tunnel barrier lowers the RA product by orders of magnitude, and values for the NiFe/graphene contacts on bulk wafers fall well within the range required to generate high local MR. Reducing the RA product also has a positive effect on the electrical properties of the spin device, as lowering the resistance reduces noise and increases the speed of an electrical circuit.92

The 3T devices with graphene tunnel barriers provide insight into the properties of a spin-polarized electron current and spin accumulation that occur directly underneath the injecting contact. A pure spin current can be generated in a 4T nonlocal spin valve contact geometry, as illustrated in Figure 1.19a. In the nonlocal detection geometry, spinpolarized electrons are injected into the Si from contact 2, producing both a spin-polarized electron drift/diffusion current which flows with an applied bias from contacts 2 to 1, and a diffusive spin current which flows to the right from contact 2. This pure spin current produces a net spin polarization and an imbalance in the spin-dependent electrochemical potential, which is detected as a voltage by the magnetic contact 3 relative to the reference contact 4. No charge current flows in the detection circuit defined by reference contact 3 and magnetic detector contact 4, thus excluding spurious contributions from AMR and local Hall effects. The voltage measured at contact 3 is sensitive to the relative orientation of the contact magnetization and the net spin orientation in the Si itself.

We use electron-beam lithography to define the magnetic contacts. The device shown in Figure 1.19b has a 200-nm and a 1- μ m wide contact separated by 200 nm. The magnetic contacts have been used as a hard mask to etch away the graphene between the electrodes with a mild O₂ plasma. This is to make sure that the graphene is used as a tunnel barrier and that the pure spin current diffuses through the Si channel rather than the graphene.

At large negative magnetic fields applied along the long axis of the contacts, the magnetizations of the 200-nm and 1- μ m wide contacts are parallel, and the nonlocal resistance is at a maximum. As the field is increased, the 1 μ m contact switches, resulting in an antiparallel orientation and a



FIGURE 1.19 (a) Schematic of nonlocal measurement: A current is applied from contact 2 to 1. The voltage is measured outside of the charge path across contacts 3 and 4. (b) SEM image of two inner contacts (2 and 3) on Si/graphene nonlocal device; dashed line indicates the active area. (c) Nonlocal resistance versus in-plane magnetic field measured using lock-in techniques. Clear parallel and antiparallel magnetic states are observed.

minimum in the nonlocal resistance. As the field increases further, the 200-nm contact also switches, so that the contact magnetizations are again parallel, and the nonlocal resistance returns to its maximum value. The sequence is reversed as the magnetic field is swept from positive to negative. The maximum resistance change is ~2.5 m Ω , close to the value that has been observed previously with MgO barriers.^{71,72}

1.4 SUMMARY

In this chapter, we have shown the unique role that graphene can play in the field of spintronics as a tunnel barrier. We have shown that while graphene exhibits metallic conductivity inplane, it serves effectively as an insulator for transport perpendicular to the plane and provides the first demonstration of two potential applications. First, we showed how a single layer of graphene could be used as an atomically thin tunnel barrier in a MTJ, preserving the spin polarization of the electrons while providing thickness control unattainable with traditional oxide tunnel barrier materials. We have measured out-of-plane transport through a single layer of graphene by fabricating metal-graphene-metal junctions using two FM metals in an MTJ structure. We observed spin-polarized electron tunneling, clearly measureable even above room temperature. Second, we demonstrated the use of graphene as a tunnel barrier for spin injection into a Si channel. The spin injection resistances achieved are three orders of magnitude lower than for comparable oxide tunnel barrier contacts and fall within a critical window of values required for practical devices. These results enable realization of semiconductor spintronic devices such as spin-based transistors, logic, and memory.

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2 Modeling and Simulation of the Elastic Properties of Kevlar Reinforced by Graphene

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ABSTRACT

The compressive strength of composites in the form of a polymer fiber, such as Kevlar, with a thin outer layer of multilayered graphene was investigated and modeled. Polymer chains of Kevlar are linked into a locally planar structure by hydrogen bonds across the chains, with transversal strength considerably weaker than a longitudinal one. This suggests that introducing an outer enveloping layer of graphene, linked to polymer chains by strong chemical bonds may significantly strengthen the Kevlar fiber with respect to transversal deformations. Such a composite structure may be fabricated by introducing strong chemical bonds linking together the fiber and graphene sheets. Chemical functionalization of graphene and a polymer fiber may be achieved by modification of appropriate surface-bound functional (e.g., carboxylic acid) groups on their surfaces. We studied the elastic response of the composite fiber to the unidirectional in-plane applied load with load peaks along the diameter. The 2D linear elasticity model predicts that significant yield strengthening occurs when the radius of graphene outer layers is about 4% of the Kevlar yarn radius, assuming that graphene layers are strongly linked together to form an isotropic structure. In case of weak interlayer graphene coupling, weaker yield strengthening is predicted by the model (however, the fiber may still be held together by the enveloping graphene layer even beyond the fiber yield limit).

2.1 INTRODUCTION

The discovery of graphene [1] and graphene-based polymer nanocomposites has shown many unique properties such as the quantum Hall effect, high carrier mobility at room temperature, large specific surface area, superior optical transparency, high Young's modulus, and exceptional conductivity [2]. Graphene-based polymer nanocomposites represent one of the most technologically promising developments to emerge from the interface of graphene-based structures and polymer materials. However, there are still many challenges that must be addressed for these nanocomposites to achieve their full potential. The preparation methods of polymer nanocomposites depend on the polymer molecular weight, polarity, hydrophobicity, precursors, reactive groups, solvent viscosity, and other [3].

There are three basic pathways for incorporating the polymer at the core of the host-layered materials. In the in situ intercalative polymerization method, graphene or modified graphene is first swollen within the liquid monomer. The appropriate initiator is added and polymerization is initiated either by heat or radiation [4]. A large number of polymer nanocomposites have been prepared in this method, that is, polystyrene/graphene, poly-methylmethacrylate (PMMA) expanded graphite (EG), polystyrene sulfonate-layered double hydroxide, polyimide, polyethylene terephthalate (PET), etc. [5–8]. In the solution intercalation method, the polymer or prepolymer was dissolved in the solvent system and graphene or modified graphene layers were allowed to swell [9]. Graphene or modified graphene is dispersed in a suitable solvent like water, acetone, chloroform, tetrahydrofuran, dimethyl formamide, or toluene; then the polymer adsorbs on to the delaminated sheets, and finally the solvent is evaporated [10]. The polyethylene-grafted maleic anhydride graphite polymer nanocomposites [11], epoxy/layered double hydroxide (LDH) [12,13], polystyrene-graphene [14], polypropylene-graphene [15], polyvinyl alcoholgraphene [16], polyvinylchloride-carbon nanotubes [17], ethylene vinyl acetate LDH [18], etc., have been prepared by this method.

