

Chapter 2

Technologies of Carbon Materials. Syntheses and Preparations

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In carbon materials technology the degree of development can be used to classify the various kinds of available carbon materials in three different stages (Fig. 2.1). Conventional carbon materials include graphite blocks, the family of carbon blacks, activated carbons and diamond. Among the newly developed materials two types can be distinguished: nanotextured carbons and nanosized carbons. Nanotextured carbons comprise a wide range of carbon structures from carbon fibers, glass-like carbons or pyrolytic carbons to diamond-like carbon materials. Among nanosized carbons (or nanocarbons) fullerenes, carbon nanotubes (CNT) and graphene can be quoted [1–3].

After a basic overview on bulk carbon materials, we will focus the presentation on the production, synthesis and technology of the recently developed carbons, as they lead the trend of the application of carbons for sensing. Nanotextured carbon based thin films are presented first; afterwards the main methods to synthesize nanosized crystalline carbons are introduced. A special emphasis is dedicated to CNTs and graphene as they concentrate the current advances based on nanomaterials, including the field of sensing. Brief review of several available techniques is included and timely reference works are listed to support the reader. To conclude the section, a few general considerations on carbon nanomaterials post-synthesis/production processing are given, and the main challenges for applications and device fabrication highlighted. Particularly, integration of graphene and CNTs is discussed based on particular examples from the standpoint of technology.

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Crystal /Micro Structure	Classic	Synthetic Conventional	Synthetic Nanotexture	Synthetic Nanosize	Orientation/ Symmetry
3D isotropic	Natural diamond	Diamond SiC			Bulk
3D anisotropic	Natural graphite	Artificial Graphite Pyrolytic Carbons	Flaky Graphites Pyrolytic Carbons Cokes		Planar
2D		C-C Composites	Intercalation Compounds Amorphous C Thin Films	Graphene	Film Thin film
1D		Carbon Fibers	Carbon Nanofibers	Carbon Nanotubes	Axial
0D		Carbon Blacks		Fullerenes Nanodiamond	Point
Amorphous or Disordered	Carbonaceous Materials Hydrocarbons	Activated Carbons Polymers	Diamond-like Carbons Glass-like Carbons		Random

Fig. 2.1 The cloud of carbons; their synthesis, production, morphological and structural classification

2.1 Conventional Carbon Materials

Among the crystalline carbons described in Chap. 1 graphite and diamond occur naturally, although at different ratios since graphitic forms are more thermodynamically stable for carbon under standard conditions.

Mineral graphite results mainly from metamorphism in rocks, by the reduction of sedimentary carbon compounds. Depending on the ore deposit crystalline flake graphite (plate-like particles), amorphous graphite (fine particles from thermal metamorphism of coal) or lump graphite (vein graphite) are found. Among synthetic graphite it stands out highly oriented/ordered pyrolytic graphite (HOPG), whose graphite sheets have an angular misalignment of less than 1° .

As an industrial material, graphite can be seen technically as the highest grade of coal, mainly used for lubricants, pencils, etc., while anthracite would be immediately below, being the highest rank of the coals for fuel applications.

As for natural diamond, it is actually a metastable allotrope of carbon, although its conversion rate is negligible in normal conditions. Natural diamond formed at high temperature and high pressure conditions in the 140–190 km depth of the Earth's mantle. Synthetic diamond can be produced by mimicking Earth's mantle conditions or alternatively by chemical vapour deposition (CVD).

Diamond applications are derived from the superlative physical properties of high hardness (the highest) and high thermal conductivity of diamond, owed to the strong covalent bonding between carbon atoms. Diamond is used in industrial applications for cutting and polishing tools, as well as knives and anvil cells for scientific applications, and as luxury good in jewellery. Another hard carbon-containing material is silicon carbide, whose sensing application is discussed in Chap. 7.

A particular category of diamond, nanodiamond, which name stands for a considerable variety of nanostructures depending on size, purity, etc., is currently the focus of scientists due to its potential as a material, for example, for drug delivery or optoelectronic devices. Gas phase nucleation at ambient pressure and high pressure high temperature graphite transformation within a shock wave are among the synthetic methods used. See [4–7] for some review materials on nanodiamond production. Sensing based on diamond is discussed in Chap. 9.

Bulk and massive material applications of carbon mostly correspond to the graphitic forms. This is due to the fact that large scale production of carbon materials correspond mainly to the graphite family forms. Graphitic carbon can act as a constituent of functional or structural materials (graphite lubricants or steel, respectively) or simply to make up structures, such as in refractories.

Yet, natural graphite is profusely used. Apart from the range of coal materials used as fuels, coke, mainly consisting in carbon, is derived from coal by baking without oxygen at high temperatures (as high as 1000 °C). Coke outstands for its metallurgical applications, such as steelmaking after further refining. A compound made of a kind of coke, the petroleum coke, is the raw material of graphite electrodes, fabricated by extrusion, shaping, baking for binder carbonization and final graphitization at 3000 °C.

For laptop computers heat sinks made of expanded graphite are used. Expanded graphite is produced by forcing the crystal lattice planes apart by the immersion of graphite into chromic acid and subsequently in concentrated sulphuric acid [8, 9]. The expanded graphite is made a foil, which is also used for other structural applications that benefit from its thermal properties. Using a somehow similar method, intercalation compounds of graphite [10] are obtained by the introduction of certain metal or small molecules between the graphite layers, such as in KC_8 , which has superconducting properties [11]. Very remarkably techniques based on graphite intercalation compounds have gained interest as a convenient route towards obtaining graphene (Fig. 2.2). Intercalation compounds of graphite and carbon fibers would typically be classified as newly developed carbons, [2] then categorized within the nanotextured carbon materials that will be described in next section.

Synthetic graphite was actually discovered in the mid-1890s by Acheson as a product of carborundum overheating [12]. Nowadays, a similar approach is used for graphene growth on SiC wafers. Additional processing involving synthetic graphite comes from a recent trend in applications of the last decades, such as energizing portable electronic devices; the use of synthetic graphite for batteries [13]. Graphite demand is expected to significantly rise as electric vehicles are being developed due to the amount of graphite used in their batteries. The remarkable

