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Graphene

Synthesis, Properties, and Phenomena

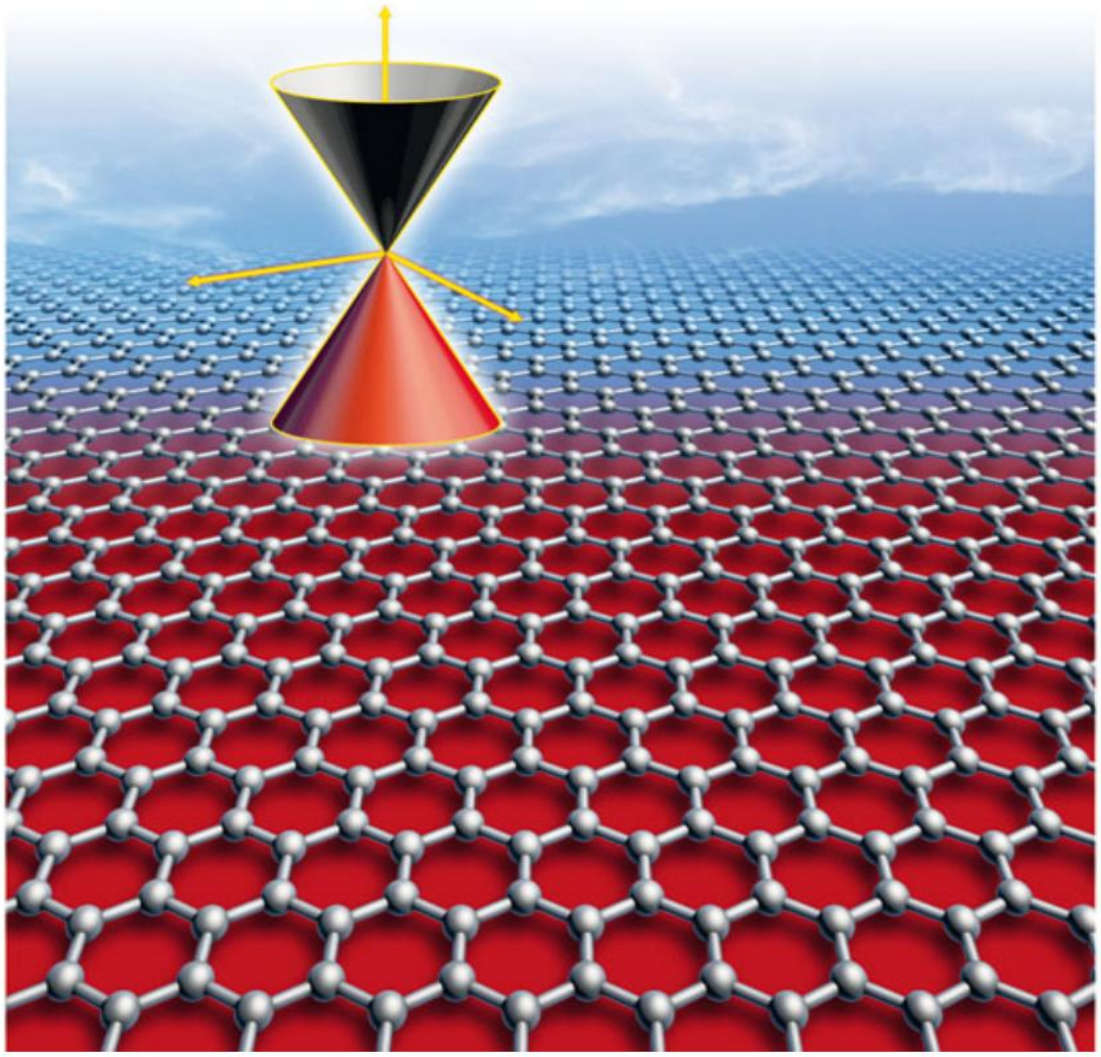

Table of Contents

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Preface

Graphene is a fascinating subject of recent origin, its first isolation being made possible through micromechanical cleavage of a graphite crystal. Since its discovery, graphene has caused great sensation because of its unusual electronic properties, and scientists from all over the world have been working on the varied facets of graphene. Thus, there has been much effort to synthesize both single-layer and few-layer graphenes by a number of methods. A variety of properties and phenomena have been investigated, and many of the studies have been directed toward understanding the physical and chemical properties of graphene. Raman spectroscopy has been particularly useful in unraveling various aspects of graphene. A graphene field-effect transistor, a basic building block of nanodevices, is a single-element laboratory to study electron–phonon interactions using Raman scattering. The low-frequency electrical noise or the flicker noise in graphene devices defines the figure of merit of a device and has contrasting behavior for single- and bilayer-graphene devices. Magnetic properties have been of equal interest with the indication that graphene may be ferromagnetic at room temperature, exhibiting magnetoresistance. Graphene nanoribbons have attracted attention because of their unique electronic structure and properties. Graphene also provides a playground for exploring many quantum field related phenomena such as Klein tunneling, antilocalization, zitterbewegung, vacuum collapse by Lorenz boost and so on. Suspended graphene devices have been used to study nanoscale electromechanics and quantum Hall effect.

A variety of applications of graphene have come to the fore. Its use in supercapacitors and batteries has been explored. Other properties of graphene, which are

