1
Introduction – The Carbon Age

The continuing trend towards miniaturization of optoelectronic devices leads to fundamental physical limits of conventional silicon-based materials. The search for new concepts has moved low-dimensional carbon nanostructures into the focus of current research [1–5]. They are represented by a variety of different metallic and semiconducting materials with unique optical, electronic, and mechanical properties [2, 3].

The main carbon material is graphite. It consists of multiple flat layers of sp^2-hybridized carbon atoms arranged in a hexagonal lattice [6]. While the σ-bonds between the carbon atoms are very strong, the Van der Waals coupling between different layers is rather weak and can be easily broken. Therefore, graphite is a suitable material for example for pencils.

In 1985, a new carbon structure named fullerene was discovered [7]. Its most common form C_{60} is a spherical carbon molecule with a mean diameter of 0.68 nm, cp. Figure 1.1c. Since the charge carriers are spatially confined in all directions, fullerenes are zero-dimensional carbon nanostructures. For their discovery, Richard Smalley, Robert Curl, and James Heath obtained the Nobel Prize in Chemistry in 1996.

Carbon nanotubes (CNTs) represent another low-dimensional carbon nanostructure, which was found for the first time in 1991 by Iijima [8, 9] and has attracted large scientific and technological interest. Nanotubes are tiny, hollow cylinders constructed by rolling up a single layer of graphite, cp. Figure 1.1b. They have diameters in the range of one nanometer, while their length can reach several micrometers. As a result, they are prototypical one-dimensional systems, in which carriers can move freely only along the axis of the cylinder. Arising from a specific geometry quantum confinement, they can be either metallic or semiconducting with a tunable bandgap. This makes them excellent materials for various technological applications.

In 2004, graphene was discovered – a perfect two-dimensional carbon nanostructure consisting of a monolayer of carbon atoms [10]. Graphene can be considered as the basic carbon material and it can be rolled up into a one-dimensional carbon nanotube, wrapped into a zero-dimensional fullerene, and stacked into a three-dimensional graphite, cp. Figure 1.1. Up to its discovery, graphene was considered as an academic material [6] that could not exist in reality due to thermodynamic
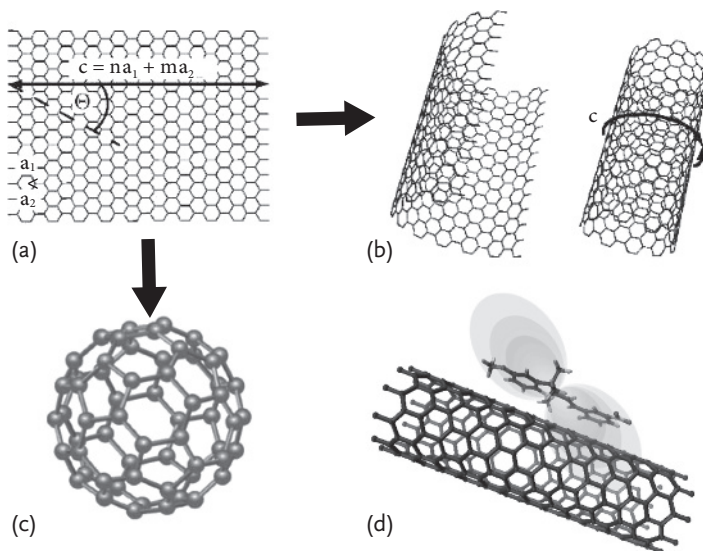
Figure 1.1 Schematic illustration of different carbon-based nanostructures. (a) Graphene as a two-dimensional material consisting of a single layer of carbon atoms can be rolled up into (b) one-dimensional carbon nanotubes, wrapped into (c) zero-dimensional fullerenes, or stacked into three-dimensional graphite (multilayered graphene). (d) Exemplary car-bon-based hybrid nanostructure consisting of a nanotube functionalized with merocyanine molecules. The latter creates a strong dipole field giving rise to changes in the optical and electronic properties of the nanotube. Figure parts (a) and (b) adapted from [14], part (c) from [15].

instabilities of two-dimensional structures on a nanometer scale [11–13]. However, Konstantin Novoselov and Andre Geim from the University of Manchester succeeded to mechanically exfoliate a single layer of graphite and revealed a completely new structure with exceptional properties. They were awarded the Nobel Prize for Physics in 2010.

