Chapter 1
Introduction

Hassan Raza

Abstract  This chapter serves as a glue for the contributed chapters in this monograph. Here, we try to summarize the multi- and inter-disciplinary topics covered in various chapters. All chapters are written in a tutorial and review fashion, to serve not only as the state-of-the-art reference for practitioners but also as a useful tutorial for incoming researchers. Each chapter leads the reader from introduction to advanced topics and relates to the topics covered in other chapters wherever applicable. We start with a brief introduction to the atomic and electronic structure of graphene and its various nanostructures, leaving a more detailed discussion to later chapters. We then discuss the historical development of graphene research in post-2004 era and relate it to the efforts in pre-2004 time frame. Finally, we focus on the metrology, synthesis, properties and applications of graphene nanomembranes and nanostructures, which relates to the contributed chapters divided into three sections. This chapter is not a review of graphene nanoscience and nanotechnology research and the history of graphene in any way.

1.1 Overview

Graphene is a two-dimensional single-atom thick membrane of carbon atoms arranged in a honeycomb crystal [1–4]. It is a perfect example of a two-dimensional electron system for a physicist, an elegant form of a two-dimensional organic macromolecule consisting of benzene rings for a chemist and a material with immense possibilities for an engineer due to its excellent electrical, magnetic, thermal, optical and mechanical properties. Bilayer graphene is also an important
Fig. 1.1 Graphene and its nanostructures. Two graphene membranes with Bernal stacking order form bilayer graphene. One-dimensional nanoribbons with armchair and zigzag edges conceptually extracted from the two-dimensional graphene are shown. Atomic visualization was done using Hückel-NV [17].

Another direction is of nanopatterned graphene structures, most notably graphene nanoribbons [8–16] consisting of one-dimensional stripes of the honeycomb arrangement, which lead to bandgap opening, edge functionalization, etc. Depending on the edge shape, two important nanoribbons are armchair graphene nanoribbons and zigzag graphene nanoribbons shown in Fig. 1.1. Finally, when multiple graphene layers are stacked, one obtains graphitic materials, and multiple nanoribbons stacking leads to multilayer graphene nanoribbons.

Historically, the word graphene comes from the Greek word graphein, which means to write – one of the earliest uses of this material. In the 1800s, the name graphite was given to the bulk material used in pencils by the German chemist Wagner. For some time, graphite was mistakenly thought to be a form of lead. The confusion of lead pencils comes from that misunderstanding. Nonetheless, graphene and graphite have been of immense use to mankind both in physical sciences and in technology as well as in the art form. The inspiring arrangement of carbon atoms leads to the artistic and architectural lattice shell structures – most notable perhaps is Bucky ball by Buckminster Fuller.

The most important historical application of graphite was in the molds to make cannon balls. It was truly a strategic material. In fact, the British crown imposed
embargo on graphite during the Napoleonic wars. Other historical uses of graphite include crucibles due to its refractory nature, lubrication because graphene planes can slide against each other with ease, electrodes and motor/generator brushes due to high conductivity, and materials processing e.g. steel and alloy making. The intercalation compounds of graphite were first reported in the 1840s and have been extensively studied since the 1930s [18]. In recent history, the use of graphite as a neutron moderator to thermalize high energy neutrons in nuclear reactors has been of great significance. The fundamental breakthroughs towards the physical understanding of graphene and graphite were routed in the 1940s and 1950s. Modern derivatives also include carbon nanofibres (with diameters less than 10 nm) prepared and studied extensively in the 1970s and 1980s [2, 19]. Graphene can also be conceptually thought of as a mother material for Bucky ball molecules and carbon nanotubes. Their discoverers in the 1980s (by R. F. Curl Jr, H. W. Kroto, R. E. Smalley, J. R. Heath and co-workers) and 1990s (by S. Iijima), respectively, formed the basis of not only new fundamental research areas, but also exciting new set of applications [19–21].