noteworthy, are those that enable its use in nanoelectronics, field emission and catalysis. Biological aspects of graphene have been investigated by a number of workers, with emphasis on its toxicity and its possible use for drug delivery.

In this book, we have tried to cover many of the salient aspects of graphene, which are of current interest. Although the book mostly deals with graphene, we have included some material on graphene-like inorganic layered materials. It is possible, however, that some topics have been left out owing to constraints on the size of the book and possible errors in judgement. We trust that the book will be useful to students, teachers, and practitioners, and serves as an introduction to those who want to take part in the exciting developments of this subject.

June 2012

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Chapter 1

Synthesis, Characterization, and Selected Properties of Graphene

C. N. R. Rao, Urmimala Maitra and H. S. S. Ramakrishna Matte

1.1 Introduction

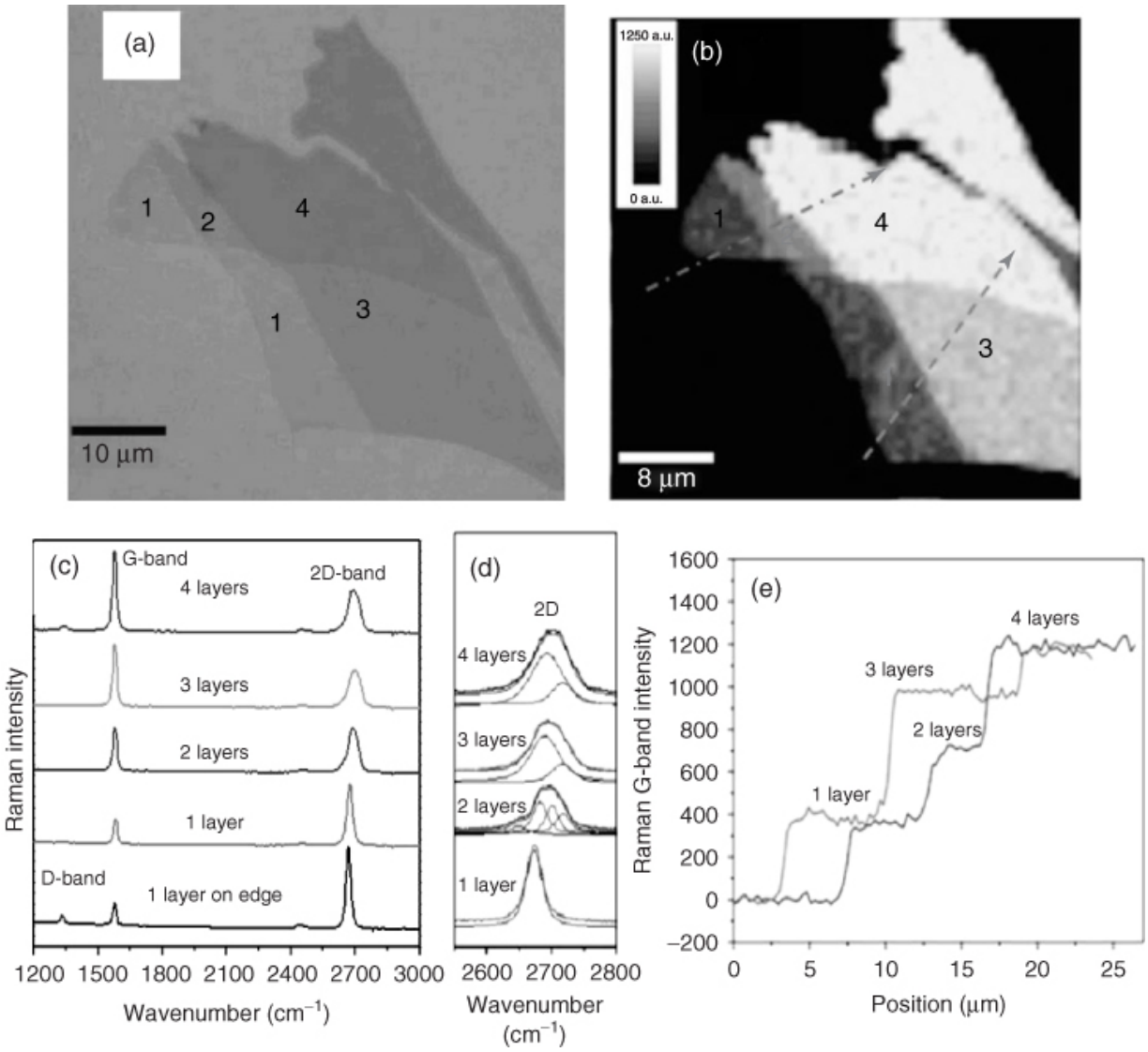
Carbon nanotubes (CNTs) and graphene are two of the most studied materials today. Two-dimensional graphene has specially attracted a lot of attention because of its unique electrical properties such as very high carrier mobility [1–4], the quantum Hall effect at room temperature [2, 5], and ambipolar electric field effect along with ballistic conduction of charge carriers [1]. Some other properties of graphene that are equally interesting include its unexpectedly high absorption of white light [6], high elasticity [7], unusual magnetic properties [8, 9], high surface area [10], gas adsorption [11], and charge-transfer interactions with molecules [12, 13]. We discuss some of these aspects in this chapter. While graphene normally refers to a single layer of sp^2 bonded carbon atoms, there are important investigations on bi- and few-layered graphenes (FGs) as well. In the very first experimental study on graphene by Novoselov *et al*. [1, 2] in 2004, graphene was prepared by micromechanical cleavage from graphite flakes. Since then, there has been much progress in the synthesis of graphene and a number of methods have been devised to prepare