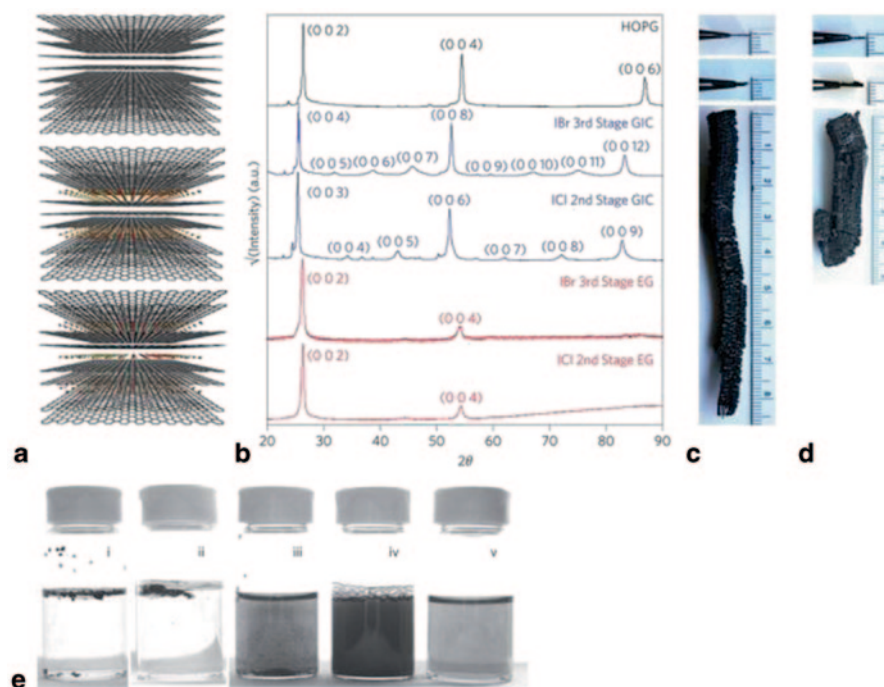


Fig. 2.2 Graphite intercalation compounds **a** structural model. **b** changes in XRD spectra from HOPG to various kinds of GICs. **c** macroscopic images, and **d** variability of GIC solubility. (Reprinted by permission from Macmillan Publishers Ltd: (Nature Nanotech 6, p. 439) Chih-Jens Shih et al. copyright (2011))

potential of carbon for electrochemical applications is covered in Chap. 6, for the case of biological sensing. Nuclear reactors also use synthetic graphite as neutron moderators [14, 15].

Axial-oriented synthetic graphite forms can be produced as well. Carbon fibers are used as plastic reinforcement, benefiting from an enhancement of the mechanical properties, or heat-resistant composites [16]. Carbon fiber is produced from polymer precursors such as polyacrylonitrile (PAN) in the form of filament yarns by two step carbonization to drive off non-carbon contents. Polymer fiber is heated at low temperature (300 °C) for H bonds break and oxidation, followed by high temperature treatment (2000 °C) in an inert gas (Ar). Chap. 3 addresses specifically a comprehensive description on dispersing CNTs and graphene into polymer matrices.

Among conventional carbons, perhaps the most interesting graphitic carbon forms for sensing are carbon black and activated carbon. Carbon blacks and activated carbons are commonly used in several industrial applications, such as material reinforcement, pigments, purification, respirators, filters... (Fig. 2.3) [17].

Carbon blacks are named after their production process of gas-phase carbonization, the incomplete combustion of petroleum products. The term includes several

Fig. 2.3 Macroscopic images of (*left*) activated carbon and (*right*) carbon blacks. (Used under a Creative Commons Attribution/Share-alike License)



types, such as, for example, thermal black, furnace black or acetylene black. The morphological characteristics of their particles strongly differ on the size and aggregation of the primary particles. They comprise graphitic carbon point forms, either concentric or radially oriented, which result from the size of precursor particles and heat treatment temperature or the composition of primary particles and applied pressure, respectively.

Activated carbon refers to a group of light carbon materials that are obtained from carbonaceous precursor materials, such as coal, wood, nutshells, etc. The activation methods are the following. Physical reactivation using hot gases can be done by either carbonization (600–900 °C in the absence of oxygen, preferably in Ar or N₂ atmosphere) or activation/oxidation (precursor material is exposed to oxidizing atmospheres at temperatures above 250 °C). Chemical activation consists in carbonization after the raw material has been impregnated with certain chemicals. Graphitic microstructure of activated carbons is randomly oriented.

As understood from their applications a characteristic of both carbon black and activated carbon is their remarkable porosity. Porous material also implies large surface area which makes them suitable for adsorption, catalytic and sensing applications. This characteristic is together with transduction optimization the reason to explore nanostructured interfaces. In the next section we present the synthesis and deposition methods of some of the relevant carbon nanotextured materials.

To conclude this section, we have looked over the main aspects of conventional carbon forms and their production, from natural materials and their conversion into desired forms to synthetic methods to obtain crystalline carbon materials, mainly structured in graphitic phase. The variations in terms of characteristics and microstructure, from pure and crystalline layered graphite and solid diamond to a variety of synthetic carbon including porous materials, determines their application as functional and structural materials.

2.2 Nanotextured Carbon Materials

Graphitization degree is commonly determined as a measure of the average stacking of the forming (graphene) layers. Graphitic stacking can occur in both the ABAB and ABCABC stacking. When no interlayer alignment occurs (disorientated) the

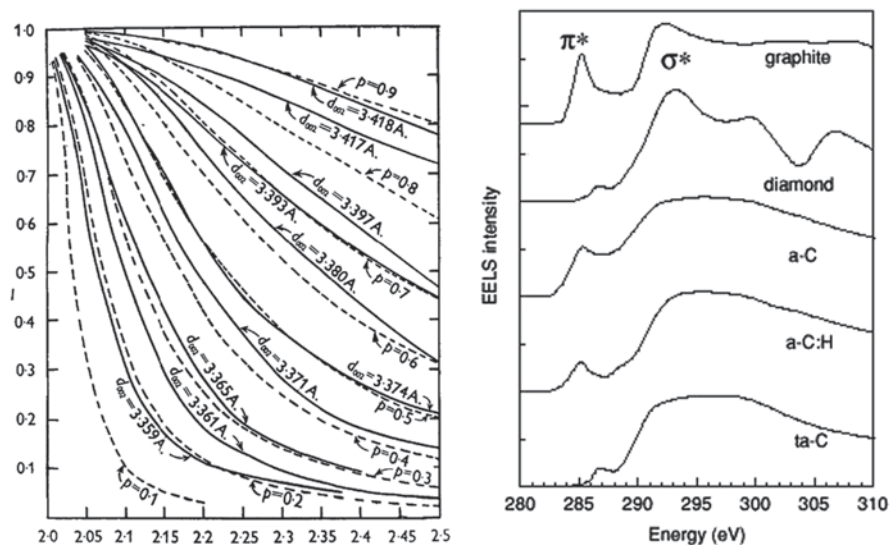


Fig. 2.4 (Left) Shape in reciprocal space in (112) line for graphitic carbons. (R. E. Franklin, Acta Cryst. (1951), 4, 253). (Right) Electron energy loss spectra of graphite, diamond, a-C:H, sp² a-C and ta-C. (J. Robertson, Semiconductor Science and Technology 18 (2003) S12-S19, IOP Publishing)

graphitic materials is named as turbostratic to indicate that there is a lack of periodic stacking, which results in an increased interlayer space, from the 3.354 Å of graphite up to 3.44 Å (Fig. 2.4, left). This variability basically depends on the starting materials and from the treatment conditions during growth. Disorientation has revealed very interesting electronic properties for few layers graphene. In relation to their production, the differences in the graphitization degree (stacking), lead to the classification of carbon materials into graphitizing carbon and non-graphitizing carbon. They are also known as graphitizable (or soft) and non-graphitizable (or hard) carbons.

The properties of a (crystalline) material depend on their crystallography, crystal size, and domains orientation (Fig. 2.4, right). For intrinsically anisotropic materials, such as graphite-like carbon layers the relevance of nanotexture is increasingly marked. The crystallite growth is actually driven by two parameters, an increase in crystallite size (L_a) and the propagation in thickness of parallel stacking (L_c). Nanotexture characteristics assist the understanding of their functional properties, but it also determines its metastability under high temperature treatment. However, there exists no strict classification for nanotextured carbons, precisely because they show very different behaviour at high T treatment, while they have similar average microstructure as resolved by common characterization methods [2].