Polyurethane was used as the interlayer between the Kevlar fiber and carbon materials to bind the carbon materials to the Kevlar fiber [19]. The graphene nanoribbons onto Kevlar fibers were fabricated through layer-by-layer spray coating. These flexible coated Kevlar fibers have the potential to be used for conductive wires in wearable electronics and battery-heated armors. Zhang et al. [3] prepared PET/graphene nanocomposites using the melt-compounding method. Polycarbonate (PC)/graphene nanocomposites with functionalized graphene sheets (FGS) nanocomposites were prepared by the melt-compounding method [21]. The tensile modulus of the PC/FGS nanocomposites was higher than that of the neat PC. Polyvinylidene fluoride (PVDF)/graphene nanocomposites were prepared from graphene oxide (GO) and EG by solution processing and compression molding [4]. The thermal stability of PVDF/FGS nanocomposite was higher than that of PVDF/EG nanocomposite. The mechanical properties of both the composites were higher than that of the neat PVDF.

Wang et al. [22] prepared $poly(\varepsilon$ -caprolactone)-GO nanocomposites using the in situ polymerization method. These nanocomposites showed excellent mechanical properties and robustness under bending. Liu et al. [23] fabricated GO-reinforced epoxy resin nanocomposites by transferring GO from water to acetone. Incorporation of 1 wt% of GO showed a significant improvement in flexural strength, flexural modulus, impact strength, and storage modulus. Poly(lactic acid)-graphene nanocomposites were prepared using the response surface method [24], which showed that graphene loading had a significant effect on tensile strength.

Reinforced polymer fibers have been studied intensively in search of superior fabrics for a broad range of applications, including bulletproof vests, protective clothing, and high-performance composites for aircraft and automotive industries [25,26]. For most structural materials, the compressive strength is much greater than the tensile strength. Fiber-reinforced composites are among a few materials that exhibit greater tensile strength than compressive strength. This behavior results from the fiber microbuckling compressive failure mechanism in fiber composites. Static compressive strengths of unidirectional composites have been studied by several research groups in the past few decades [27–30].

A major step forward in the protection of personnel against ballistic threats has been achieved by the introduction of Kevlar synthetic fibers and textiles. The most common approaches for the fabrication of reinforced composite fibers have been melt processing and solution coagulation spinning [31,32]. Kevlar fibers are produced by wet-spinning from sulfuric acid solutions [33]. While in an acid solution, Kevlar forms a liquid crystalline phase, with rod-like polymer chains well aligned parallel to each other, and bonded by hydrogen bonds across to form strong planar sheets [34]. Such sheets are stacked radially to form a Kevlar fiber. As a result, the fiber is much stronger with respect to longitudinal deformations than to transversal deformations.

On the other hand, the carbon nanotubes (CN) and graphene sheets (GS) have been proposed as one of the most promising additives for the fabrication of ultrastrong polymer composites due to their advanced mechanical properties [9,35]. It is well known that CN and GS have Young's modulus and tensile strength above 1 TPa and 60 GPa [36-40], respectively, while their densities can be as low as 1.3 g/cm³. They may exist as single-layered or multilayer structures. It is possible to harness the multifunctional properties of graphene sheets and design a novel class of advanced composites with superior mechanical and electric performance [40,41]. Thus, various polymeric-CN and polymeric-GS composites and their chemical functionalizations have become a subject of intensive research and technological development over the last few years [42,43]. Recently, a significant mechanical enhancement of Kevlar fibers has been demonstrated by incorporation of surface-modified carbon nanotubes achieved by using the N-methylpyrrolidone (NMP) solvent [44,45]. The maximum values observed were for Young's modulus 115-207 GPa; yield strength 4.7–5.9 GPa; strain at break 4.0–5.4%; and toughness 63-99 J/g [44].

In this chapter, we present the 2D linear elasticity model to predict the mechanical properties of the Kevlar fibers reinforced by depositing an outer shell of graphene, rigidly attached to the Kevlar fiber through chemical bonds. The graphene outer layer can be formed by soaking a single Kevlar fiber with graphene dispersed in the NMP solvent. By using a spinning technique, it will be possible to create a composite structure by depositing an outer layer of graphene enveloping the Kevlar fiber. This leads us to hypothesize that graphene could be incorporated into swelled Kevlar fibers by soaking fibers in a dispersion of graphene in NMP. Chemical functionalization of graphene and Kevlar may be achieved by modification of appropriate surface-bound functional (e.g., carboxylic acid) groups on their surfaces. We anticipate that the outer graphene layer enveloping the Kevlar fiber may stabilize radially stacked hydrogen-bonded planar sheets, forming Kevlar fibers with respect to transversal deformations.

The main goal of this chapter is to model the mechanical behavior of Kevlar–graphene fibers and to predict the optimal thickness of the outer layer of graphene for strengthening. We show that within a 2D linear elasticity model, and taking realistic Young's modulus and Poisson's ratios for transversal deformations, reinforcement starts to occur when the outer hard shell radius is about 4% of the Kevlar fiber radius (corresponding to about 8% weight). We assume that the applied load has a narrow load peak along the diameter, which we may take to be the *Y* axis, as shown in Figure 2.1.

A commercially available Kevlar fiber has a radius of about 6 μ m. In that case, assuming strongly linked multilayer graphene, we will need about 240 nm of functionalized graphene for substantial twofold yield strength improvement. At such a scale, a continuous elasticity model may be used.

Our modeling assumes that graphene flakes envelop the fiber and are tied up together by covalent bonds, which may



FIGURE 2.1 (a) Applied force per unit transverse area, as a function of polar angle. Force is in the *Y* direction and is nonzero in an interval of width $\theta w = (\pi/16)$ centered at $\theta = \pm (\pi/2)$; (b) σ_{rr} is component of material stress on the outer boundary, as a function of the polar angle θ ; (c) $\sigma_{r\theta}$ is component of material stress on the outer boundary, as a function of the polar angle θ .

be achieved by graphene functionalization. In the presence of strong interlayer covalent bonds, we may assume that bonded graphene flakes will have high Young's modulus and tensile strength in all directions, and we can model it by an isotropic continuous model. Our model also allows us to investigate anisotropic material. Our computation shows that if interlayer coupling is weakened, yield reinforcement drops, as a normal load is more easily transferred to the fiber inside graphene layers. In particular, there is no significant reinforcement by a thin outer layer when elastic constants are those of graphite, which has much softer response to load in the direction normal to the layers.

