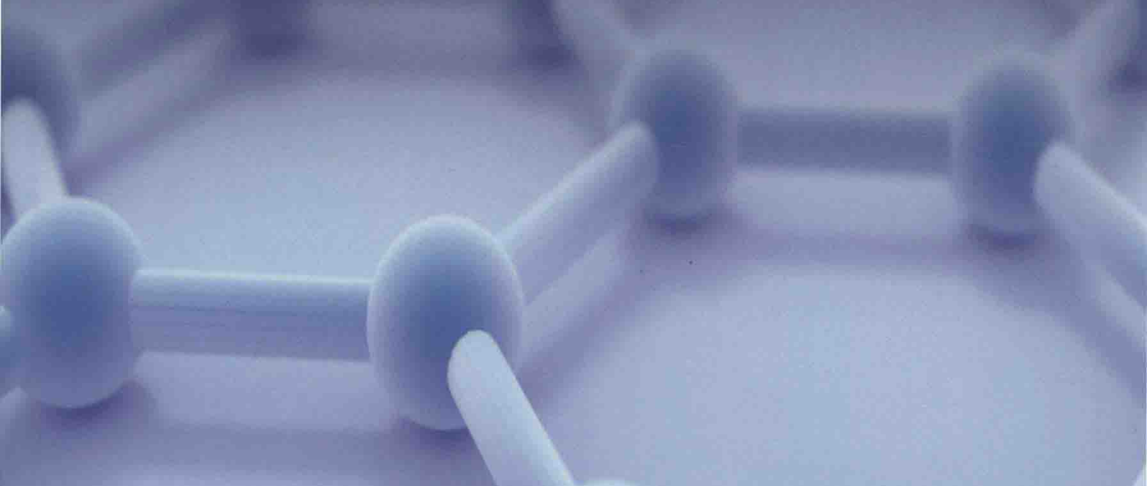
NANOMATERIALS

Graphene Nanomaterials



Kal R. Sharma

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Graphene Nanomaterials

The book is dedicated to R. Hari Subrahmanyan Sharma (alias Ramkishan), my eldest son, who turns thirteen on August 13th 2014, with love.

Abstract

Graphene Nanomaterials is expected to fill a void in knowledge among practitioners generated by the discovery of graphene as a distinct allotrope of carbon (2010 Nobel Prize in Physics) with the potential to affect further increases in speed of microprocessors beyond 30 peta hertz. It has other interesting performance properties. Identified in 2004, currently the number of patents in graphene is 7,351 and the number is rising rapidly. This book provides information on the synthesis, characterization, application development, scale-up, stability analysis using a pencil and paper, and structure-property relations. With less than 24,000 atoms/25 nm, the nanosheet form is metastable. Thirty-nine different nanostructuring methods were reviewed in an earlier book including epitaxy, lithography, deposition, exfoliation, etc. With the thickness of only a few atomic layers, graphene has superior field emitter properties, is 100 times stronger than steel, flexible as rubber, tougher than diamond, and is 13 times more conductive than copper. Electron mobility in graphene has been found to be 200,000 $cm^2V^{-1}s^{-1}$.

Different methods of fabrication of graphenes are elaborated and the cost of production can be optimized by consideration of total cost as a sum of capital cost and operating costs. High temperatures needed in the reactor may increase the operating costs. The different processes to make graphene that are discussed in this book are roll-to-roll transfer process, low pressure chemical vapor deposition, atmospheric plug flow reactor, APFR performance analysis, dispersion using NMP, exfoliation from carbonizing catalyst, ion implantation and layer thickness control, chemical method, large area synthesis by phase separation, unzipping CNTs and chemical thermal method, nanoribbon alternation, electrophoretic deposition and reduction, flash cooling, gas intercalation and exfoliation, graphene shell formation, and coal tar pitch as source. The diffusion time calculations in intercalation and exfoliation processes are shown for both Fick and hyperbolic diffusion models. The methods of handling surface reactions, sublimation transport, auto-catalysis, and layer transfer are considered. The characterization methods discussed are Raman Spectroscopy, TEM, SEM, SPM, HeIM, EIS, and morphology analysis.

The cost to prepare a single layer of graphene needs to be reduced. Currently, the cost of production of graphenes is high. The cost depends on the substrate used. A 50 × 50 mm monolayer thin film of graphene from Graphene-Square is $250 for copper substrates and $808 for PET substrates. Graphene nanoplatelets (5 to 8 nm thick) are sold at $218 to $240 per kg. Graphene sheets may have an area with length greater than or equal to 1 mm and fall in a range of 1 mm to 1,000 mm along the transverse and longitudinal directions. The electrical, optical, thermal, magnetic, chemical, quantum, and other properties of graphenes are discussed in detail.