Nanotexture is controlled by the processes used in their production, so decomposing nanotexture into qualitative features can assist the rough classification

of a range of distinguishable useful graphitic materials (Fig. 2.1). Essentially, we can separate nanotextured carbon materials into two categories; those having oriented nanotexture and those randomly oriented nanotexture. Carbons with oriented nanotexture present three distribution possibilities: planar, axial and point orientation. Planar orientation corresponds to carbon nanocrystallites which align respect to a single reference plane, such as in flaky graphites, pyrolytic carbons and cokes. Nanotexture following an axial orientation may refer to either graphitic carbon nanotubes, coaxial layers aligned respect to a longitudinal reference axis, or crystallites radially oriented respect to the longitudinal axis of materials in the form of wires, like carbon fibers having some kind of radial orientation of the graphitic layers and carbon forming fibers of nanometer size in diameter. Point oriented nanotexture can be concentric, like in fullerenes, or radial, exemplified by carbon blacks.

Carbon materials having a randomly oriented nanotexture present a highly variable to complete lack of (mutual) orientation of the very carbon-carbon bonds and the crystallites [2, 18]. They can be a combination of several of the latter oriented nanotextures. In the next subsection we address a brief introduction on carbon thin films deposition, with special attention to various amorphous carbon materials.

2.2.1 Carbon Thin Films

Conventional thin film deposition techniques are able to grow thin films with thickness control of a few nanometers [19]. Among other variables, as the thickness of the materials considered as thin films is typically in a relatively wide range, from a few micrometers to sub-nanometer scale, no standard thin film deposition technique is established. The growth methods are typically categorized as either physical or chemical methods depending on the nature of primary process driving the thin film material deposition. Chemical methods include CVD, spin coating, plating and so on, while physical deposition techniques range from conventional sputtering and thermal evaporation to assisted processes like plasma, laser beam, etc. [20].

Specifically for carbon deposition, as atomic carbon arranges in various allotropes (sp^3 , sp^2 and sp^1 hybridizations of the C–C bonds) and additionally it can be shaped in very distinctive morphologies (planar versus curved sp^2 , fibers, porous materials, etc.) the carbon thin film growth is a non-trivial issue. Basically, three kinds of carbon films can be distinguished: polymer films (plasma polymer or plasticized monomers), diamond-like carbon (DLC) films and crystalline carbon films (CVD diamond or graphite films). In brief, the development of carbon thin film deposition methods is driven by applications while the process parameters (growth conditions) are determined by the specifications of the intended carbon thin film. A paradigmatic example is graphene [21], the single atom layer of strongly bonded sp^2 C atoms forming a hexagonal web. Its isolation and confirmation of extreme properties revolutionized not only the scientific community, but the industry and

the market. Yet its on-purpose growth control is immature, although progressing rapidly. Graphene synthesis will be covered in the next section.

Among the nanotextured carbon materials, carbon thin film membranes can show particularly good performance for sensing applications as they can be used, for instance, to avoid reactions at the interface of the analyte and metal electrode, which otherwise cause signal interference. Other relevant industrial applications of carbon thin films are focused on physical properties such as hardness and wear characteristics of diamond (e.g. abrasive wear protection, cutting tools) and graphite (e.g. friction reduction, adhesive wear protection). Next, we present the main thin film deposition techniques and characteristics for randomly oriented and amorphous carbon materials.

For DLC materials, which key property is its sp^3 bonding, the tetrahedral arrangement can be promoted by ion bombardment. The growth mechanism of DLC is understood as a result of subplantation of incident ions; the incoming ions impact on the growing film induces the sp^3 bonding (ion dominated deposition process) [22] instead of the chemical-driven stabilization of sp^3 bonding in CVD diamond. As a physically driven process, two methods are commonly considered, evaporation, where the coating material is a melted precursor; and sputtering, where the coating material is in solid form. We summarize the main DLC deposition techniques from the Robertson's seminal review paper as follows [18].

In the ion beam deposition of DLC typically the system consists in a graphite cathode irradiated by an ion source, such as Ar, causing the generation of carbon ions. Decomposition of hydrocarbons in plasma can also be used to create the carbon ions. Subsequently carbon ions are shaped as a beam and accelerated towards the sample surface by using electromagnetic fields and apertures. A sophisticated version of ion beam deposition uses small ion energy spread carbon ions that have been accelerated to 5–40 kV and filtered by a magnetic filter thanks to their e/m value. The deposition is done after slowing down and focusing the selected species. The technique is called mass selected ion beam deposition and is very appropriate to deposit C thin films, e.g. ta-C film, with high control in spite of its low rate and high cost. Similar techniques are also applied for example to fullerene deposition. We will briefly describe some particular version of ion beam assisted deposition of DLC in Sect. 2.4.

Sputtering is the most conventional technique for industrial deposition of DLC. It generally consists on the use of argon plasma to ablate a graphite electrode by means of dc and rf fields, or magnetron for increased sputtering yield. It allows to deposit a-C:H films, as well as a-CN_x films if argon plasma is combined with nitrogen, but sputtered films are not the hardest grade among the DLC films.

Another particular technique used for DLC thin film deposition is the so-called cathodic arc method. It is based on the high ion density formed by a striker on a graphite electrode. The plasma and particulates are produced as an arc in high vacuum ambient. Low energy plasma for the actual deposition on the target substrate is obtained after magnetic filtering (and eventually accelerated by dc or rf fields) and

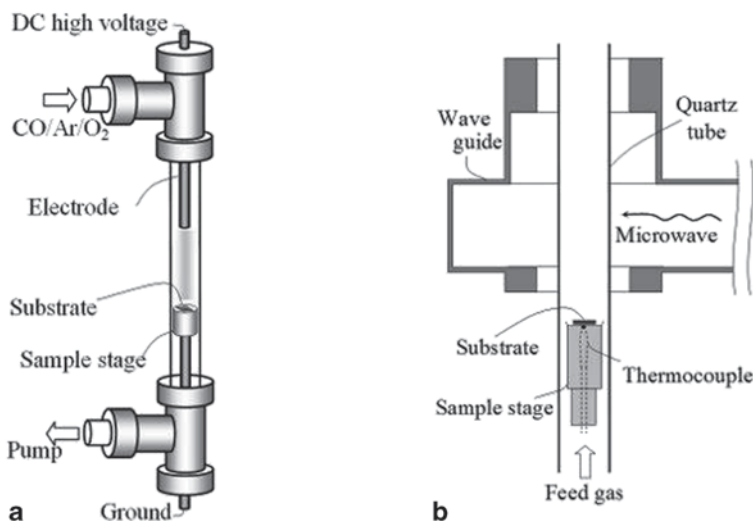


Fig. 2.5 Examples for plasma reactor systems used in nanocarbons deposition. S. Mori and M. Suzuki (2010). Non-catalytic, low-temperature synthesis of Carbon nanofibers by plasma-enhanced chemical vapor deposition, Nanofibers, Ashok Kumar (Ed.), ISBN: 978-953-7619-86-2, InTech, DOI: 10.5772/8159. (Available from: <http://www.intechopen.com/books/nanofibers/non-catalytic-low-temperature-synthesis-of-carbon-nanofibers-by-plasma-enhanced-chemical-vapor-depos>)

provides ta-C films with high deposition rate and low cost. Pulsed laser deposition also roots in the use of a carbon plasma plume which materialization is induced by pulsed excimer laser such as ArF. The deposition dynamics basically depends on the fluence of the laser pulse and the obtained films are typically ta-C.