We note that if reinforcement is insufficient and stresses in the fiber are above the fiber yield limit, the fiber may experience plastic response. However, even if that is the case, but strong enveloping outer graphene layers do not disintegrate, the composite fiber may still survive and not break apart, being contained by strong outer graphene shell. For investigation of such a high load, a high displacement regime has to go beyond the linear elasticity model investigated here.

2.2 SOLVING ANISOTROPIC ELASTICITY EQUATIONS

Linear elasticity is mathematically well developed and widely used. There are many excellent references, for example, Reference 46. In case when elastic properties in the fiber cross section are isotropic, the solution of elasticity equations is given in terms of the Airy function in Reference 47. In anisotropic case, we will solve elasticity equations in terms of displacements, given in the polar coordinates (r, θ) :

$$\mathbf{u} = (u_r, u_\theta). \tag{2.1}$$

We assume that $\mathbf{u}(0) = 0$. We expand displacements, as well as strains and stresses, in the Fourier series with respect to the polar angle

$$u_r = \sum_{m=-\infty}^{\infty} \hat{u}_r(r,m) e^{\imath m \theta}, \quad u_{\theta} = \sum_{m=-\infty}^{\infty} \hat{u}_{\theta}(r,m) e^{\imath m \theta}, \quad \iota^2 = -1. \quad (2.2)$$

Hook's law for an orthotropic material yields stresses in terms of the strains:

$$\hat{\sigma}_{rr}(r,m) = c_{11}\hat{u}'_r + c_{12}\frac{\mathrm{Um}\hat{u}_{\theta} + \hat{u}_r}{r},$$

$$\hat{\sigma}_{r\theta}(r,m) = c_{66}\left(\hat{u}'_{\theta} + \frac{\mathrm{Um}\hat{u}_r + \hat{u}_{\theta}}{r}\right) \qquad (2.3)$$

$$\hat{\sigma}_{\theta\theta}(r,m) = c_{22}\frac{\mathrm{Um}\hat{u}_{\theta} + \hat{u}_r}{r} + c_{12}\hat{u}'_r;$$

here, $\hat{u}'_{\alpha} = (d/dr)\hat{u}_{\alpha}, c_{\alpha\beta}$ are stiffness constants in the orthotropic case.

Elasticity equations are given by

$$\hat{\sigma}_{rr}' + \frac{\mathrm{t}m\,\hat{\sigma}_{r\theta} + \hat{\sigma}_{rr} - \hat{\sigma}_{\theta\theta}}{r} = 0,$$

$$\hat{\sigma}_{r\theta}' + \frac{\mathrm{t}m\,\hat{\sigma}_{\theta\theta} + 2\hat{\sigma}_{r\theta}}{r} = 0.$$
(2.4)

In terms of displacements, those equations are

$$\frac{d}{dr}\Phi(r,m) = \begin{pmatrix} -\frac{1}{r} & -\frac{\mathrm{t}m(c_{12}+c_{66})}{rc_{11}} \\ -\frac{\mathrm{t}m(c_{12}+c_{66})}{rc_{66}} & -\frac{1}{r} \\ 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Phi(r,m) = \begin{pmatrix} \frac{a_{22} + m^2 c_{66}}{r^2 c_{11}} & \frac{4m(c_{22} + c_{66})}{r^2 c_{11}} \\ -\frac{4m(c_{22} + c_{66})}{r^2 c_{66}} & \frac{m^2 c_{22} + c_{66}}{r^2 c_{66}} \\ 0 & 0 \\ 0 & 0 \end{pmatrix}, \quad m = 0, \pm 1, \pm 2, \dots$$

$$\Phi(r,m) = \begin{pmatrix} \hat{u}'_r(r,m) \\ \hat{u}'_{\theta}(r,m) \\ \hat{u}_{\theta}(r,m) \\ \hat{u}_{\theta}(r,m) \end{pmatrix}, \quad m = 0, \pm 1, \pm 2, \dots$$

$$(2.5)$$

We pick a small radius r_0 . Let Φ_i , i = 1,...4 be solutions of Equation 2.5 with the initial condition $\Phi_i(r_0) = \mathbf{e}_i$, where \mathbf{e}_i are standard basis vectors in \mathbb{R}^4 (i.e., \mathbf{e}_i is a column vector with 1 in position *i* and 0 elsewhere). Basis solutions Φ_i can be computed by iteration (with \mathbf{e}_i being the initial approximation) or by numerical Runge–Kutta methods. Iterative solution will have logarithmic terms in *r*, not just powers of *r* or (1/*r*). It can be seen that Φ_1 and Φ_2 are the solutions regular at r = 0, in the sense that

$$\lim_{\epsilon \to 0^+} \lim_{r_0 \to 0^+} \Phi_i((1+\epsilon)r_0, m) = e_i.$$
(2.6)

We take region 1 to be the fiber region, $x^2 + y^2 \le R_1^2$, and region 2 to be the outer reinforcing ring, $R_1^2 \le x^2 + y^2 \le R_2^2$. In region 1, a solution of Equation 2.5 is a linear combination of Φ_1 and Φ_2 , computed using the stiffness constants of region 1:

$$\Phi^{(1)}(r,m) = \sum_{i=1}^{2} \chi_i(m) \Phi_i^{(1)}(r,m), \quad m = 0, \pm 1, \pm 2, \dots \quad (2.7)$$

(we indicate the region by a superscript in parenthesis). In region 2, a solution of Equation 2.5 is a linear combination of all four basis solutions Φ_i , i = 1, ..., 4, computed using the stiffness constants of region 2:

$$\Phi^{(2)}(r,m) = \sum_{i=1}^{4} \xi_i(m) \Phi_i^{(2)}(r,m), \quad m = 0, \pm 1, \pm 2, \dots$$
 (2.8)

The sixth unknown constants per mode, $\xi_i(m)$, i = 1, ... 4, $\chi_i(m)$, i = 1, ... 2 are found from the following six conditions:

$$\hat{\sigma}_{rr}(R_2,m), \hat{\sigma}_{r\theta}(R_2,m) \text{ are determined by} \\ \text{loading force per unit area} (1,2) \\ \hat{\sigma}_{rr}(R_1,m), \hat{\sigma}_{r\theta}(R_1,m) \text{ are continous;} (3,4) (2.9) \\ \hat{u}(R_1,m), \hat{u}_{\theta}(R_1,m) \text{ are continous.} (5,6)$$

Stresses and displacements can be expressed via components of $\Phi^{(1)}$, $\Phi^{(2)}$, and their first derivative with respect to *r*; in particular, the stresses are given by Equation 2.3. Thus, Equation 2.9 is a system of six linear equations for the six constants $\xi_i(m)$, $i = 1, ..., 4, \chi_i(m)$, i = 1, 2, for each of the Fourier modes $m = 0, \pm 1, \pm 2,...$ Solving the linear system (Equation 2.9), we find those constants, for any external loading. That gives us functions $\Phi^{(1)}(r, m)$, $\Phi^{(2)}(r, m)$ (Equations 2.7 and 2.8), which enables us to compute displacements and stresses (for any external loading).