Meanwhile, also carbon-based hybrid materials consisting of a nanostructure functionalized with molecules have moved into the focus of current research [16–18], cp. Figure 1.1d. Carbon materials offer a variety of metallic and semiconducting substrates, which show a large sensitivity to changes in their surrounding environment. Thus, they are excellent structures for functionalization with molecules [17, 19], which offers the possibility to control and optimize certain properties. As a result, functionalization is a promising strategy to exploit the great application potential of carbon nanostructures [18, 20, 21].

1.1
Graphene

Properties   Since its discovery [10], graphene has attracted tremendous interest in fundamental research and industry [5, 22]. Graphene has an exceptional band structure exhibiting crossing points between the valence and the conduction band at the six corners of the Brillouin zone [6]. Around these so-called Dirac points, the energy dispersion is linear giving rise to unique optical and electronic properties [3, 15]. The electrons behave like relativistic massless particles and can be described by a Dirac-like equation [15]. One consequence is for example the anomalous fractional quantum Hall effect [23].

Consisting of just a single layer of carbon atoms, graphene is the thinnest known material. Because of the sp^2-bonds between the hexagonally arranged carbon atoms, it is also one of the strongest structures that we know of [24]. Furthermore, it is an excellent conductor of electricity and heat, which can be traced back to its excellent carrier mobility at room temperature. The carriers can move freely without scattering events over length scales of some hundreds of nanometers (ballistic transport) [3, 25, 26]. Moreover, graphene is flexible and almost transparent in the optical frequency range [27–29]. As a result, it is a promising material for applications in nanoelectronics and optoelectronics [3, 30].

Synthesis   Graphene was first obtained by mechanical exfoliation [10]. Konstantin Novoselov and Andre Geim used a common adhesive tape to repeatedly split graphite crystals into increasingly small flakes, cp. Figure 1.2. Then, they transferred the thinnest flakes onto a SiO_2 substrate of a specific width. Finally, they could visualize monolayers of carbon atoms under a simple optical microscope. The procedure is known as the scotch tape or drawing method, since the mechanical exfoliation resembles writing with a pencil. Such exfoliated graphene exhibits a high crystal quality resulting in a large carrier mobility. This method is ideal
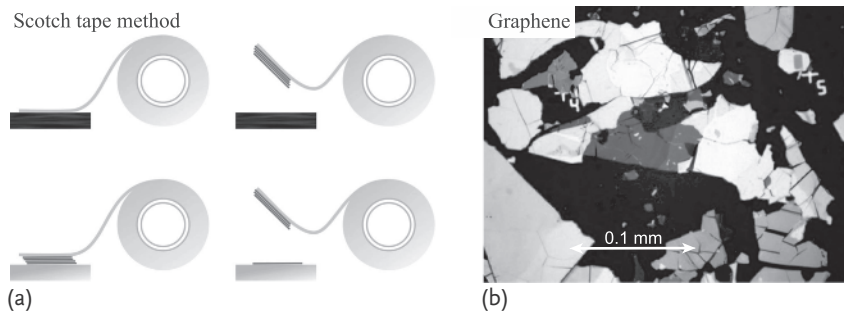

Scotch tape method

Graphene

0.1 mm

(a)   (b)

Figure 1.2   (a) Schematic illustration of the scotch tape method applied to mechanically exfoliate graphene from bulk graphite. (b) Thin flakes of graphite on a SiO_2 substrate account for various colors, which represent their thickness reaching values from 100 nm (white flakes) to a few nanometers corresponding to just a few monolayers (black flakes). Figure adapted from [5].

for producing samples for fundamental research. However, the sample size is too small (around 10 μm) for technological applications. Thus, other methods allowing large-scale exfoliation are required to exploit the great application potential of graphene [30]. The most promising growth technique for the mass production of large area graphene films is chemical vapor deposition (CVD). Graphene samples with a size of over 75 cm have already been reported [31]. However, the structural quality of the produced graphene layers is so far lower compared to exfoliated or epitaxially grown samples.

