



Graphene

Properties, preparation,
characterisation and devices

Edited by Viera Skákalová and Alan B. Kaiser

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and devices

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Graphene

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Graphene burst onto the world science scene as the new miracle material in 2004. It caught the imagination of the general public as well as materials scientists. Who would have thought 50 years ago that it would be possible to image a single layer of atoms?

The excitement of the discovery was reminiscent of the discovery of high-temperature superconductors in 1986, with hundreds of scientists trying to push the superconducting onset temperature T_c up to room temperature. Alex Müller and Georg Bednorz took the record for the fastest Nobel Prize when they were awarded the Nobel Prize for Physics the following year (1987). Unfortunately, T_c never got to room temperature (at least so far), although high- T_c superconductors are in service in many practical applications.

The Nobel Prize for graphene to Andrei Geim and Kostya Novoselov was not so immediate, but at 6 years after their discovery it was still unusually rapid. As is usually the case, other groups were working at the same time to achieve the same goal. Here the goal was separating from a graphite crystal just a single plane, the now familiar hexagonal pattern of a single layer of carbon atoms. One of the promising ideas considered at Columbia University by Philip Kim's group was using an Atomic Force Microscopy (AFM) instrument tip made of graphite and pressing it against a substrate in the hope that some trace of graphite might be a single graphitic plane.

Finally, the method successfully used by Geim and Novoselov to separate graphene layers was hardly at the cutting edge of technology, in fact just the opposite – a piece of sticky tape took with it layers of graphene when it was pulled off a piece of graphite. Some of the carbon layers were one atom thick (monolayers), others bilayers or multilayers. In fact, it turns out that we have all made graphene monolayers just by writing on paper with a graphite pencil – but we didn't know it! The problem is not so much forming graphene sheets but identifying their existence.

Was it good luck that the silicon substrate that was used for depositing graphene was covered with 300 nm oxide layer? It became clear later that

this was the best substrate which, under an optical microscope, yielded very strong contrast owing to favourable interference of light reflected from the bottom and top interfaces of the silicon oxide layer. Geim and Novoselov and their team were able in this way to identify the number of layers of graphene on a silicon substrate.

But why was this discovery worthy of the Nobel Prize? Most importantly, Geim and Novoselov with contributions from others went on to perform many experiments that demonstrated what an amazingly novel material graphene is. It was these 'groundbreaking experiments' revealing the behaviour of electrons in a two-dimensional (2D) material that had not been observed previously that amply justified the Nobel Prize. In addition, the large variety of possibilities for applications of graphene owing to its great strength as well as its unusual electronic properties over a wide range of temperatures mean that graphene is or will be incorporated in many devices for use in our everyday life.

Regarding graphene, the theorists were far ahead of experiments. The now-famous paper of the Canadian physicist Philip Wallace in 1947 calculated the electronic band structure of electrons in a 2D graphene layer (i.e. the energy of the different available states of the electrons in the layer). This calculation is much easier for the 2D graphene sheet than for 3D graphite. Wallace showed that the band structure of graphene is quite different from that in ordinary metals or semiconductors. Graphene could be called a metal with zero density of states at Fermi level or, equally well, it could be called a semiconductor with a zero band gap.

This band structure of graphene means that its properties can be dramatically altered and controlled by doping that can be provided either through a field effect transistor (FET) device or by chemical or electrochemical approaches. Thus, the graphene layer can be used for various applications in electronics.

We should mention that other novel forms of carbon closely related to graphene have been discovered, in fact before graphene. A structural modification leads to a change in the electronic properties of the material. This is why each member of the 'graphene family' has its own character and a different perspective for industrial application. The important modified structures based on graphene are fullerenes (miniature carbon 'soccer balls' formed by changing specific hexagons to pentagons), nanohorns of conical shapes, nanowalls grown perpendicular to the substrate, and nanofoam with the topology extended to 3D space.

Carbon nanotubes deserve special attention: if a sheet of graphene is rolled up with the carbon atoms on opposite edges matched up, a carbon nanotube is formed. These hollow carbon tubes can be single-wall with diameters down to less than one nanometre, or could consist of multiple shells (multiwall carbon nanotubes). Carbon nanotubes, like graphene, have

a range of very attractive properties, such as, for example, strength, flexibility, and electrical and thermal conduction, that are finding applications in nanoscale electronics and composite materials. In this respect, carbon nanotubes represent the most serious competitor to graphene.

In this book, the articles take an in-depth look at the key aspects of graphene, both a single layer of graphene (monolayer) as well as bilayers and few-layer graphene. We start with chapters that introduce the most developed methods of preparation of graphene in Part I. The methods discussed are epitaxial growth of graphene through thermal decomposition of a SiC crystal, chemical vapour deposition growth of large-area graphene on catalytic substrates, and layer-exfoliation from graphite using chemical and electrochemical routes. Each of the methods produces graphene of different quality, size, and amount. In order to evaluate these factors we need to characterize synthesized graphene.

Part II contains chapters describing the most powerful techniques for characterization of graphene atomic and electronic structures. The principles and applications of particular characterization techniques are discussed. Transmission electron microscopy visualises the structure of suspended graphene down to the atomic level, giving information on crystalline grain size and structural defects as well as chemical modifications. Scanning tunnelling microscopy can give an atomic resolution image of graphene either grown *in situ* or transferred onto a conductive surface. In the spectroscopy mode, the electronic structure of graphene under various environmental conditions can be obtained through recording differential conductivity while sweeping the bias voltage between the conductive tip and substrate. Raman and photoemission spectroscopies provide us with a detailed picture of electronic structure that is affected by structural disorder, bending and thickness. Important insight into these spectroscopic methods is offered by the two last chapters in Part II.

The focus of Part III is on electronic transport in monolayer and in bilayer graphene and on electronic devices towards applications. In addition to presenting the unusual and fascinating electronic transport properties, the effect of absorbents on electronic transport is analysed. Quantum (single-electron) transport through a constricted area of graphene and a very strong effect of electronic disorder on the transport properties are discussed in a separate chapter. The final chapters cover graphene spintronics and graphene nanoelectromechanical systems (NEMS) where graphene is shown to be a promising material for these technological applications.



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