2.3 ANALYZING SOLUTION

For illustration, we assume that unidirectional transversal compression is applied along a diameter, in a small neighborhood of points of contact. We assume that the load is uniform in a small region of contact.

The load we use in our study is shown in Figure 2.1. Compressing force is applied on the outer boundary in the (-Y) direction in a small neighborhood of *Y* axis intercept, with an opposite balancing force applied in diametrically opposite region. Magnitude of the force per transversal to the *Y* surface area element, as a function of the polar angle θ , has narrow peaks centered at $\theta = \pm(\pi/2)$; we take the magnitude to be constant at such peaks, and we take width of the peak to be $w = (\pi/16)$. Outside of the peaks, we take a smooth interpolation to a zero value in a small angular region of width ε . Thus, f_Y , the *Y* axis projection of the applied force per transversal to *Y* area element, as a function of polar angle is given by

$$f_{y}(\theta) = \begin{cases} -1, \left| \theta - \frac{\pi}{2} \right| \le \frac{\theta_{w}}{2} \\ 1, \left| \theta + \frac{\pi}{2} \right| \le \frac{\theta_{w}}{2} \\ 0, \left| \theta \pm \frac{\pi}{2} \right| \le \theta_{W} + \epsilon \end{cases}$$
(2.10)

Corresponding stresses applied on the outer boundary, as functions of polar angle, are

$$\sigma_{rr}(\theta) = f_{y}(\theta) |\sin \theta| \sin \theta,$$

$$\sigma_{r\theta}(\theta) = f_{y}(\theta) |\sin \theta| \cos \theta;$$
(2.11)

 f_y as a function of the polar angle θ is shown in Figure 2.1a. In Figure 2.1b and c, we plot components of the stress tensor σ_{rr} and $\sigma_{r\theta}$, induced in the material by such applied load, as a function of the polar angle; here r, θ are polar coordinates. Stress σ_{rr} corresponds to a compression in the vicinity of two diametrically opposite points on the *Y* axis. Stress $\sigma_{r\theta}$ rapidly changes sign at those points, since projection of f_y onto the polar unit vector e_{θ} changes sign.

2.3.1 VON MISES YIELD CRITERIA

Yield criteria for a broad class of materials may be given in terms of the Von Mises stress. The Von Mises stress is proportional to the square root of the sum of squares of characteristic values of the trace-free part of the stress tensor. Since a Kevlar fiber is transversally isotropic and the transversal yield strength of the Kevlar fiber is much lower than the longitudinal one, we will use a 2D version of the Von Mises stress:

$$\sigma_M = \sqrt{(\sigma_{xx} - \sigma_{yy})^2 4 \sigma_{xy}^2}.$$
 (2.12)

To illustrate how the Von Mises stress is distributed on the Kevlar–graphene domain, we plotted the Von Mises stress (Equation 2.12) on the Kevlar fiber region (Figure 2.2), in the case when $r_1 = (R_1/R_2) = 0.96$, for various values of anisotropic stiffness constants of reinforcing multilayered graphene. The external applied load is along the *Y* axis and has a sharp peak of polar angle width ($\pi/16$), as in Equations 2.10 and 2.11. If multilayers of graphene are linked together into a strong 3D structure, there is a sharp drop of the Von Mises stress occurring in the stronger outer graphene layer, with a more than two-fold decrease of stress in the Kevlar fiber compared to the case of no graphene reinforcement (Figure 2.2a). On the Kevlar fiber domain, the Von Mises stress is larger in the outmost region and near the *Y* axis where the external stress is applied. There is smaller drop of Von Mises stress in case if multilayers



FIGURE 2.2 Von Mises stress σ_M is shown in the fiber region only, in the case where the ratio of the inner to outer radius (R_1/R_2) is 0.96. Applied force per unit area is ±1 unit and is a compression along the *Y* axis; it is applied on the outer boundary within a polar angle interval of width $\pi/16$ centered at $\theta = (\pi/2)$, with an opposite force applied in the diametrically opposite region. Fiber stiffness constants are $c_{11} = c_{22} = 8$, $c_{12} = 4.3$, $c_{66} = 1.85$ GPa. Reinforcement graphene layer is (a) isotropic, with stiffness constants $c_{11} = c_{12} = 613.6$, $c_{12} = 68.2$, $c_{66} = 272.7$ GPa, (b) anisotropic, with softer constants normal to the graphene layers, $c_{11} = 306$, $c_{22} = 613.6$, $c_{12} = 69$, $c_{66} = 272.3$ GPa, and (c) has stiffness constants of "turbo-g" graphite, $c_{11} = 36.5$, $c_{22} = 1060$, $c_{12} = 15$, $c_{66} = 0.15$ GPa.

coupling is softer in the direction normal to the layers (Figure 2.2b). If the thin reinforcing layer, $r_1 = (R_1/R_2) = 0.96$, has stiffness constants of graphite, that is, "turbo-g" graphite [48], the drop in Von Mises stress is very small compared to the case of no reinforcement; Von Mises stresses in that case are shown in Figure 2.2c.

Von Mises yield criterion is that yield occurs when σ_{max} , the maximum value of the Von Mises stress σ_M taken over the domain, becomes greater or equal to the critical value yield σ_{yield} , specific for the material. For Kevlar, $\sigma_{yield} \approx 2.9$ GPa for longitudinal loads, but for transversal loads it is lower (e.g., for Kevlar/PEKK composite the transversal strength is 21 MPa [34,49,50]). If Von Mises stress is reduced by the outer reinforcing layer, fiber yield strength increases by the same factor (about twofold increase in the case of strongly coupled graphene layers, $r_1 = (R_1/R_2) = 0.96$; essentially unchanged in the case of a thin layer of graphite).

For loads exceeding yield limit, it is expected that fiber response becomes plastic. However, if enveloping reinforcing layers (either weakly or strongly coupled) do not disintegrate, the fiber may still not break apart. Detailed investigation of such a high load case is beyond the scope of the present work, as nonlinear elasticity theory is required.