To conclude with the techniques for DLC deposition, plasma enhanced CVD is probably the most widely used among scientists (Fig. 2.5) [23–25]. It consists in a pair of asymmetric electrodes between which plasma is created. Accounting for the higher mobility of electrons respect to ions positive space charges (sheath) are formed onto both electrodes. The smaller electrode acquires net negative sheath voltage (cathode) and therefore is used to hold the sample, as the positive ions are accelerated toward its surface. The effective ion energy does not correspond to sheath voltage but depends on ambient pressure and ion collisions. This causes a certain ion energy distribution that could be minimized by the use of low pressure, which contrarily would be detrimental to the strike probability (i.e. deposition). To overcome this the magnetic confinement of the plasma can be used (namely plasma beam source), apart from further sophisticated systems. Nonetheless a-C:H films are effectively grown whose characteristics strongly depend on the gas precursors used; the hydrocarbons, such as benzene, acetylene, propane, ethane or methane, and hydrogen as carrier/dilution gas are the more common.

Somehow a counterpart of DLC for not amorphous but randomly oriented texture graphite-like material is glass-like carbon, also referred as glassy carbon or

vitreous carbon [26]. Commonly used as electrode material in electrochemistry is defined as a non-graphitizing carbon that combines glass and ceramics properties (hardness, high temperature resistance...) with those of graphite (low electrical resistance, low friction...). It was discovered in the mid-1950s as a product of the firing of cello tape in an inert atmosphere. Chemically modified electrodes made of glassy carbon paste, glassy carbon, etc. have been used for organic molecules sensing. Good review materials including synthesis and characteristics of glassy carbon thin films can be found in [27].

2.3 Nanosized Carbon Materials

Intrinsically nanosized materials, and more precisely carbon nanomaterials, are one of the major spotlights of nanotechnology. The merit resides in two aspects; either they present novel properties or their show promise for value-added performance. For crystalline carbon nanomaterials, fullerenes, CNTs and graphene, the synthesis itself represents a landmark. Its discovery, its structural comprehension, encouraged much research to exploit their potential novel functionalities, where their controlled synthesis and production is essential. Yet carbon nanomaterials still show some defiance to be completely and precisely tailored.

We provide in the following an overview of CNTs and graphene synthesis. The main methods will be shortly described along with a discursive summary of their main morphological, structural and functional features. As in present book we leave the relevant fullerenes (and metallofullerenes) out of the description on carbon sensing devices, literature on fullerene synthesis is listed here [28–33].

2.3.1 Carbon Nanotubes

The relevance of the CNTs as a low dimensional entity is that it constitutes not a solid fiber or wire, as its name indicates, but a hollow very anisotropic nanostructure (of top length-to-diameter ratio). At the time of the discovery of (multiwalled) CNTs (MWCNT) [34] carbon nanofibers were long-known and produced nanomaterials [35, 36]. But TEM revealed the possibility of forming a novel carbon crystalline nanostructure in addition to the fullerenes; now concentrically ordered graphene layers were arranged along a longitudinal axis, forming a cylinder (Fig. 2.6).

The synthesis of a single walled CNT (SWCNT) just followed and CNTs became an archetype of the materialization of quantized properties occurring in nanomaterials, precisely because of the size in the nanometer scale order. In other words, the most special characteristic of SWCNTs derives from its extremely small diameter, which typically is around 1 nm, and how the atomic C arranges with respect to the SWCNT longitudinal axis, which it determines its electronic band structure.

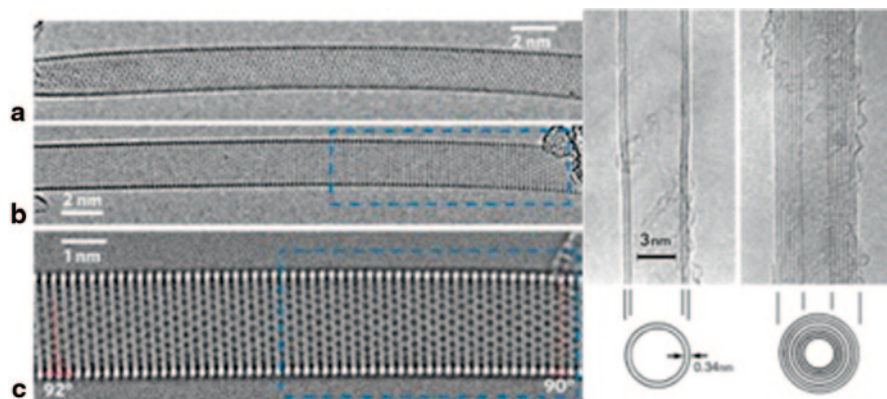


Fig. 2.6 (left) HRTEM of SWCNTs with different chirality. Reprinted by permission from Macmillan Publishers Ltd: (Nature Materials 10, p. 958) J.H. Warner et al., copyright (2011) (right) HRTEM of double walled CNT and MWCNTs. (Reprinted by permission from Macmillan Publishers Ltd: (Nature 354, p. 56) Iijima, copyright (1991))

The representation of the C atoms position can be expressed in terms of a pair of indices (n , m), where the integers are unit vectors along two directions of the constituent rolled graphene layer. Coarsely explained, the calculation of the SWCNT electronic band structure as a function of (n , m) indices reveals the band gap opening for SWCNTs with $n \neq m$, which leads to semiconducting (and metallic) SWCNTs. Being able to synthesize SWCNTs of specific chirality is a major challenge of SWCNT growth, but, specially, a strict requirement for certain applications. Instead, MWCNTs consist of multiple rolled graphene layers and they always show metallic behaviour as electrical conductors.

In both cases, other properties, like thermal and mechanical characteristics, of SWCNTs and MWCNTs are also remarkably outstanding. These properties are a signature of the strong C–C bonds, the sp^2 hybridization, which makes them all really useful for a number of applications. Examples include CNTs as additives in all sorts of structural materials and, obviously, for various devices, such as sensors [37–39].

Arc discharge was the original method used to produce both the first observed CNTs and the first intentional synthesis of CNTs. It relies on the sublimation of carbon from a negative graphite electrode due to high discharge temperature. The obtained CNTs are structurally of high quality, with few defects, but the soot is a mixture of CNTs with other carbon deposits, such as various types of amorphous carbon. In addition, it is difficult to control the CNT structural characteristics, such as thickness (SWCNTs, MWCNTs), diameter and length.

Other methods such as laser ablation enable obtaining amount of CNTs with higher purity ratios. Laser ablation relies on the vaporization of a graphite target by pulsed laser inside a high-temperature reactor in an inert gas atmosphere. Vaporized carbon condenses in the form of CNTs in the cooler surfaces of the reactor (e.g. some water cooled substrate intentionally placed to collect the CNTs). Using a

composite of graphite and metal particles SWCNTs of controllable diameter can be synthesized. Particularly, cobalt-nickel alloy and determined process temperatures give the best yield and controllability. As a significant drawback, the technique is more expensive than other methods, such as chemical vapour deposition.