Since graphene is just an atomic plane of graphite, it was known to humans in the form of graphite deposits around the globe at least for few centuries and was effectively discovered since the invention of X-ray crystallography. It was important to isolate this atomic plane and, much more important, to show that this is a unique material worth further studying. Initial theoretical effort to study its 2D electronic structure was made by P. R. Wallace in 1947 [1] followed by its extension to the electronic structure of 3D graphite by D. F. Johnston, J. W. McClure and M. Yamazaki [22–24]. J. W. McClure also emphasized that the quasiparticles were Dirac-like, which was re-iterated by G. Semenoff [25].

In a nutshell, the results suggested that graphene is a semi-metal, i.e. it has zero bandgap, with linear dispersion around the chemical potential leading to cones in two-dimensional reciprocal space. This was quite a surprising result because most of the matter waves have quadratic dispersions following Schrödinger equation, which is first order in time and second order in space. In the simplest model, it leads to the following dispersion for the conduction and valence bands, respectively:

\[ E_S(k) = E_{c,v} + \frac{\hbar^2 |k|^2}{2m_{c,v}} \]  

(1.1)

where \( E_{c,v} \) are the conduction and valence band edges and \( m_{c,v} \) are the effective masses of electrons in conduction band and holes in valence band, respectively (\( m_e \) is negative, \( S \equiv \text{Schrödinger} \)). One gets zero bandgap for \( E_c = E_v \); however, the dispersion still remains quadratic.

In contrast to the Schrödinger equation, the dispersion for the Dirac equation is

\[ E_D(k) = \pm \sqrt{m^2c^4 + \hbar^2c^2|k|^2}, \]  

(1.2)

where \( c \) is the speed of light and \( m \) is the relativistic mass (\( D \equiv \text{Dirac} \)). The positive and negative dispersion plots are shown in Fig. 1.2, which give rise to a
mass-dependent gap of $2mc^2$ between the positive energy of matter (electron in this case) and the negative energy of anti-matter (positron) – the $mc^2$ product for an electron is about 0.512 MeV. In the limiting case of $m = 0$, clearly the gap becomes zero. Furthermore, (1.2) becomes

$$E_D(k) = \pm \hbar c |k|$$

which is plotted in Fig. 1.2 depicting the linear dispersion with zero bandgap, the energy scale on the order of MeV and the speed equal to that of light.

As a reference, the band structure of graphene is shown in Fig. 1.2, which follows the following equation based on tight-binding description [2]:

$$E_G(k) = \pm t \sqrt{1 + 4 \cos \left( \frac{3k_x a_{cc}}{2} \right) \cos \left( \frac{\sqrt{3}k_y a_{cc}}{2} \right) + 4 \cos^2 \left( \frac{\sqrt{3}k_y a_{cc}}{2} \right)} ,$$

where $a_{cc} = 1.42 \text{Å}$ is the C–C bond length and $t$ is the first nearest-neighbour tight-binding parameter ($G \equiv \text{graphene}$). Clearly the bandgap is zero and dispersion is linear around the points where conduction and valence bands meet with a renormalized velocity $v$ resulting in

Fig. 1.2 Graphene band structure. Dirac dispersions with $2mc^2$ gap are shown. In the limit of $m = 0$, the gap becomes zero with a linear dispersion, where the energy scale is on the order of MeV. In analogy, the graphene band structure also has a linear dispersion with zero gap around the Dirac point, albeit with the energy in eV range.
\[ E_G(k) = \pm \hbar v |k| \] 

(1.5)

similar to the dispersion of Dirac’s in (1.3). Readers are encouraged to see Chap. 8 for more discussion about the electronic structure in detail.

This analogy led to the suggestion that electrons and holes act like Dirac fermions in graphene with zero mass and hence zero gap. In other words, charge carriers are mass-less relativistic Dirac fermions with point of intersection between conduction and valence bands labelled as Dirac point and the dispersion cones usually referred to as Dirac cones. Based on this analogy, sometimes phrases like quantum relativity in our pencils have been used. Furthermore, there are six points over the Brillouin zone where the conduction and the valence bands meet as shown in Fig. 1.2. Although, one may think that there are six Dirac points, with careful analysis, one concludes that only two points are inequivalent. Moreover, these two points are also related by the time-inversion symmetry.