2.4 CONCLUSIONS

Strengthening of Kevlar–graphene fibers, with the increase of thickness of the outer layer of graphene, was predicted by analyzing solution of equations of 2D linear elasticity.

In the case of tightly bonded graphene layers, results of computation of Von Mises stress in Kevlar–graphene composite demonstrated a twofold increase in the yield strength for different transversal loadings, when the outer graphene shell radius was about 4% (corresponding to about 8% weight) of the Kevlar fiber radius. Within a linear elasticity model, reinforcement weakens if transversal bonding of graphene layers is weakened. Weaker composite fibers may not disintegrate even with the onset of plasticity; however, investigation of such a high displacement regime is outside the scope of linear elasticity model.

The theoretical results presented here can potentially be used to guide experimental work and to model strengthening of other fiber-reinforced composites.

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3 Size Control Methods and Size-Dependent Properties of Graphene

Guoxin Zhang and Xiaoming Sun

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ABSTRACT

Graphene, one of whose lateral sizes is confined to being oneatom thick, has grabbed enormous attention ever since the discovery of this atomic thin layer of carbon crystal or polymer which was theoretically proved to be thermodynamically unstable. Size effects of the other two dimensions were then found and investigated. To precisely control the planar size of graphene and chemically convert graphene into nanoribbons or nanoshapes with regularity remains a challengiein this field. A few research groups including ours have pioneered some fundamental work on the size control of this atomic thin carbon layer, which we will summarize and expand in details here in this section. Meanwhile, variations in corresponding properties between different lateral sizes will be depicted. Furthermore, some unsolved problems preventing further progress will be illuminated and possible solutions to them will be given.

3.1 INTRODUCTION

When the lateral size of materials is reduced down to the critical size of nanoscale, the nanomaterials normally behave distinctly other than the bulk. For instance, quantum dots, the nanoscale semiconductor particles, emit photons with different wavelengths upon the same excitation.¹ This intriguing variation is termed as the small size effect. Unlike semiconductor due to the huge π system in the basal plane which can greatly

facilitate the carrier mobility. The massless carriers, Dirac fermions, can move without scattering as long as there is no confinement at the boundaries. Measurements show graphene has room-temperature mobilities of 10⁴ cm⁻² s⁻¹.² Meanwhile, an unusual half-integer quantum Hall effect (QHE) for both electron and hole carriers in graphene has been observed by adjusting the chemical potential using the electric field effect.³ In addition, graphene is highly transparent, with an absorption of only ~2.3% per layer toward visible light.⁴ Its thermal conductivity, k, is measured with a value of 5000 W mK⁻¹ for a single-layer sheet at room temperature.⁵ Graphene also possesses excellent mechanical strength. The intrinsic mechanical properties of free-standing monolayer graphene membranes were measured by nanoindentation under an atomic force microscope.⁶ The breaking strength was found to be 42 N m⁻¹ and Young's modulus 1.0 TPa, indicating it is one of the strongest materials ever measured.

Till now, hundreds of papers have revealed a definite relationship existing between the properties and the morphologies of graphene, where the morphologies can be ascribed to both sizes and shapes. The sizes and shapes of graphene were shown dictating their electrical, optical, magnetic, and chemical properties. Ever since the finding of graphene by Novosolov et al.,² numerous papers had reported the methodologies to fabricate graphene with various sizes and morphologies as well as how its properties are governed by its different sizes and shapes. In this chapter, methods to obtain size-controlled graphene and several cases of graphene nanostructures with size-dependent properties will be discussed.

3.2 SIZE CONTROL METHODOLOGY

One prerequisite for specific practical use is the availability of graphene with appropriate sizes. A few efficient pathways have been established and applied to certain areas such as devices fabrication,² biomaterials,⁷ and so forth. Effective methods to control the size and shape of graphene are initially summarized in Table 3.1 together with their advantages and disadvantages, which will be expanded on later. Graphene with different sizes and shapes will also be discussed and it will be elaborated how their given size is related to concerned properties.

3.2.1 Nanoscale Cutting

Sonication is widely used to disperse nanoparticles and cut nanomaterials down to nanorange in liquid media. Acoustic waves in liquids can generate small cavitation bubbles; the cavitation bubble nuclei then quickly grow through rectified diffusion and coalescence.⁸ After reaching a critical size, these bubbles collapse violently, creating a strong hydrodynamic flow field in the surrounding liquid. This phenomenon, known as cavitation, can explain the efficiency of sonication in disrupting nanoparticle aggregates and even at exfoliating or cutting nanomaterials.⁸ Sonication to reduce the size of graphene oxide (GO) was shown to be remarkably useful. With the initial GO size of 1.573 μ m, 4 min of horn sonication (~400 W) can reduce the lateral size (LS) down to an average size of 400 nm. Continual sonication brings the size reducing effect further till a size limit is reached at about 170 nm, whose tendency is shown in Figure 3.1. The ln(LS/nm) function (LS stands for lateral size) was further shown to depend on the ln(t/nm) which is in line with the equation

$$\ln\left(\frac{LS}{\mathrm{nm}}\right) = 6.53 - 0.36\ln\left(\frac{t}{\mathrm{min}}\right) \tag{3.1}$$

Surprisingly, the sonication method can also be used to produce graphene nanoribbons (GNRs), as reported by Li et al.9 As schematically shown in Figure 3.2, they firstly exfoliated commercial expandable graphite by 60-s heating to 1000°C to form gas (3% hydrogen in argon). The resulting exfoliated graphite was dispersed in a 1,2-dichloroethane (DCE) solution of poly(m-phenylenevinylene-co-2,5-dioctoxy-pphenylenevinylene) (PmPV) by sonication for 30 min to form a homogeneous suspension. Centrifugation was done to remove large pieces of materials from the supernatant. The GNRs were solution phase-derived, stably suspended in solvents with noncovalent polymer functionalization, and exhibited ultrasmooth edges with possibly well-defined zigzag or armchairedge structures. Electrical transport experiments showed that, unlike single-walled carbon nanotubes (CNTs), all of the sub-10-nm GNRs produced were semiconductors and afforded graphene field-effect transistors with on-off ratios of about 107 at room temperature.