CVD or catalytic vapour deposition of CNTs is based on the chemical reaction of some carbon precursor gas, usually mixed with some carrier gas such as H_2 , Ar, etc., with some tiny particles acting as nucleation points for the tube formation [40]. The reactor can be very simple, typically consisting in a high temperature furnace (~ 700 – $1000^\circ C$), which chamber can be operated in vacuum or atmosphere pressure. A reactor is equipped with the gas inlets and outlets, and corresponding flow meters and valves, either manually or electronically controlled.

Carbon feedstock gases used for CNT growth are generally organic compounds such as hydrocarbons, methane, ethane and so forth, but alcohols can be used as well. The simplest, methane, is probably the most widely used as its thermal and catalytic decomposition products would result the simplest and more uniform. Obviously, process parameters strongly determine the CNT deposition, i.e. realization of the synthesis in crystalline form. Temperature, chamber pressure and gases ratio are the key variables. However, the crucial element of the crystalline CNT formation by CVD is the catalyst [41].

Fine particles of metals such as Ni, Co or Fe are very efficient for CNT formation and alloyed particles can be used as well. Oxides are also appropriate when they are reduced by certain temperature conditions. A key aspect for the CNT formation is the formation of the catalyst particle, as discussed below. In this respect, two types of CNT growth mechanisms are identified; tip growth and base growth (sometimes also called extrusion or root growth) (Fig. 2.7). In tip growth, the body of the nanotube is formed by piling atomic carbon beneath the metal particle, so that metal particle displaces as the CNT grows. As a result CNTs have the minute catalyst particle at the tip of the tube. Instead, in the base growth the carbon progressively incorporates to the semi-fullerene cap, essential antecedent of CVD CNT synthesis, which has formed onto the catalyst particle. In consequence, CNT nucleation particle is not at the CNT tip, but resting in its original position. Dissolution rate of atomic carbon into the various metal tiny particles is a major factor on driving the actual growth mechanism.

An additional aspect of the role of the catalyst in the CNT growth is the catalyst particle size, as the CNT size is very much related to the tube diameter. There are various strategies to provide the minute particles for CNT CVD growth. One option is directly to use catalyst particles of (single digit) nanometer size. In this case the challenge is to avoid the agglomeration of the particles, which melting at process high temperature, would promote the formation of bigger particles, even preventing CNT growth. Isolated catalyst particles can be dispersed on a substrate, for instance, by dissolution and spin coating; otherwise, one should find the appropriate catalyst preparation method, also very much depending on the desired CNTs architecture. Although controlling the CNT growth by means of the catalyst particle is very attractive, for example, using spinel particles, and great achievements have certainly been obtained, it shows practical limitations [42, 43]. As it relies on engineering the

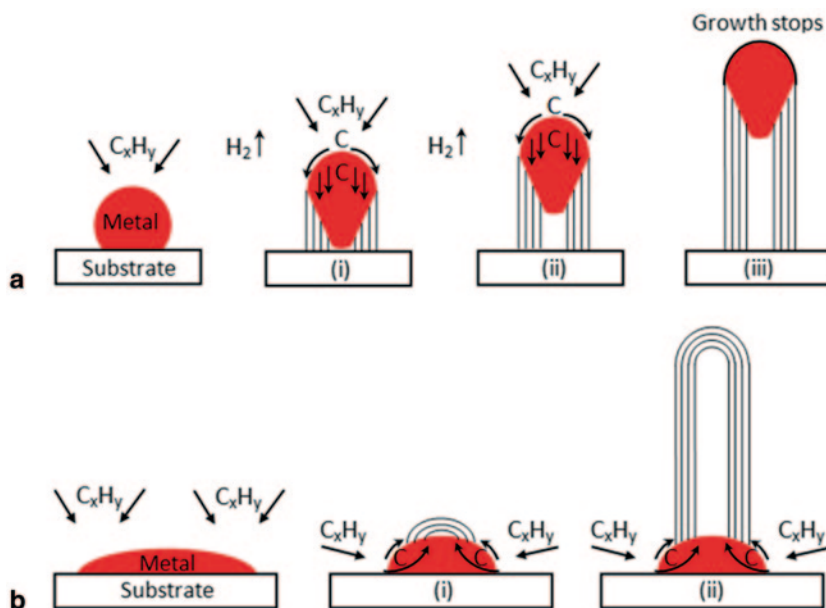


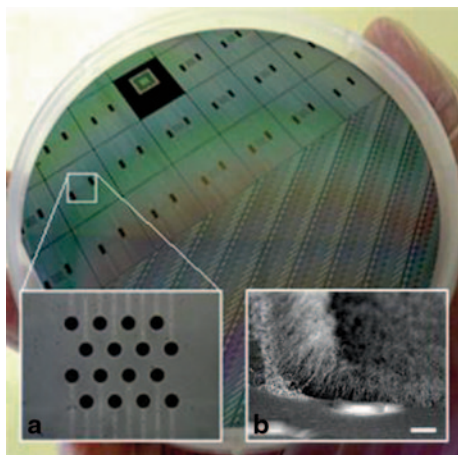
Fig. 2.7 Accepted CNT growth models; tip growth (*upper row*) and base growth (*lower row*). Mukul Kumar (2011). Carbon nanotube synthesis and growth mechanism, Carbon nanotubes—synthesis, characterization, applications, Dr. Siva Yellampalli (Ed.), ISBN: 978-953-307-497-9, InTech, DOI: 10.5772/19331. (Available from: <http://www.intechopen.com/books/carbon-nanotubes-synthesis-characterization-applications/carbon-nanotube-synthesis-and-growth-mechanism>)

same particle, the particle synthesis tolerances, again together with the thermally-induced changes, are very severe especially when the goal is to control strictly the SWCNTs chirality/diameter.

As another main alternative for catalyst preparation, many groups use the thermal decomposition of ultrathin metal layers to obtain the metal particles that initiate the CNT formation under the CVD growth feedstock gases. In this case, pre-CNT growth conditions such as heating rate and pressure play a critical role in the particle formation. Formation of large particles due to melting is particularly serious on ultraflat technical substrates, such as thermal SiO_2 surface. In this case, a very simple solution that can be applied to certain cases is the use of the so-called buffer layer underneath the metal thin film. In particular, films such as Al_2O_3 , having finite roughness, help the metal layer to break into convenient tiny catalyst particles [44]. Other original methods to induce the CNT formation consist in space constrictions, such as the growth based on nanometer size porous materials, and even relying on the metals embedded on those materials or other molecules as catalysts [45].

Actually, tip versus tube growth had actually been understood thanks to the synthesis of vertical oriented CNTs. Intrinsically highly anisotropic CNTs can be synthesized in various arrangements respect to the substrate; namely, 1) laying on

Fig. 2.8 Integration of vertically aligned CNTs on Platinum electrodes for biosensing, Microelectronic Engineering 86 (2009) 806–808 [45]



the substrate—horizontally oriented CNTs; 2) perpendicular to the substrate—vertically oriented CNTs or arrays (Fig. 2.10); and 3) randomly oriented CNTs or forests. The ability to control the orientation of the grown CNTs very much depends on the growth parameters in precise coordination with the catalyst preparation and the processing conditions [46, 47].