There have been several efforts geared towards graphene synthesis. H. P. Boehm et al. [27] observed ultra-thin graphitic samples using electron microscopy in 1962. A. J. van Bommel et al. [28] studied thin graphitic fragments on the basal faces of SiC in 1975 by using graphitization of SiC pioneered by E. Acheson in the 1890s [29]. Since the fundamental understanding of photoelectric effect provided by A. Einstein, it has been well known that adsorbates severely affect surface properties. Carbon deposition on metal substrates has been well studied since the 1960s, see e.g. the literature review in [30]. In the surface science community, sometimes graphitic features were observed on metal surfaces, see e.g. [31]. With the discovery of scanning tunnelling microscopy (STM) in the early 1980s [32], visualizing graphite substrates became a routine practice to obtain atomic resolution images. Around the turn of the century, efforts were started to manipulate graphite samples to obtain graphene [33–36].

It is quite interesting that the sample preparation for STM involves pealing graphite samples using scotch tape to expose fresh basal planes of graphene. Understandably, researchers used to throw away the scotch tape with graphitic flakes on it. In 2004, instead of throwing away the tape, Manchester group transfered some of the flakes on a silicon substrate with 300 nm of silicon oxide film and isolated graphene to study the field effect [37]. With the right thickness of the silicon oxide film, it was not only possible to image graphene using an optical microscope but also possible to determine the number of layers from the colour difference or reflection variations as shown in Fig. 1.3. This ground-breaking discovery of transferring graphene onto an arbitrary substrate from graphite led to an immense interest in this material system. The ambipolar field effect in graphene and few layer graphene was demonstrated [37,38] and at the same time very high electronic quality was observed despite its atomic thickness and being placed on atomically rough substrate and covered with all sorts of adsorbates. No one could have predicted that the material could be so good electronically given the common wisdom that the thinner the film the worse its quality. The present day graphene boom is precisely due to this excellent electronic quality. In comparison, monolayer dichalchogenides also
show field effect but with poor electronic quality and hence not as attractive for nanoelectronics [38].

The important breakthrough that propelled graphene research to its heights was the publication of back-to-back papers from the Manchester and Columbia groups [5,39,40] that demonstrated an unusual quantum Hall effect in monolayer graphene. This put to rest any doubts about reproducibility of the previous Manchester results and, from this point, the research community has eagerly embraced the paradigm of one atom thick experimental system with exceptionally high crystal and electronic quality and exotic electron transport properties. Shortly, the field effect in few layer thin epitaxial graphitic layers on SiC was also reported, although the effect was small and the resistance changed by less than 1% because screening becomes important in multilayer devices and does not allow change the carrier concentration across the whole device’s thickness [41]. For these groundbreaking experiments, 2010 Physics Nobel prize was awarded to Geim and Novoselov (from Manchester group).

Although seemingly low-tech and humble, the Scotch tape method has allowed researchers to obtain graphene in sufficient quantities for studying fundamental physics and making proof-of-concept devices, which has proved invaluable for advancing graphene research. However, the isolation method is not scalable to be useful in any technology. Therefore, novel synthesis methods are required for large-scale synthesis of graphene membranes. Since the initial discovery, the community has scaled the thin film growth methods of graphite to mono- and multilayer graphene. As of today, epitaxial growth of graphene on SiC by thermal decomposition [42–44], chemical vapour deposition method of graphene synthesis
on metal substrates \cite{45–48} and chemical methods of graphene synthesis have been achieved \cite{49}. All these methods hold great promise for enabling future integrated circuits using graphene-based nanoelectronic devices. However, it is still a long way to achieve the goal of producing high quality wafer scale graphene reproducibly with defect densities on the order of today’s state-of-the-art silicon processing.

### 1.2 Book Summary

This book covers key topics related to graphene nanoelectronics from science and technology perspectives. The contents of most of these chapters are multi- and inter-disciplinary, which makes the integration challenging in a monograph form. However, the distinguished contributing authors have worked closely to make the book coherent and wherever applicable, have cross-referenced the material presented in other chapters. Furthermore, the contributed authors have not only tried to make this book a good reference by providing a review of the state of the art in their respective area of expertise but also presented the material in a tutorial form to make it a good starting point for the newcomers.