The crystalline quality of graphene grown epitaxially on silicon carbide or metal substrates via high-temperature annealing is very high [32, 33]. However, the growth strongly depends on which side of the SiC graphene layers are grown. On the Si-face a single layer of highly doped graphene is formed on top of a buffer layer [34]. On the C-face rotationally twisted graphene multilayers are produced, which do not exhibit Bernal stacking order but are rotationally twisted against each other resulting in a negligible coupling and a graphene-like behavior [32]. A more detailed discussion of growth methods can be found in Section 3.4.

Applications   Graphene is considered a very promising future material for nanoelectronics [3, 5, 30, 35]. It is characterized by huge carrier mobilities, optical transparency, flexibility, robustness, and environmental stability giving rise to a large variety of applications ranging from solar cells and light-emitting devices to touch screens, photodetectors, and ultrafast lasers [30, 35].

In particular, the observed ballistic transport and the resulting exceptional carrier mobility can be exploited to build highly efficient transistors. Recently, IBM researchers reported on a graphene-based field-effect transistor with an on–off rate of 100 GHz exceeding the speed of corresponding silicon transistors [36, 37], cp. Figure 1.3a. Since graphene is almost transparent and at the same time an excellent conductor it is also a promising material for transparent electrodes required in touch screens and displays. Its mechanical strength and flexibility make it more suitable than indium tin oxide [5, 30, 38].

The exceptional carrier mobility and absorption over a large spectral range from terahertz to ultraviolet also suggest application as ultrafast, spectrally broad photodetectors [35, 39]. Recently, terahertz emission and amplification was observed in optically pumped graphene demonstrating the feasibility of active graphene-based terahertz devices [30]. Furthermore, graphene can be applied as a broadband and fast saturable absorber in ultrafast laser systems [40, 41] due to its ultrafast carrier dynamics, broadband absorption, and efficient Pauli blocking – in contrast to conventional materials with a narrow spectral range requiring costly bandgap engineering. Finally, graphene has already been applied in composite materials to achieve improved mechanic and electric properties [42].

Challenges   Despite the impressive progress in the short time since its discovery, there are still substantial challenges on the way to graphene-based nanoelectronics. In particular, further progress in epitaxial growth techniques is needed to obtain high-quality graphene films complying with industrial standards including suffi-
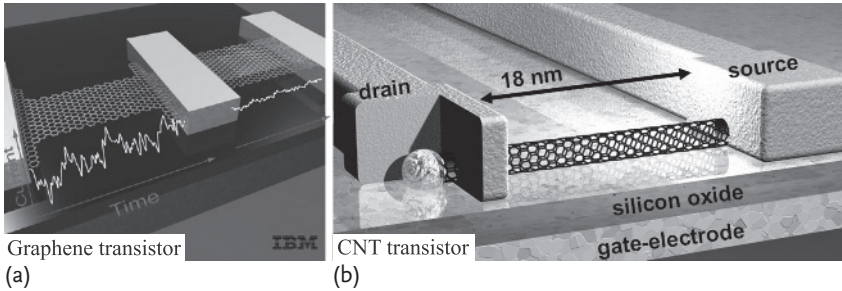
Graphene transistor IBM CNT transistor

(a) (b)

Figure 1.3 Prototypes of field-effect transistors based on (a) graphene (IBM) [36, 37] and (b) carbon nanotubes (Infineon) [46]. Source IBM and Infineon, respectively.

cient reproducibility and control of specific features in graphene devices. Furthermore, for many applications it is necessary to induce a bandgap at the Dirac point. This can be achieved by cutting graphene into thin ribbons exhibiting a series of subbands due to the spatial confinement similar to carbon nanotubes [43, 44]. The bandgap can then be tailored by changing the width of nanoribbons. The other strategy is to use bilayer graphene, where a bandgap of up to 250 meV can be opened by applying an electrical field [45].