The capability to grow horizontally oriented CNTs is essential for establishing CNT-based nanoelectronics, preferably, the ability to synthesize site-specific direction oriented growth of either semiconducting or metallic CNTs. Patterning the catalyst is a good strategy to predetermine the location where the CNTs are deposited by CVD. In combination with the CNT growth conditions and other preparations, catalyst patterning adds remarkable potential, e.g. for enabling specific electronic device applications, such as CNT-sensor electrodes integrated into microelectronic circuits (Fig. 2.8).

Continuing with the attractive potential of SWCNTs in terms of electronics, real applications are actually benefiting from the tolerance of MWCNTs in terms of growth, while very apparently SWCNTs are not able yet to represent a significant alternative to Si-based devices. Nevertheless much progress has been accomplished and the knowledge in terms of synthesis and characteristics generated towards the goal of SWCNT-based logic electronics undoubtedly represents valuable information for any domain related to CNTs.

To conclude with CVD deposition of CNTs, although CVD method does not provide the highest quality CNTs (less defective), it is undoubtedly the preferred technique. It is not only most versatile for producing a number of CNT architectures as illustrated above but it allows outstanding control of the characteristics of CNT products and processing reproducibility. Remarkably it is a scalable and relatively cheap process so CVD route is making viable the commercialization of CNTs.

Physically enhanced CVD technique can often be used to boost the yield (towards massive production) and influence the structure of synthetic nanosized carbons (multiplying the possibilities and fulfilling the needs of application-oriented approaches), as it will be presented later. Additional aspects related to the production and manipulation of CNTs as required for applications, for instance, removal of the metal catalyst particle are covered in Chap. 3 (dispersion of CNT in polymer matrices) and 4 (functionalization). Formation of yarns, cables, fibers, sheets, sponges, etc. can be consulted for example in Refs. [48–51].

2.3.2 Graphene

Graphene is a single atom thick layer of carbon atoms forming a regular hexagonal web. At the time of its isolation [21] graphene was the missing piece of the low dimensional graphite-like nanosized carbon materials. Together with the curved graphite-based nanoentities the fullerenes structural family (the 0D structure) and the CNTs (the 1D structure) were completed with the 2D representative: graphene. The relevance and attention that graphene receives nowadays may owe a great deal to CNTs and fullerenes and in general to the scientific and technological frame created by Nanotechnology as a separate field.

Graphene is seen as a paradigmatic material likely to revolutionize transversally and to impact any aspect of our present lives. However its wide potential as a functional material lies in some cases on the compliance with graphene pristine characteristics which becomes a challenge for technologists, engineers... The list of graphene applications include lightweight actuators for space applications, hydrogen storage, water filtration, etc. and all sorts of novel and more efficient electronics-related devices, ranging from sensors and batteries to transparent displays and solar cells [52, 53].

In any case, graphene is structurally a very special case as it can be considered in the limit of shape versus bulk structure crystalline nanomaterials. The current interest and (re)consideration of the potential other 2D crystalline (nano)materials is a consequence of graphene investigations (Fig. 2.9) [54].

Actually graphene discovery is but the confirmation of the very special characteristics theoretically derived from a strict 2D carbon structure. While initially defying conventional calculations on material stability, graphene electronics demonstrated electron behaviour as mass-less Dirac particle which would have tremendous implications in electronic devices [55]. Subsequently superior thermal and mechanical characteristics were confirmed as well [56, 57]. Nonetheless, graphene re-nurtured and completed the threshold envisioned for the potential of nanomaterials, as an application-oriented aspiration of the market as well; as one of the pillars of a technology revolution.

First materialization of graphene started nearly as a game. The so-called mechanical exfoliation of graphite consists of transferring a graphene microcrystal by

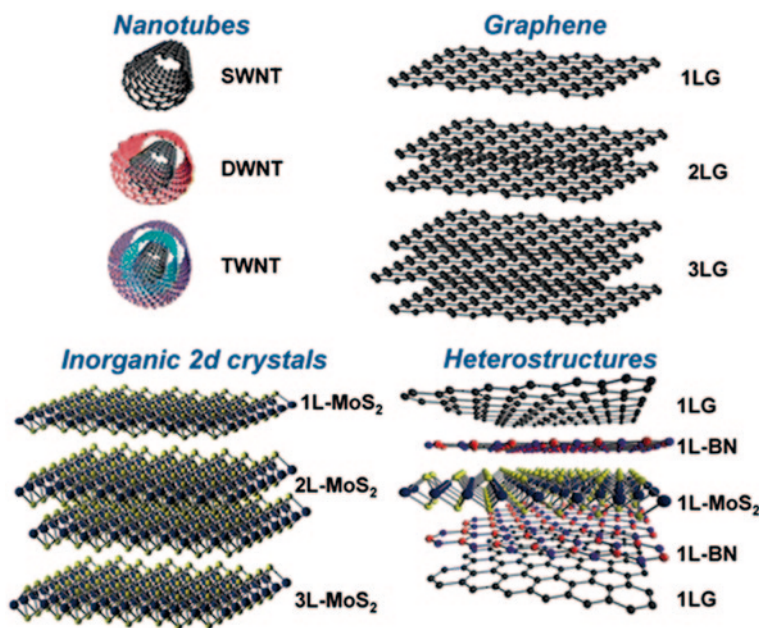


Fig. 2.9 Family of layered nanomaterials. (*Carbon*) nanotubes and graphene have promoted the reconsideration of other inorganic 2D materials and the potential of heterostructures based on their combination. (Reprinted with permission from Bonaccorso et al. ACS Nano vol. 7, 1838–1844. Copyright (2013) American Chemical Society)

picking some graphite thin layer with a piece of cello tape and rubbing it onto the target substrate, e.g. silicon dioxide. Although some attempts have been done, for example, on applying or developing thermal tapes from more reliable transfer, it is clear that the technique is technologically irrelevant, e.g. intrinsically excludes graphene synthesis, especially because of its limited throughput, scalability, controllability, etc. Therefore it is not suitable for real practical applications. Yet best (pristine) graphene characteristics have been observed on mechanically exfoliated graphene from HOPG.

Similar to the status of SWCNTs technology as an alternative to Si within integrated circuits, the integration of graphene as a standard/routine material in microelectronics, namely planar technology, is considerably far from been established. However the possibility to obtain high quality graphene formed directly on SiC crystal wafers is very promising.

The formation of graphene layers on SiC wafers due to high temperature treatment had long been known [58] but it was then considered rather inconvenient as there was no awareness of the relevance of graphene. Nowadays on the contrary the interest upon the feasibility and then consolidation of a graphene-on-SiC [59] is boosting definitely both graphene and SiC investigations (Fig. 2.10) as a sort of reciprocal benefit for their development, either separately or together.