high-quality single-layer graphenes (SLGs) and FGs, some of which are described in this chapter.

Characterization of graphene forms an important part of graphene research and involves measurements based on various microscopic and spectroscopic techniques. Characterization involves determination of the number of layers and the purity of sample in terms of absence or presence of defects. Optical contrast of graphene layers on different substrates is the most simple and effective method for the identification of the number of layers. This method is based on the contrast arising from the interference of the reflected light beams at the air-to-graphene, graphene-to-dielectric, and (in the case of thin dielectric films) dielectric-to-substrate interfaces [14]. SLG, bilayer-, and multiple-layer graphenes (<10 layers) on Si substrate with a 285 nm SiO_2 are differentiated using contrast spectra, generated from the reflection light of a white-light source (Figure 1.1a) [15]. A total color difference (TCD) method, based on a combination of the reflection spectrum calculation and the International Commission on Illumination (CIE) color space is also used to quantitatively investigate the effect of light source and substrate on the optical imaging of graphene for determining the thickness of the flakes. It is found that 72 nm thick Al_2O_3 film is much better at characterizing graphene than SiO_2 and Si_3N_4 films [16].

Figure 1.1 (a) Optical image of graphene with one, two, three, and four layers; (b) Raman image plotted by the intensity of G-band; (c) Raman spectra as a function of the number of layers; (d) zoom-in view of the Raman 2D-band; and (e) the cross section of the Raman image, which corresponds to the dashed lines in (b).

(Source: Reprinted with permission from Ref. [15].)