Application development of graphene nanomaterials is examined for the following; Supercapacitor, Barristor, Microprocessor Speed Increases Beyond 30 peta Hertz, Pollutant Capture, Heat Conduction, High Capacity Electrodes, Solar Cells – AR Coating, Carbon Composites, Panel in Wireless Telephones, Thermal Managements, Medical Applications, Genome Analysis using Graphene, Drug Delivery, Piezoelectric Sensors, Desalination, Molecular Sieve, Antibacterial, Quantum Dots, and Transistors. The graphene market is expected to grow to a size of $126 million by the year 2020. By the year 2015, the nanotechnology market is expected to be 3 trillion. Triple-junction solar cells with a light-power conversion efficiency of 41% have been reported by Siemens and Semprius Inc.

2D nanosheets cannot be generated without an epitaxial substrate, which can be used to provide atomic bonding in the third dimension (Landau-Pearls argument). Different stability considerations are discussed in detail, which includes, Free Energy Considerations, Enthalpy Considerations, Epitaxial Stability, Landau-Pearls Stability, Euler Stability, Kekule Structure, Mackay's Radius of Gyration, "Negative" and "Positive" Curvature of Sheets, Puckering and Wrinkling, Island Formation, Metastability, Interface Formation, and Surface Tension.

Keywords

single-layer graphenes, barristor, ultracapacitor, carbon allotrope, thinnest material, deposition, milling, scotch tape, honey comb structure, 2D lattice, unscrolled CNT, industrial electronics, nanomaterials, transparent

electrodes and other applications, cost of production, roll-to-roll transfer and other fabrication processes, APFR, diffusion times, Raman spectroscopy, TEM, HeIM and other characterization methods, hexagonal anion rings, magnetic, surface, electrical, and mechanical properties, quantum hall effect, electrorheological properties, catalysts, thermodynamic stability-free energy of reaction, scroll stability, surface reactivity, interfacial stability, edge stability, metastability, defects

Preface

Graphene has been discovered as a distinct allotrope of carbon (2010 Physics Nobel Prize). It has a two-dimensional unique hexagonal lattice structure made of planar sheets of sp^2-hybridized carbon atoms different from the Bravais lattices known in materials science. *Graphene Nanomaterials* describes the discovery, prospects, characterization methods, applications, stability considerations, fabrication methods, and properties of graphene. It possesses interesting electronic, optical, mechanical, and thermal properties. A number of interesting applications are expected for single-layer graphene in the areas of computing, energy, and medicine. Interest in development of graphene is increasing worldwide including investments in the European Union, Russia, Korea, and the United States (National Nanotechnology Initiative). It has the potential to effect further increases in microprocessor speeds beyond 30 pHz. It has other interesting performance properties. Identified in 2004, the number of patents on graphene is 7,351 and rising rapidly. Less than 24,000 atoms/25-nm nanosheet form is metastable. Thirty-nine different nanostructuring methods were reviewed in an earlier book including epitaxy, lithography, deposition, exfoliation, and so forth. One or more atom layers in thickness, graphene has superior field emitter properties, is 100 times stronger than steel, flexible as rubber, tougher than diamond, and is 13 times more conductive than copper. Electron mobility in graphene has been found to be 200,000 $cm^2\ V^{-1}\ s^{-1}$.

According to a recent Lux report, the projected market value of graphene by 2018 is $180 million. According to the British Broadcasting Corporation (BBC), by 2020, the market value of graphene will be $675 million. The Lux report did not include an economically scalable model of fabrication of graphene in their estimates. A number of scalable methods to make graphene are discussed in Chapter 5. The cost of production of graphene is expected to come down as the technologists move past the learning curve. It costs $60 per square inch of graphene on a copper substrate. Expectations are high for the costs to come down to $1 per square inch for industrial electronic applications and 10 cents per square inch for use in touch-screen displays. Different methods of fabrication of graphenes are ellaborated. In processes where operating costs are high, an optimal cost solution may exist. The different processes to make graphene that are discussed are roll-to-roll transfer process in an atmospheric plug flow reactor, dispersion using *N*-methyl-2-pyrrolidone, exfoliation from a carbonizing catalyst, ion implantation and layer thickness control, chemical method, large-area synthesis by phase separation, unzipping carbon nanotubes, and chemical–thermal method, nanoribbon alternation, electrophoretic deposition and reduction, flash cooling, gas intercalation and exfoliation, graphene shell formation, and coal tar pitch as the source. The diffusion time calculations in intercalation and exfoliation processes are shown for both Fick and hyperbolic diffusion models. It is shown how to handle surface reactions, sublimation transport, autocatalysis, and layer transfer.