In this collection, the topics range from metrology and synthesis to physical properties as well as device applications. For the sake of clarity, we have divided the book into three parts as described below. However, one should be careful that many chapters discuss topics listed in other parts as well. In the next few sections, we outline the three parts of the book and discuss the topics covered briefly to relate them to various chapters.

#### Part I: Metrology and Synthesis

In this part, the contributed authors discuss metrology and characterization of graphene samples as well as graphene synthesis and device fabrication. This part starts with the introduction and application of Raman spectroscopy in Chap. 2, which has been an extremely valuable tool for studying and characterizing carbon-based nanomaterials for over 40 years. Raman spectra give quantitative information to various physical properties of graphene, e.g. defects, edges, number of layers and doping. Electronic structure and other physical processes contribute to the Raman spectra, which are discussed in detail. The discussion about the Raman spectroscopy of graphene would be concluded with the near-field optics and coherent phonon spectroscopy.

Chapter 3 discusses scanning tunnelling microscopy (STM) and spectroscopy (STS), which is an extremely valuable and versatile tool for probing local properties of graphene and its various nanostructures and edges. Discussion will be provided about the use of STM and STS to experimentally study and characterize the atomic structure, electronic structure, Landau level spectroscopy, defects, edge
states, interactions, substrate effects, localization, dislocations and misalignments in graphene, multilayer graphene, nanoribbons, etc. Another useful avenue is STM-based nanolithography of graphene to form nanostructures.

ARPES (angle-resolved photoemission spectroscopy) has been widely used to study the band structures of graphene and multilayer graphene. Chapter 4 starts with an introduction and a review of ARPES for various graphene structures. It further discusses the effect of adsorbates on graphene and multilayer graphene. Adsorbates are an important consideration in graphene, which are also conceptually related to intercalation graphitic compounds. Unintentional adsorbates can undesirably change the properties and band structure. Whereas, a controlled deposition of adsorbates can lead to systematic effects, e.g. doping, and magnetism.

The next three chapters mainly discuss graphene synthesis and device fabrication. Chapter 5 starts the discussion along these lines with an introduction to graphitization of SiC(0001) surface to form graphene in a historical perspective. The science and technology discussed in this chapter may lead to large-scale fabrication of graphene nano-electronic devices [41,42,44]. The next chapter carries on the discussion along the same lines, i.e. the fabrication of electronic and spintronic devices using the state-of-the-art tools, starting with epitaxial graphene on SiC. Chapter 6 provides details about the electrical characterization of graphene electronic and spintronic devices. In short, these chapters take a reader through steps of growth, material characterization, device fabrication, atomic layer deposition dielectric growth and finally transport characterization.

Although epitaxial growth is a viable candidate for both large-scale fabrication of electronic and spintronic devices, another growth method holds promise for the same application, notably for spintronics. Chapter 7 discusses this alternate fabrication method, i.e. chemical vapour deposition (CVD) of graphene on metallic substrates. This chapters discusses the growth mechanism, characterization and magnetic effects.

\textbf{Part II: Electronic Structure and Transport Properties}

This part of the book begins with Chap. 8, which provides a thorough introduction to the tight-binding model of graphene and bilayer graphene. Furthermore, the connection of the tight-binding model to the Dirac-like Hamiltonian is discussed. Advanced concepts related to these material systems are explained in a tutorial manner, e.g. chirality, pseudospin, Berry phases, trigonal warping ($\gamma_3$), Lifshitz transition, Landau level spectrum, quantum Hall effect and gate-induced bandgap opening, etc.

With the introduction to the electronic structure of the two-dimensional graphene and bilayer graphene, Chap. 9 discusses the effect of quantization and edge shapes on the electronic spectrum and the transport properties of the one-dimensional graphene nanoribbons. Interesting features like edge localization in zigzag nanoribbons near the equilibrium chemical potential and their absence in the
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Armchair graphene nanoribbons are discussed. Furthermore, the effect of disorder and impurity scattering is discussed in detail. The chapter concludes with the effect of edge shape on zero conductance Fano resonance in graphene nanojunctions.