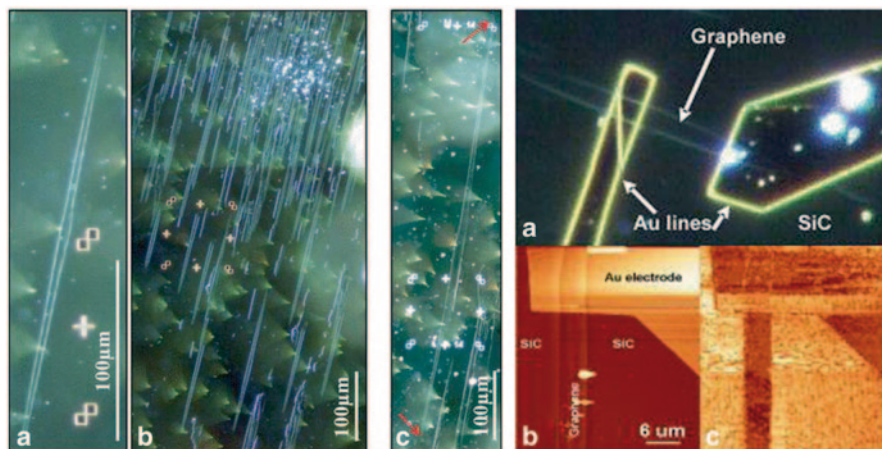


Fig. 2.10 Anisotropic growth of graphene flakes on SiC wafers by thermal decomposition. (Left) The elongated graphene flakes result from the use of a graphitic cap. (Reprinted from Camara et al. Phys Rev B 80, 125410 (2009) under the creative commons attribution 3.0 license (CC-BY); (right) **a** OM image of graphene flake electronic devices fabricated by using EBL; AFM images of the electrically biased device. **b** topography signal and **c** electrical force microscopy signal. G. Rius et al. J. Vac. Sci. Technol. B 27 (2009) 2691)

The deposition of graphene on SiC occurs at high temperatures (typically $> 1500^{\circ}\text{C}$) due to the difference in the vapour pressures of Si and C. The sublimation of atomic Si leaves the surface supersaturated with carbon. At this temperature crystallization as graphite structure is thermodynamically favourable; the so-called epitaxial graphene on SiC can be obtained in both low (vacuum) and atmospheric pressure conditions.

The main limitation lies in the fact that graphene growth onto/from a SiC crystal is an extrinsic phenomenon; based on the decomposition of the SiC substrate. Consequently, the graphene deposition variables strongly depend on: (i) the characteristics and initial state of the SiC crystal; (ii) the ex situ and in situ conditioning of the SiC surface; (iii) the thermal treatment conditions (temperature, pressure ...); (iv) the dynamics of the crystallization. Accordingly, the characteristics of the deposited graphene, such as crystal size/domain, number of layers, etc., but especially graphene electronic properties will be particularly influenced by the reconstruction of the SiC underneath (e.g. width of the terraces, height of the steps) and the graphene-SiC interface (charge transfer, graphene conformality to SiC, etc.). See the special issue on epitaxial graphene on SiC [59].

In short the deposition of epitaxial graphene on SiC is dominated by two growth factors: nucleation and growth propagation. Nucleation is directly connected to the presence of defects and impurities as well as SiC step bunching while growth propagation will be very much determined by the factors affecting the carbon mobility such as width of the SiC terraces, e.g. height of the steps and pressure.

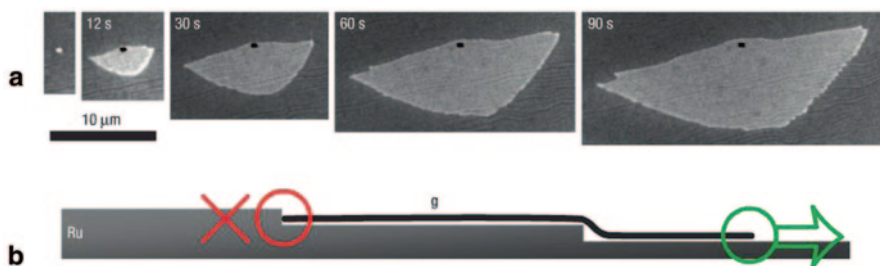


Fig. 2.11 Growth of epitaxial graphene on Ru as a function of time **(a)** and sketch of a growth propagation model **(b)**. (Reprinted by permission from Macmillan Publishers Ltd: (Nature Materials 7, p. 406) P.W. Sutter et al. copyright (2008))

From the viewpoint of the graphite crystallography graphitization (graphenization) can be thought as function of the increase of the crystal size in the basal plane (L_a) and the stacking of graphene layers (L_c). When L_c increases multilayer graphene is obtained. In epitaxial graphene on SiC the control over both L_a and L_c is very much affected for example by the morphology of the SiC substrate.

Similar considerations can be applied to the deposition of graphene by CVD technique. The morphology and dimensions of the graphene crystal are determined to a large extent by the characteristics and conditioning of the catalyst material and substrate. As expected, growth is also very dependent on the process conditions of temperature, pressure, carbon precursor (e.g. feedstock gases, but also solid sources) as in the case of the CNT growth.

Concerning the materials used as catalyst a list of transition metals has been explored for graphene deposition and in relation to aspects such as lattice match. Among others ruthenium (Fig. 2.11), iridium, platinum, palladium, rhenium and rhodium show very particular characteristics due to the metal-graphene interaction. A nice review highlighting the effect of the metal-graphene interface can be found in [60] covering aspects such as effect of corrugation and shift of π -band.

Because graphene is intrinsically an all interface material its characteristics can be dominated by the environment as it also happens with the growth of graphene. For example, graphene layers can be formed on iron carbides under certain cooling rates [61]. In this case the graphene deposition can be analyzed in terms of the phase diagrams. The high affinity of Fe and C makes favourable the formation of stable carbide but graphite (graphene) precipitation can be forced by fast cooling [61].

A similar analysis can be applied to the CVD growth of graphene on Ni. The solubility of C in Ni is high at temperatures above $\sim 800^\circ\text{C}$ leading to the formation of a solid solution. A decrease in the temperature implies lowering the solubility so that C tends to diffuse out of Ni. In these conditions the graphite phase is stable and graphitization effectively occurs. Preferential precipitation however happens at the grain boundaries of polycrystalline Ni which becomes a main drawback for single layer graphene deposition preventing a uniform distribution of the grown graphene upon the Ni surface. This growth mechanism is commonly referred as dissolution-precipitation method [62].

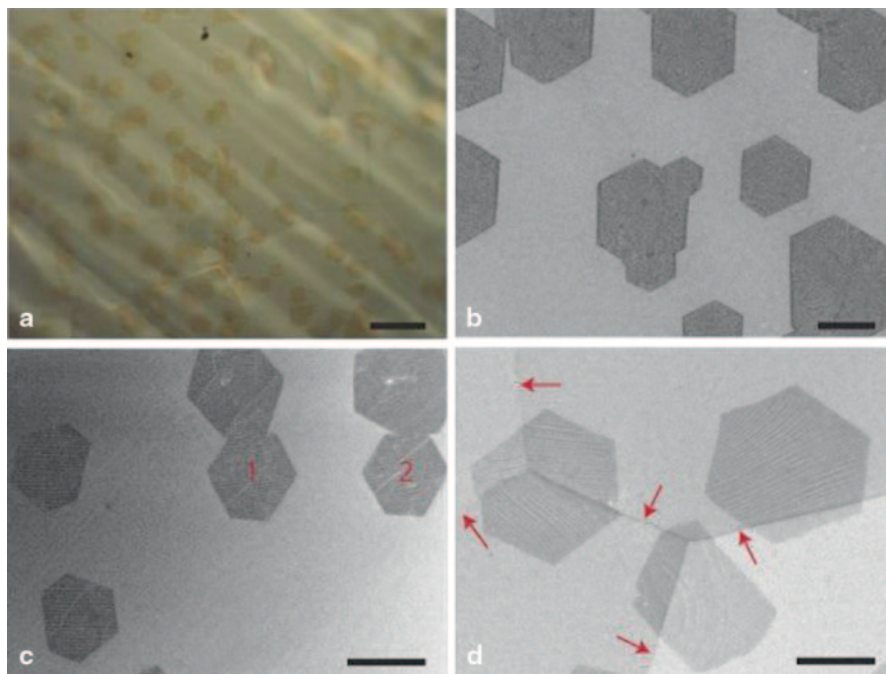


Fig. 2.12 CVD graphene grown on Cu. Single crystal domains can be formed across Cu grain boundaries (d). (Reprinted by permission from Macmillan Publishers Ltd: (Nature Materials 10, p. 443) Qingkai Yu et al. copyright (2011))