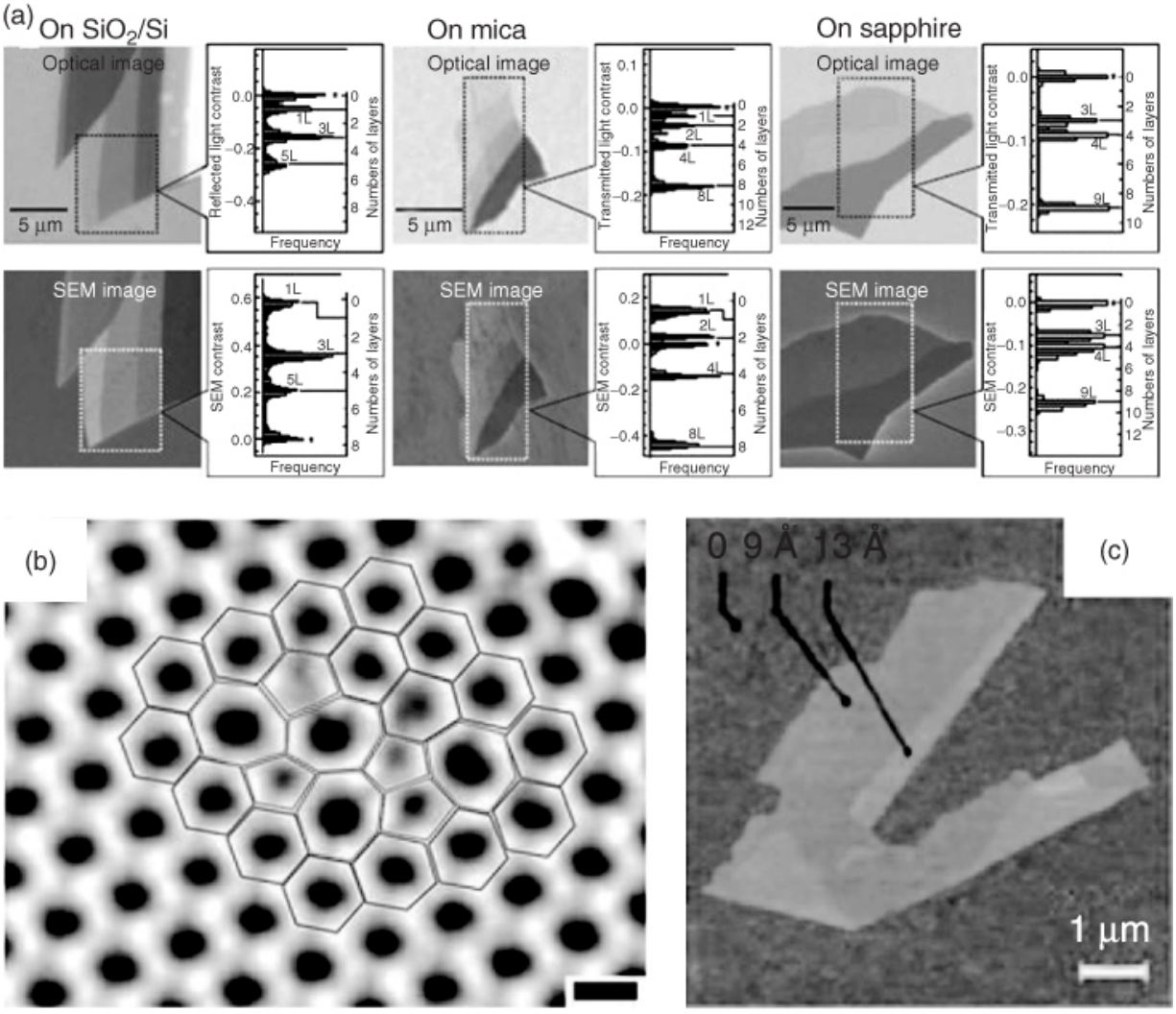


Contrast in scanning electron microscopic (SEM) images is another way to determine the number of layers. The secondary electron intensity from the sample operating at low electron acceleration voltage has a linear relationship with the number of graphene layers (Figure 1.2a) [17]. A quantitative estimation of the layer thicknesses is obtained using attenuated secondary electrons emitted from the substrate with an in-column low-energy electron detector [18]. Transmission electron microscopy (TEM) can be directly used to observe the number of layers on viewing the edges of the sample, each layers corresponding to a dark line. Gass *et al*. [19] observed individual atoms in graphene by