Chapter 10 builds on the discussion provided in the previous two chapters to study the electronic structure of quantum rings and superlattices made out of graphene to introduce periodicity in nanoconstricted graphene via boundary conditions and explicit potential, respectively. With properly engineered rings, an effective magnetic flux through the rings leads to unique features in the energy spectrum and a persistent current through the ring. On the other hand, a superlattice structure leads to new Dirac points at equilibrium chemical potential, which gives rise to conductance resonances in the quantum transport through these systems.

Chapter 11 extends the discussion in Chap. 8 by providing analysis of the electronic structure of arbitrarily stacked multilayer graphene with and without a magnetic field. The energy band structure, Landau-level spectrum and low-energy effective theory of multilayer graphene are discussed. This chapter concludes with the discussion about the quantum Hall effect, optical conductivity and electrical conductivity.

Chapter 12 reports the state of the art in the macroscopic semi-classical transport through graphene in the presence of disorder and impurities and compare it with the quantum transport theory of graphene and recent experiments. The main topics covered in this context are graphene screening within the random phase approximation (RPA), the self-consistent approximation for ground state properties and effective medium theory for the charge transport.

At the nanoscale, one needs the quantum transport theory. Chapter 13 along with Chaps. 15–18 in Part III provides a set of quantum transport theoretical framework based on Green’s function formalism. In this context, Chap. 13 starts with the discussion about conductance quantization of $e^2/h$ per channel per spin in graphene nanoribbons and the effect of edge disorder, dislocations, adsorbates and impurities on the electrical conduction through nanoribbons. The topic of localization discussed in this chapter also relates to the discussion in Chap. 3.

Chapter 14 is a unique chapter about the graphene oxide. This chapter discusses comprehensively the synthesis, fabrication, characterization, ab initio analysis of the bonding and electronic structures. A detailed discussion about its applications is further provided. This chapter relates potential applications with graphene oxide to some of the other topics discussed in the book as a whole.

Part III: From Physics and Chemistry of Graphene to Device Applications

This part of the book is about device applications utilizing graphene and its various nanostructures. However, they also complement the electronic structure and transport discussion of the second part of the book. Nonetheless, the emphasis on device physics makes the chapters in this part very unique. These chapters are
mostly theoretical in nature, but experimental results are comprehensively discussed wherever applicable.

A PN junction diode is the most basic device which is formed by metallurgically joining p-type and n-type semiconducting regions. While graphene is in fact a semi-metal, it is still possible to make PN junction devices. Chapter 14 discusses the transport properties of such PN junctions based on graphene. It further discusses the angular selective nature of transmission and Klein tunnelling. Magneto-transport through these junctions is also discussed in the context of snake orbits, edge effects, disorder and strain. Finally, details about the numerical modelling of the quantum transport are provided.

The next chapter is about field effect transistors (FETs) using monolayer and bilayer graphene nanoribbons with armchair and zigzag edges. FETs are the workhorse of today’s integrated circuits. This chapter discusses the performance analysis of Schottky barrier field effect transistor using armchair-edged and doped zigzag edged bilayer graphene nanoribbons. Finally, nanoelectromechanical switches are discussed for memory applications.

Chapter 17 discusses the electric field modulation in graphene nanostructures. Bandgap opening in bilayer and multilayer graphene has already been discussed in Chaps. 8 and 11. This chapter extends the discussion along these lines in the presence of misalignments and strain as well as provides a review of the modulation effects in armchair and zigzag nanoribbons with and without edge roughness. Device applications for these material systems are also discussed in detail.

The final (Chap. 18) takes the reader from device characteristics to the integration of individual devices into integrated circuits for scalable applications. In particular, discussion about graphene inverter characteristics is provided. With this, the book concludes with an overarching theme of a unique source of review and tutorial material for graphene nanoelectronics research from basic and applied perspectives.

1.3 Outlook

The area of graphene research is progressing by leaps and bounds. Everyday, new discoveries are being made. Given the exponential growth trend, we anticipate that another monograph within 5–10 years will cover the more advanced topics in graphene nanoelectronics, once the facts of graphene gold rush have been established on solid footings.

We also anticipate that once the basic science of graphene is established on a more solid footing, novel applications in very diverse areas [50–52] utilizing this exceptional material will follow suit.

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References