Yet sonication methods inevitably loosely control the aspect of size distribution as revealed by the long error bar of each data point in Figure 3.1a. Normally, it is hard to narrow the

TABLE 3.1

Advantages and	Disadvantages of	of Methods for	Controlling t	the Size and t	the Shape of Graphene
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Defect Degree	Repeatability	Damage	Size Control	Layer Control	Shape Control	Reference
Low	Good	Low	100 nm ⁻¹ mm	No	Yes	9,10
Medium	Poor	Medium	10–100 nm	No	No	11-18
Low	Good	N/A	10 nm-100 µm	Yes	Yes	19–24
High	Good	Very low	10–100 μm	No	No	31
High	Good	Very low	5 nm–5 µm	Yes	No	35,37
	Defect Degree Low Medium Low High High	Defect Degree Repeatability Low Good Medium Poor Low Good High Good High Good	Defect DegreeRepeatabilityDamageLowGoodLowMediumPoorMediumLowGoodN/AHighGoodVery lowHighGoodVery low	Defect Degree Repeatability Damage Size Control Low Good Low 100 nm ⁻¹ mm Medium Poor Medium 10–100 nm Low Good N/A 10 nm–100 µm High Good Very low 10–100 µm High Good Very low 5 nm–5 µm	Defect DegreeRepeatabilityDamageSize ControlLayer ControlLowGoodLow100 nm ⁻¹ mmNoMediumPoorMedium10–100 nmNoLowGoodN/A10 nm–100 μmYesHighGoodVery low10–100 μmNoHighGoodYery low5 nm–5 μmYes	Defect DegreeRepeatabilityDamageSize ControlLayer ControlShape ControlLowGoodLow100 nm ⁻¹ nmNoYesMediumPoorMedium10-100 nmNoNoLowGoodN/A10 nm-100 μmYesYesHighGoodVery low10-100 μmNoNoHighGoodYery low5 nm-5 μmYesNo



FIGURE 3.1 (a) The lateral size of aqueous GO in the function of sonication duration time under the power of ~400 W. Then the initial size of GO is approximately 1.573 μ m. (b) The log of lateral sizes of GO based in e is found having a linear relationship with that of the duration of sonication. The slope is -0.36 and 6.53 for the intercept. (Unpublished data of the authors of this chapter.)



FIGURE 3.2 Chemically derived graphene nanoribbons down to sub-10-nm width. (a) (Left) Photograph of a polymer PmPV/DCE solution with GNRs stably suspended in the solution. (Right) Schematic drawing of a graphene nanoribbon with two units of a PmPV polymer chain adsorbed on top of the graphene via p stacking. (b to f) AFM images of selected GNRs with widths in the 50-nm, 30-nm, 20-nm, 10 nm, and sub-10-nm regions, respectively. All scale bars indicate 100 nm. (Reproduced with permission from Li, X. et al. 2008. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* 319(5867): 1229–32. Copyright 2008, Science Publishing Group.)

distribution as well as to achieve a desirable shape. To control the shape more precisely without compromising the surface chemistry, the diamond-edge-induced nanotomy technique was developed.¹⁰ The sharp diamond knife can cut graphite into graphite blocks of nanoscale with designed shapes; and then, those graphite blocks are intercalated by solvent and exfoliated forming graphene, which was pioneered by Berry et al.¹⁰ Schematically shown in Figure 3.3, the diamond edge is kept perpendicular to the graphene planes of the highly oriented pyrolytic graphite (HOPG), which is subsequently cleaved via C-C bond stretching and crack formation in the direction of cleavage. Depending on the desired shape/size, the HOPG is cut several times, at controlled thicknesses and in different directions to produce graphite nanostructures of defined dimensions and shape. By this method, various kinds of graphene with desirable shape and size can be fabricated, including nanoribbon, -square, -rectangle, and -triangle. Results showed that the edges of the produced graphene nanostructures were straight and relatively smooth with an $I_{\rm D}/I_{\rm G}$ of 0.22–0.28 and a roughness <1 nm. Further, thin films fabricated from ribbons exhibited a band gap evolution with width reduction (0, 10, and ~35 meV for 50, 25, and 15 nm width, respectively).¹⁰ Along with the effectiveness of achieving designed shape and size, another advantage of the nanotomy technique is providing a large density as well as high quality.

3.2.2 CHEMICAL CONTROL

The one-atom thin graphene, all of whose atoms are on the surface, is very reactive and sensitive when exposed to oxidants or metal catalysts. Oxidants like oxidative acids are frequently used, including H_2SO_4 , HNO_3 , $HMnO_4$, and HIO_4 . Pan et al.¹¹ have reported a facile approach for cutting graphene into surface-functionalized zero-dimensional graphene quantum dots (GQDs) under sonication in mixed acids of H_2SO_4 and HNO_3 . The functionalized GQDs of approximate 9.6 nm mean size were found to exhibit ~430 nm bright blue photoluminescence (PL), which has never been observed in bigger graphene nanostructures.

The size and the edge structure of GO can also be tailored by the oxidation of periodic acid.12 The edges were verified to be dominant quinone structures. Under the same excitation wavelength of 365 nm, samples of S1, S2, S3, and S4, whose mean size are respectively 43, 22, 13, and 8 nm, displayed a strong emission peak and the peak shifted from 550 nm of S1, 526 nm of S2, 488 nm of S3 to 470 nm of S4, indicating a size-dependent PL behavior.¹² However, when the lateral size of GQDs reduces down to less than 5 nm and GO is gets fully oxidized, their PL properties become constant, as shown in Sun's report. GQDs with different sizes afforded similar PL which may due to the contained similar small aromatic domains.7 The domain size was inhomogeneous and ranged from small aromatic molecules to large macromolecular domains. The former was responsible for fluorescence in the visible range, while the latter gave PL in the IR range. Fujii and Enoki¹³ reported a simple approach to produce nanosized graphene on the basis of chemical oxidation followed by cutting of the sheet using a scanning probe microscopic (SPM) manipulation technique. The linear defects present in GO were observed to have a spacing of 5-10 nm and a length of >100 nm, which resulted from the linear arrangement of epoxide functional groups. The cutting experiments are directly performed on graphene sheets and cutting is initiated by a point contact between the preoxidized sheet and the atom force microscope (AFM) probe. The local mechanical stress caused by the point contact leads to rupture of the sheet, which proceeds linearly along the linear defect of the epoxide groups. They further noticed that the cut edge shape could have a well-defined alignment along the zigzag direction,¹³ which is based on a theoretical prediction that the linear epoxide groups have preferential alignment along a zigzag direction in the graphene lattice.¹⁴

A systematic study of strain-induced breakage of graphene was promoted by Wang and Ding.¹⁴ They used ab initio calculations to demonstrate that graphene could be cut into graphene nanoribbon, -rectangle, and -triangle on oxidation with the assistance of a uniaxial external tensile strain. The external strain is used to break the symmetry of the graphene honeycomb lattice and is applied along two directions: armchair (AM) and zigzag (ZZ). They found with external strain that the 90° epoxy chain has the highest binding energy and the 0° has the lowest. Further they claimed that there is an energetically preferred orientation for the epoxy chains on graphene if an external uniaxial strain is applied, indicating that linear defect formation resulting from linear epoxy chain was favorable and may benefit cutting graphene into nanostructure of desirable shape and size.