high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) in the aberration-corrected mode at an operation voltage of 100 kV. Direct visualization of defects in the graphene lattice, such as the Stone–Wales defect, has been possible by aberration-corrected TEM with monochromator (Figure 1.2b) [20]. Electron diffraction can be used for differentiating the single layer from multiple layers of graphene. In SLG, there is only the zero-order Laue zone in the reciprocal space, and the intensities of diffraction peaks do not therefore, change much with the incidence angle. In contrast, bilayer graphene exhibits changes in total intensity with different incidence angles. Thus, the weak monotonic variation in diffraction intensities with tilt angle is a reliable way to identify monolayer graphene [21]. The relative intensities of the electron diffraction pattern from the {2110} and {1100} planes can be used to determine the number of layers. If $I_{\{1100\}}/I_{\{2110\}}$ is >1, it is reported as SLG, and if the ratio is <1, it is multilayer graphene [22]. Thickness of graphene layers can be directly probed by atomic force microscopy (AFM) in tapping mode. On the basis of the interlayer distance in graphite of 3.5 Å [3], the thickness of a graphene flake or the number of layers is determined as shown in Figure 1.2c [3]. Scanning tunneling microscopy (STM) also provides high-resolution images of graphene.

Figure 1.2 (a) Comparison of the counting of layers by optical microscopy and SEM for graphene on SiO_2/Si, mica, and sapphire. For each figure is shown a histogram of the distribution of graphene layers within the rectangular area indicated by a dotted line. (Source: Reprinted with permission from Ref. [17].) (b) High-resolution transmission electron microscopic image showing the Stone–Wales defects in graphene. (Source: Reprinted with permission from Ref. [20].) (c) Atomic force microscopic image of single-layered graphene. Folded edge shows a height increase of 4 Å indicating single-layer graphene.

(Source: Reprinted with permission from Ref. [3].)



Raman spectroscopy has been extensively used as a nondestructive tool to probe the structural and electronic characteristics of graphene [3]. Figure 1.1c shows typical Raman spectra of one-, two-, three-, and four-layered graphene prepared using micromechanical cleavage technique and placed on SiO_2/Si substrate. The Raman spectrum of graphene has three major bands. The D-band located around 1300 cm^{-1} is a defect-induced band. The G-band located around 1580 cm^{-1} is due to in-plane vibrations of the sp^2 carbon atoms. The 2D-band around 2700 cm^{-1} results from a second-order process. The appearance of the D- and 2D-bands is related to the double resonance Raman scattering process [23], and with the increasing the number of layers, the 2D-band gets broadened and blue shifted. A sharp and symmetric 2D-band is found in the case of SLG as shown in Figure 1.1d. The Raman image obtained from the intensity of the G-band is shown in Figure 1.1b. A linear increase in the intensity profile of the G-band with increase in the number of layers along the dashed line is shown in Figure 1.1e [15]. Surface area, which also forms an important characteristic of graphene, is discussed later in the chapter.

1.2 Synthesis of Single-Layer and Few-Layered Graphenes

SLG and FG have been synthesized by several methods. In Table 1.1, we have listed some of these methods. The synthesis procedure can be broadly classified into

exfoliation, chemical vapor deposition (CVD), arc discharge, and reduction of graphene oxide.

Table 1.1 Synthesis of Single- and Few-Layered Graphene

Graphene synthesis	
Single layer	Few layers
Micromechanical cleavage of HOPG	Chemical reduction of exfoliated graphene oxide (2–6 layers)
CVD on metal surfaces	
Epitaxial growth on an insulator (SiC)	Thermal exfoliation of graphite oxide (2–7 layers)
Intercalation of graphite	Aerosol pyrolysis (2–40 layers)
Dispersion of graphite in water, NMP	
Reduction of single-layer graphene oxide	Arc discharge in presence of H_2 (2–4 layers)

1.2.1 Mechanical Exfoliation

Stacking of sheets in graphite is the result of overlap of partially filled p_Z or π orbital perpendicular to the plane of the sheet (involving van der Waals forces). Exfoliation is the reverse of stacking; owing to the weak bonding and large lattice spacing in the perpendicular direction compared to the small lattice spacing and stronger bonding in the hexagonal lattice plane, it has been tempting to generate graphene sheets through exfoliation of graphite (EG). Graphene sheets of different thickness can indeed be obtained through mechanical exfoliation or by peeling off layers from graphitic materials such as highly ordered pyrolytic graphite (HOPG), single-crystal graphite, or natural graphite. Peeling and manipulation of graphene sheets have been achieved through AFM and STM tips [24–29]. Greater control over folding and unfolding could be achieved by modulating the distance or bias voltage between the tip and the sample [29]. Zhang [30] obtained 10–100 nm thick graphene sheets using graphite island attached to tip of