The key prerequisite for most applications in optoelectronics is a microscopic understanding of the character of optical excitations as well as of their ultrafast relaxation dynamics. Many important aspects of experimental data have not yet been fully complemented with theoretical studies on a microscopic footing. This aspect is addressed in detail in Chapters 4 and 7 of this book.

1.2
Carbon Nanotubes

Properties   The discovery of carbon nanotubes has opened a new research field [1, 2]. CNTs are ideal model systems to study the fundamental physics of one-dimensional nanostructures. CNTs can be considered as a piece of graphene rolled up into a cylinder with a diameter of approximately one nanometer, cp. Figure 1.1. The diameter of the cylinder and the chiral angle ϕ (rolling-up angle) determine the microscopic structure of each specific nanotube [1]. Because of the hexagonal shape of the Brillouin zone of graphene, the angles can reach values between 0°–30°. The two distinguished angles correspond to zigzag nanotubes with $\phi = 0°$ and armchair nanotubes with $\phi = 30°$. The names reflect zigzag- and armchair-like chains at the edge of their unit cells, cp. Figure 1.4.

Similarly to graphene, carbon nanotubes are one of the strongest known materials due to the covalent sp^2-bonds between the carbon atoms [47]. At the same time, they are very light, because they consist of a single layer of carbon atoms. The extraordinary crystal quality gives rise to a ballistic conduction of current and heat at room temperature. As a one-dimensional material with an extreme length-to-
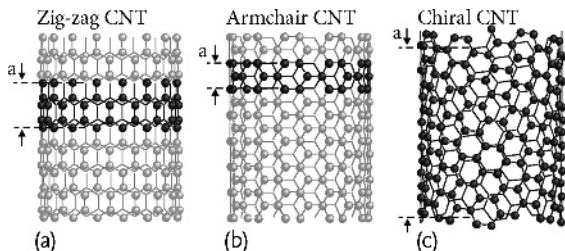
Zig-zag CNT   Armchair CNT   Chiral CNT

(a)   (b)   (c)

Figure 1.4 The classification of nanotubes according to the chiral angle ϕ describing the orientation of carbon hexagons relative to the nanotube axis: (a) zigzag tubes with $\phi = 0°$, (b) armchair tubes with $\phi = 30°$, and (c) chiral tubes (n_1, n_2) with $0° < \phi < 30°$. The names reflect the armchair- and zigzag-like edges of the corresponding unit cells (emphasized area). Figure adapted from [1].

diameter ratio, CNTs also exhibit pronounced optical properties [48]. In contrast to graphene, the further spatial confinement gives rise to a variety of metallic and semiconducting nanostructures with distinct physical properties. Depending on the chiral angle, one third of all possible nanotubes are metallic [1]. Furthermore, the bandgap of the semiconducting CNTs is tunable with the diameter of the tube. This variety of one-dimensional nanostructures with distinct physical properties accounts for the huge potential of carbon nanotubes for technological applications [2, 4, 49].

Synthesis   Carbon nanotubes can be grown by chemical vapor deposition, laser ablation, and arc discharge [14]. All methods have in common that first a carbon plasma is generated and then metal catalysts are added, which induce the growth of nanotubes. The type of catalyst and the growth conditions determine the number of nanotube walls, their diameter, and length [14].

Figure 1.5a shows an SEM image of CNT bundles grown by arc discharge [50]. Each bundle consists of 20–100 single-walled carbon nanotubes, as indicated in the high-resolution TEM image in Figure 1.5b. To obtain single-walled CNTs, the bundles are broken apart by ultrasonification and the single tubes are coated by a surfactant to prevent them from rebundling. Furthermore, CNT forests can be produced via water-assisted chemical vapor deposition [51], cp. Figure 1.5c. Additionally, the CVD technique enables the growth of CNTs in well-defined positions on patterned substrates [51], as shown in Figure 1.5d.