The characterization methods described are Raman spectroscopy, helium ion microscopy, small-angle X-ray scattering, transmission electron microscopy, surface electron microscopy, scanning probe microscopy, microwave spectroscopy, Auger electron microscopy, X-ray diffraction, and others. Application development of graphene nanomaterials is discussed in detail for the following: supercapacitors, desalination, light-emitting diodes, thermal management, transparent electrodes, solar cells, batteries, anticorrosion coating, bionic materials, electromagnetic shielding, oil spills, superconductors, rapid DNA sequencing, magnetic sensors, nanorobots, and nanoscale thermometers. Chemical modification and Rusnano initiative are also discussed. Two-dimensional nanosheets cannot be generated without an epitaxial substrate, which can be used to provide atomic bonding in the third dimension (Landau–Peierls argument). Different stability considerations are discussed in detail that include thermodynamic stability—free energy of reaction, scroll stability, surface reactivity, interfacial stability, edge stability, metastability, and defects.

The magnetic, surface, electrical, and mechanical properties of graphenes are discussed. Quantum hall effect, electrorheological properties, hexagonal onion rings, and role in catalysts of graphenes are also examined.

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CHAPTER 1

Discovery and Prospects

Chapter Objectives

- What is graphene?
- Carbon allotropes
- Graphene in news
- Market potential
- Applications
- News
- Investments in China and Russia

Carbon Allotropes

Graphene[1] is a distinct allotrope of carbon. The Nobel Prize in Physics was awarded to Prof. A. K. Geim and K. Novoselov in 2010 for their research on graphenes. Other allotropes of carbon that have received considerable attention and are of interest are as follows: (1) graphite;[2] (2) diamond;[3] (3) fullerene,[4] C_{60}; and (4) carbon nanotubes (CNTs).[5] Graphite was discovered in 1564. The energy that binds the interlayer graphene sheets is around 5.9 kJ mol^{-1}. Graphene can be obtained by exfoliating layers from the bonded sheets down to one layer. Carbon nanofoam[6] has been identified as another form of carbon. The Nobel Prize in Chemistry was awarded to Sir Harry Kroto, Richard Smalley, and Robert Curl in 1996 for their research on fullerenes. Other forms of carbon mentioned in the literature, such as lonsdaleite found in meteorites, C_{540}, and fullerene nanobuds, need better characterization and further understanding before being discussed. Vitreous carbon is a non-graphitizing carbon and can be used to make high-temperature crucibles. Substantial portions of bituminous coals[7] are made of fixed carbon (FC). Dehydrogenation of the FC residue can lead to another form of carbon. Charcoal, soot, amorphous carbon, and coke formed during catalytic reactions are also examples of sources containing carbon in predominant portions.

Fullerenes are made of sheets of pentagons and hexagons of carbon and obey the Euler stability criterion. The sheets have positive curvature and form a soccer-ball structure. In carbon nanofoams, a heptagonal structure with "negative curvature" is seen.

Graphene in News

The two-dimensional lattice structure of graphene is unique and different from the 14 three-dimensional Bravais lattices known in materials science. It can be considered a hexagonal two-dimensional lattice. Graphene is found to be superstrong. It comprises one layer of honeycomb-structured atoms. Some consider that the discovery of graphene is the next big development since the invention of James Watt's steam engine at the onset of industrial revolution and John Bardeen's invention of transistor and superconductor in the 20th century. A number of jobs can be generated by the development of graphene. Graphene is the subject of investigation in every top-notch university around the world. Multinational conglomerates are developing vision and mission plans that are geared toward market capture of graphene products.

The American Chemical Society has called graphene a "wonder material." It is a two-dimensional crystal. It possesses interesting electronic, optical, mechanical, and thermal properties. It has been called as "miracle material" because it was found to have high strength and self-healing properties. Graphene has been found to be the strongest material ever produced, surpassing another carbon allotrope, diamond; it is a conductor of electricity and has self-cooling properties.

Expectations are high for graphene to be used in applications such as solar cells,[8] cameras, transistors, computers, and touch-screen devices. With some modification, it can replace silicon in barristers and transistors. Graphene is highly reactive. A separate chapter is devoted to stability considerations from different perspectives.

The European Union is investing €1 billion as funding for 10 years in order to explore commercial applications of graphene. The Russian initiative plans to spend $8.55 billion in order to create a nanotech