In contrast, specifically using copper as the metal catalyst generally can overcome this aspect. Cu is not only convenient in terms of cost but the very low solubility of C in Cu, even at 1000 °C which is close to its melting temperature, suggests a better control of the catalysis for single layer graphene formation. As a result graphene thickness is not the main issue when performing CVD on Cu and using hydrocarbon as the feedstock gases (Fig. 2.12). Not only CVD is the preferred method, as it will be discussed and highlighted below, but it can be said that Cu has become the standard substrate for graphene CVD.

Typical growth parameters are ~1000 °C and similar to CNT growth a combination of H_2/CH_4 gases is used while growth time and pressures values reported in the literature vary a lot. This appears to be a kind of signature of the differences among reactors, such as feedstock control, and of other variables such as the catalyst conditioning.

When Cu is the catalyst usually commercially available Cu foils are employed with thickness of a few tens of microns. Cu foils are composed of randomly oriented crystals (polycrystalline) so that pre-growth treatment in an inert gas (N_2 , Ar) and H_2 annealing are key steps of the graphene growth [61, 63].

One of the most remarkable differences between the syntheses of graphene on Cu versus Ni is the growth mechanism. While dissolution-precipitation is understood

for Ni, on Cu hydrocarbon decomposition and adsorption make possible the crystallization driven by nucleation and diffusion phenomena. Due to this fact, again the pre-growth treatments (conditioning and annealing) are very important for CVD graphene on Cu: it is the route to guarantee the smoothness of the Cu surface which would enable more controlled, uniform and large graphene crystal deposition.

In summary, CVD graphene is far from providing perfect graphene crystals, but it is undoubtedly the more promising among the available techniques, combining good quality with potential in terms of cost and scalability (for large volume production). Nevertheless, the major differences in the mechanical, thermal and electronic properties of CVD graphene are not attributed to the growth, but to its manipulation (see next section), and this factor is common for most of the synthetic methods.

Alternative chemical methods for graphene production are the reduction of graphene oxide (GO) or total organic synthesis and unzipping CNTs. The unzipping CNTs by means of Ar plasma and KOH etching was originally proposed as the simplest method to provide graphene nanoribbons. Controlled synthesis of graphene nanoribbons would be extremely desirable for nanoelectronics in relation to the possibility of band gap opening, high mobility and spin properties [64].

Production of graphene-layers by the reduction of graphene oxide (GO) [65] method actually involves two steps. First graphite is oxidized by oxidants such as sulphuric acid, nitric acid and potassium permanganate following the Hummers method. GO can be easily exfoliated in water, forming stable solutions of single layer GO by using ultrasonication. Then chemical reduction is applied with reducing agents such as hydrazine and sodium borohydrate. Alternatively thermal reduction has been reported [66]. In general the resulting graphene is of poor crystal quality due to vacancies, contamination, etc., which derives from the manipulation, the use of strong chemicals and incomplete reduction. In the case of total organic synthesis this bottom-up technique referees to building up graphene from graphene-like molecules and monomers like polyacyclic hydrocarbons. It resulted successful for graphene nanoribbons on metal surface with high control.

To some extent it is actually related to the variety of products of the chemical synthesis of graphene (but also their properties and use) that a necessity to strictly define the graphene-related nomenclature for publications arose. An attempt to rationalize the nomenclature for 2D carbon materials has recently been proposed by the editorial board of Carbon journal [67].

Speaking of nomenclature and graphene structure tolerances the group of graphene-like materials include some porous structures with particular orientation respect to the substrate such as those known as carbon sheets, carbon nanowalls (CNW), etc. Those self-standing graphene flakes (the counterpart of vertically aligned CNTs) are considered particularly interesting for devices such as supercapacitors and batteries due to their high surface area a characteristic that makes them suitable for sensing too (Fig. 2.13). They are typically produced on plasma enhanced CVD methods such as inductively coupled PECVD, microwave PECVD, etc. Physically enhanced CVD techniques usually combine the capability to produce oriented growth (depending on process conditions) with higher deposition

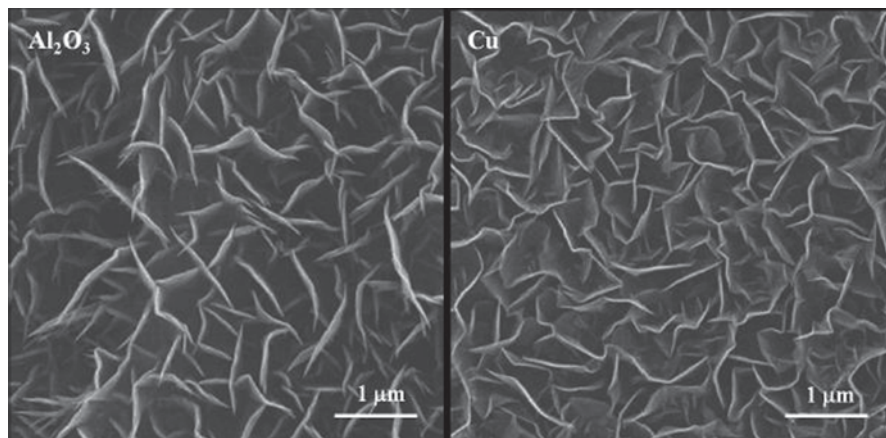


Fig. 2.13 CNWs grown on Al₂O₃ substrate (*left*) and Cu foil (*right*) by using microwave PECVD. (Rius et al. e-J. Surf. Sci. Nanotech. 10 (2012) 305)

yield. However, this often occurs at the expense of graphene crystal quality, domain size or control over the number of layers.

2.4 Carbon Nanomaterials as Functional Elements

Until here, the preparation of carbon materials has been introduced mainly based on their synthesis including mention to a few preparation strategies based on ‘simple’ modifications such as carbonization, intercalation for exfoliation/cleavage and so on. We discussed the production of the different textures desired for carbon materials applications as a brief summary of the established as well as developing methodologies.

However carbon materials in the form of raw materials hardly ever are found useful except perhaps as fuels for combustion. All sort of applications require the manipulation of the carbon materials so that they effectively become functional elements for some application. Technologically this is nowadays particularly true for newly synthesized carbon materials and most critical point for nanosized carbon materials, as the market demands their exploitation (commercialization).

While some applications require little modification of the raw carbon materials, such as polymer composites others such as CNT-FETs challenge the established methods to fabricate the devices. Polymer-carbon composites preparation, very far from being trivial (Chap. 3), can sometimes be attained following existing/conventional methods and it is the innovation provided by the elements and their compound properties what diversifies or enhances their performance as functional elements. Otherwise disruptive technologies may be required as stressed by the case of graphene and CNTs in integrated circuits. Roughly speaking two categories can be distinguished.

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