While the diameter and the length of CNTs can be controlled during growth, the control of the chiral angle remains a major challenge in current research. Usually, CNT samples exhibit a homogeneous distribution of chiral angles. Separation of metallic and semiconducting carbon nanotubes was successfully achieved by using i.a. (i) density-gradient ultracentrifugation (DGU), which separates surfactant-wrapped CNTs by the difference in their density [52], (ii) alternating current dielectrophoresis, which exploits the difference in the relative dielectric constants resulting in an opposite movement of metallic and semiconducting tubes along the electric field gradient [53], and (iii) agarose gel electrophoresis, where the rela-
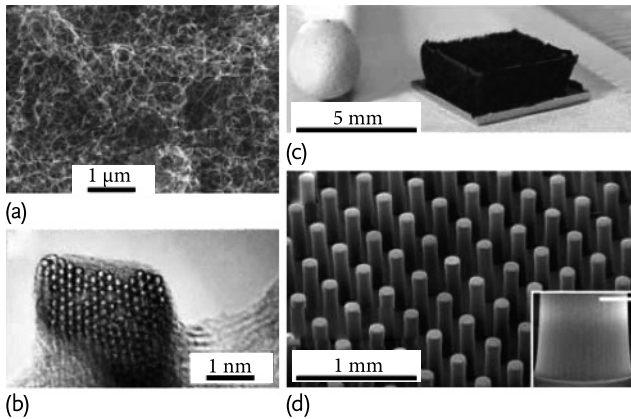
Figure 1.5 Carbon nanotubes obtained with different growth techniques including (a) CNT bundles grown by arc discharge [50], (b) cross section of such a bundle, (c) mm-thick CNT forests grown by water-assisted chemical vapor deposition [51], (d) CNTs grown in predefined places on a patterned substrate [51]. Figure taken from [14].

tive mobility through a gel is used for separation of CNTs with different molecular weights [54]. Recently, progress has also been made allowing enrichment of CNTs with a specific chirality for example by exploiting chirality-dependent wrapping of CNTs with the DNA leading to enrichments of up to 90% and more [55].

Applications   The variety of one-dimensional metallic and semiconducting carbon nanotubes with a tunable bandgap makes CNTs promising candidates for various technological applications [2, 4, 49]. In particular, nanotube-based field-effect transistors have already been demonstrated based on room-temperature ballistic transport [4, 46], cp. Figure 1.3b. Furthermore, metallic CNTs can be used in integrated circuits to conduct current and high-speed signals [56]. Consisting of a single layer of carbon atoms, CNTs exhibit a large surface-to-volume ratio, which is favorable for application as chemical or gas sensors [57]. Functionalization of CNTs can be used to improve their sensitivity and selectivity to specific chemical substances or biomolecules [58].

The strength and flexibility of CNTs on the one hand and their extraordinary conductivity on the other hand suggest engineering of transparent, electrically conductive films of CNTs for application in touch screens and flexible displays [49, 59]. CNTs have already been used in composite materials to improve their mechanical, thermal, and electronic properties [60]. Their mechanical strength is already exploited in everyday items, such as cloths, sports gear, cars and so on.

Challenges   Most technological applications require an almost perfect separation of metallic and semiconducting nanotubes. For some applications, even a separation by chiral angle is necessary. Therefore, further progress in growth and selection techniques remains the major challenge in current nanotube research [2].

Furthermore, the unambiguous characterization and identification of specific CNTs is an important issue. In this context, the well-pronounced optical transitions can be seen as an optical finger print for each individual nanotube. Optical spectroscopy methods, such as absorption, photoluminescence, Rayleigh and Raman scattering can be used for structural assignment of CNTs [61–65]. This aspect is addressed in detail in Chapter 6.

For applications in nanoelectronics, a microscopic understanding of the Coulomb- and phonon-induced ultrafast relaxation dynamics of optically excited carriers is required, in particular addressing different relaxation channels and their diameter and chirality dependence. Microscopic investigations on the carrier dynamics in CNTs are presented in Chapter 5.