FIGURE 3.3 Schematic diagram for the graphene nanoribbon production process. (a) A descriptive sketch of the nanotomy process showing the diamond-knife-based mechanical cleaving of HOPG block to produce GNBs for GNR production. Process parameters: dr = step-size and $\theta v =$ angle of cleavage. (c) sketch of the two-step nanotomy process to produce GNBs for GQD production. (b,d) GNRs and GQDs are produced by exfoliating the corresponding GNBs in chlorosulphonic acid (superacid). TEM micrographs of 30 nm GNRs and FESEM micrographs of GQDs of different shapes (square, rectangle, and triangle). (Reprinted by permission from Macmillan Publishers Ltd. *Nat. Commun.*, Mohanty, N. et al. 2012. Nanotomy-based production of transferable and dispersible graphene nanostructures of controlled shape and size. 3: 844, copyright 2012.)

Excepting oxidants, metal atoms and nanoparticles that are intimate with carbon can be also used for cutting preoxidized graphene into well-defined shapes.^{15,16} Typically, Ni nanoparticles were first deposited on HOPG plates by a dip-drawing process.15 Afterward, the sample was annealed at 500°C in Ar/ H₂ flow (Normally 1300 sccm, 15 vol% hydrogen) for 1 h, and then the temperature was immediately increased up to the cutting set point (850–1000°C). By applying a multistage cutting, they could obtain ribbons, rectangle, rhomboid, and triangle. Experimental observations and theoretical analysis indicate that the cutting directions in the graphene planes can be controlled by the size of the metal particles,¹⁶ in principle allowing graphene pieces to be cut with discrete armchair or zigzag edges. It is also observed several turns for the channels during cutting. All the angles for these turns are 120° , or 60° . This indicates that the particles move, while cutting, along symmetric directions along the graphene lattice.¹⁶ This catalyst cutting method provides a feasible pathway to fabricate size-, shape-, and edge structure-controllable graphene nanostructures, which may accelerate their usage in electronic devices.

Shape-controlled graphene, especially one-dimensional (1D) GNR, can be alternatively fabricated by unzipping a diameter-selected CNT. Unzipping multiwalled CNTs by plasma etching of nanotubes partly embedded in a polymer

film, Jiao et al. proposed a facile approach to obtain GNRs with smooth edges and controllable widths with relative high yields¹⁷ (Figure 3.4a through f). The GNRs have smooth edges and an arrow width distribution (10-20 nm). Raman spectroscopy and electrical transport measurements reveal the high quality of the GNRs. The average I_D/I_G values were, respectively, 0.38, 0.30, and 0.28 for the single-, bi-, and trilayer GNRs with 10- to 20-nm widths. Unzipping CNTs with well-defined structures in an array allow the production of GNRs with controlled widths, edge structures, placement, and alignment in scalable fashion for device integration. By using gas-phase oxidation, pristine few-layer nanoribbons can be produced by unzipping mildly gas-phase oxidized multiwalled CNTs using mechanical sonication in an organic solvent.¹⁸ The nanoribbons are of very high quality, with smooth edges, low ratios of disorder to graphitic Raman bands, and very high electrical conductance and mobility (up to 5 e² h⁻¹ and 1500 cm² V⁻¹ s⁻¹ for ribbons 10-20 nm in width).

3.2.3 CHEMICAL SYNTHESIS

Precise control over graphene is highly demanded nowadays because it is crucial for probing their fundamental physical properties and introducing them in promising applications.



FIGURE 3.4 AFM images of a nanographene film grown on various substrates synthesized under different conditions: (a) on Al_2O_3 , at 525°C, 0.14 Torr, for 3 h; (b) on sapphire, at 500°C, 0.20 Torr, for 4 h; (c) on quartz, at 500°C, 0.20 Torr, for 5 h; (d) on mica, at 525°C, 0.20 Torr, for 4 h; (e) on Si, at 525°C, 0.204 Torr, for 3 h; and (f) on SiC, at 500°C, 0.20 Torr, for 2 h. The plasma power was 100 W in each case. (With kind permission from Springer Science+Business Media: *Nano Res.*, Catalyst-free growth of nanographene films on various substrates, 4(3), 2011, 315–21, Zhang, L. et al.)

Considering practical uses that need repeatability and scalability, bottom-up graphene synthesis with precise control over sizes and chemical compositions has an indispensable position in the fabrication of fine graphene nanostructures.

Remarkable progress on chemical vapor deposition (CVD) graphene synthesis has been achieved in the last 10 years.¹⁹ To date, Zhang et al.²⁰ developed a new method to grow uniform small graphene directly on various substrates, such as insulators, semiconductors, and even metals, without using any catalyst, as visually and graphically depicted in Figure 3.4. The growth was carried out using a remote plasma enhancement chemical vapor deposition (r-PECVD) system at relatively low temperature. Scanning tunneling microscopy (STM) confirmed that the films are made up of nanocrystalline graphene particles of tens of nanometers in lateral size.

Liu et al.^{21,22} reported a CVD approach that allowed the direct synthesis of uniform single-layered, large-size (up to 10,000 μ m²), spatially self-aligned, and single-crystalline hexagonal graphene flakes (HGFs) by using liquid copper as the substrate (Figure 3.5). These HGFs showed an average two-dimensional resistivity of $609 \pm 200 \Omega$ and saturation current density of 0. $96 \pm 0.15 \text{ mA/}\mu\text{m}$, demonstrating their good conductivity and capability for carrying high current density. Size control could be achieved by differing the annealing temperature and time to vary the nucleation distribution and density.

Müllen et al. devoted much effort to the atomically precise synthesis of nanographene and GNRs for decades. Nanographene and GNRs of various sizes and shapes have been obtained in bulk scale, thus offering an opportunity for additional solution/vacuum processing and device fabrication. The bottom-up synthesis of graphene was initiated through the versatile organic chemistry of polycyclic aromatic hydrocarbons (PAHs).^{23,24} By far, the largest synthesized nanographene molecule consists of 222 carbon atoms with a disk diameter of 3.2 nm, while one of the smallest has a size of approximately 1.4 nm.²⁵ By appropriately choosing the synthetic units, normally the high-molecular-weight oligophenylene precursors, we can obtain various types of graphene nanostructure²⁶: the triangle, the ribbon, and Chevron-like shape.

3.2.4 Post Synthesis Separation (Chemically Converted Graphene)

3.2.4.1 Differential Separation

Differential separation comes up as one time-efficient and low-cost way to get graphene sheets with wide size distribution. The sedimentation rate of particles in a medium with given density ρ_m and viscosity η_m , in a centripetal force field g', can be described as²⁷

$$U = \frac{2g'(\rho_{\rm p} - \rho_{\rm m})(r+t)^2}{9\eta_{\rm m}}$$
(3.2)

Here *r* denotes the radius of the core particle, *t* is the thickness of the solvated shell,²⁸ and ρ_p denotes the apparent density of the particle. Equation 3.1 indicates that the colloid



FIGURE 3.5 The growth of HGFs on flat liquid Cu surfaces on W substrates. (a) Scheme showing CVD process for the synthesis of HGFs on liquid Cu surface. (b) SEM image showing partially covered and well-dispersed HGFs using 6 sccm $CH_4/300$ sccm H_2 at 1,120°C for 30 min. (c) SEM image of HGFs showing a compact assembly of HGFs in which the dark and bright parts represent HGFs and the Cu surface, respectively. (d) SEM image of a near-perfect 2D lattice composed of similar-sized HGFs. (e) SEM image of the sample for 2 h growth showing the continuous graphene film with uniform contrast. (f and g) SEM images of large sized HGFs showing that the average sizes are approximately 50 μ m and approximately 120 μ m using 1140°C and 1160°C, respectively. Experimental conditions from (c) and (d) are the same, using 6 sccm $CH_4/300$ sccm H_2 at 1120°C for 38 min. (Geng, D. et al. Uniform hexagonal graphene flakes and films grown on liquid copper surface. *Proc. Natl. Acad. Sci.* 109(21): 7992–6, Copyright 2012, National Academy of Sciences, U.S.A.)

sedimentation rate U depends on both the colloid core radius r (that is why large particles sediment faster than small ones) and the properties of the medium (ρ_m and η_m). The density difference between ρ_p and ρ_m is the dominant term. The particles stop sedimentation when they reach the medium of the same density (i.e., $\rho_{\rm p} - \rho_{\rm m} = 0$). This is how we estimate the apparent density of colloids by differential separation. As long as the graphene, mostly chemically converted graphene (CCG), can be solvated by given solvents such as the polar solvents like water (H₂O), N-methyl-2-pyrrolidone (NMP), and dimethyl formamide (DMF), or the nonpolar solvents like tetrachloromethane (CCl₄) and cyclohexane, those graphene derivatives can be sorted by adjusting separation rate and time. After combining the solvated shell and balancing the buoyancy, graphene will sedimentate down to the bottom if the buoyancy cannot match the centrifugal force; or they will stay where the buoyancy matches the centrifugal force, forming the supernatant. The CCG staying in the supernatant is definitely more easily solvated than the remnant left in the bottom. Further, the ability of contacting solvents or being solvated by them will diversify their applications. This strategy is almost universally available for all kinds of CCG. For the case of low oxidized GO, they normally have a very thin solvated shell, which means they can be easily separated from the liquid phase. All we need is to adjust the rate to a lower level in order to achieve a smaller centrifugal force.²⁹ The above-mentioned separation is based on the neutral aqueous system. If CCG has very small I_D/I_G , we should use other solvents to alter the aqueous system. For instance, NMP and DMF, two very strong polar solvents, are capable of solving small I_D/I_G CCG and sorting CCG according to their size when combining differential separation. Now that buoyancy is highly related to the solvated shell, the overall separation effect should be influenced by thinning or expanding the solvated shell like adjusting the pH value.³⁰

By analyzing the zeta potentials of GO with two kinds of sizes under varied pH values, Shi et al.31 found that there existed a certain pH range at which two kinds of GO (Figure 3.6), f1 and f2, had right opposite zeta potential, which means f1 the small GO remains soluble while f2 the big GO is protonated so f2 can be easily expelled from the suspension. Meanwhile, they found f1 had more oxygen content than f2. This size effect inherited into the Langmuir-Blodgett (LB) film and greatly influenced the films' resistance and transmittance; higher oxygen content leads to higher sheet resistance. Because of lower oxygen content in bigger GO, the LB film fabricated from f2 showed to have lower resistance and higher transmittance. Generally speaking, the differential separation methods are effective and of low cost as long as we do not put too much emphasis on the precise size distribution. Besides, they fit the practical usages well due to the scalable production of CCG with rough size distribution. Yet there are some occasions that need precise control of the size distribution, aiming at more advanced research. Then we should probably use a modified version of differential separation, that is, density gradient separation (DGS).



FIGURE 3.6 Separation of graphene oxide by adjusting pH value. Size of graphene oxide can greatly affect properties of GO, such as resistance and transparency. (Reprinted with permission from Wang, X., Bai, H., and Shi, G. Size fractionation of graphene oxide sheets by pH-assisted selective sedimentation. *J. Am. Chem. Soc.* 133(16): 6338–42. Copyright 2011 American Chemical Society.)

3.2.4.2 Density Gradient Separation

3.2.4.2.1 Zonal Centrifugation

By using a differential separation, rough size distributions can be achieved by either a one-step or multistep separation process. For more precise cases, the researchers may turn to DGS, which originate from the separation of biomacromolecules. Once this method was transplanted to sort inorganic nanomaterials, hundreds of investigated cases had shown this strategy effective for nearly all nanocrystals including zero-dimensional FeCo@C,28 gold nanoparticles,¹ CdSe nanodots,¹ 1D CdS nanorods,³² CNTs,^{33,34} and of course, 2D CCGs.³⁵ Schematically shown in Figure 3.7, gradients of different densities are first layered bottom up. Then the analyst suspension with appropriate solvent is placed on top of the gradients. Once the centrifugation begins, the analyst particles start to move down to the bottom. The larger and heavier particles have a higher sedimentation rate after balancing the centrifugal force against buoyancy and viscous drag. Higher density and viscosity could slow down the smaller graphene sheets while allowing larger and heavier sheets to pass through.



FIGURE 3.7 Schematic illustration of the mechanism of DGUR separation of CMG sheets with different sizes. (Reprinted with permission from Sun, X. et al. Monodisperse chemically modified graphene obtained by density gradient ultracentrifugal rate separation. *ACS Nano* 4(6): 3381–9. Copyright 2010 American Chemical Society.)