Chapter 2
Preparation Methods

The first report on the fabrication of two-dimensional carbon nanostructures dates back more than 10 years. Ando et al. [1] found petal-like “carbon roses” during the fabrication of carbon nanotubes in 1997. In 2002, Wu et al. [2] reported the fabrication of two-dimensional carbon nanostructures, “carbon nanowalls,” standing vertically on catalyzed substrates. Both cases were found incidentally during the fabrication of carbon nanotubes. Shang et al. [3] prepared carbon nanoflake films using hot filament chemical vapor deposition (CVD). To date, carbon nanowalls and similar structures have been grown using various CVD methods such as microwave plasma [2, 4, 5], radio frequency (RF) inductively coupled plasma [6], RF capacitively coupled plasma assisted by H radical injection [7, 8], DC plasma [9], helicon-wave plasma [10], electron beam excited plasma [11], hot-filament CVD [3, 12], and even by sputtering of a glassy carbon target [13, 14].

This chapter is devoted to introduce experimental methods for synthesizing carbon nanowalls. Synthesis techniques for carbon nanowalls are similar to those used for diamond films and carbon nanotubes. In general, a mixture of hydrocarbon and hydrogen or argon gases, typically CH₄ and H₂, is used as source gases for the synthesis of carbon nanowalls. High-density plasmas such as microwave plasma and inductively coupled plasma are suitable for decomposing H₂ molecules efficiently because it is considered that a large amount of H atoms is required for the growth of carbon nanowalls, which is similar to the case for diamond growth. Metal catalysts such as Fe and Co are required for the growth of carbon nanotubes, whereas the situation for the growth of carbon nanowalls is not so critical and carbon nanowalls do not require for their nucleation such catalysts in many cases. Consequently, carbon nanowalls have been fabricated on several substrates, including Si, SiO₂, Al₂O₃, Ni, and stainless steel, at substrate temperatures of 500–700°C without the use of catalysts [15].
2.1 Microwave Plasma Enhanced Chemical Vapor Deposition

Microwave plasma is one of high-density plasmas and is suitable for decomposing H₂ molecules to generate H atoms effectively. Figure 2.1a, b show two types of microwave plasma-enhanced chemical vapor deposition (MWPCVD), which have been called NIRIM (the National Institute of Research of Inorganic Materials, Japan) type and ASTeX (Applied Science and Technology, Inc.) type, respectively. These systems have been extensively used for the growth of diamond films.

In the case of NIRIM-type MWPCVD system, the CH₄/H₂ plasma is generated in a cylindrical quartz tube, which intersects a rectangular waveguide, as shown in Fig. 2.1a. The dimensions of the waveguide are chosen to drive the TE₉₀ mode of a 2.45 GHz microwave provided by a power generator. A short circuit stub can be adjusted to obtain a stationary wave with the maximum in electric field located in the center part of the tube. Three tuning stubs allow the minimization of the reflected power. The plasma provides the substrate heating. The major advantages of NIRIM-type reactors are (1) simple reactor design with relatively low set-up costs and (2) flexible variation of substrate position relative to the plasma. On the other hand, the size of substrate is limited to approximately a few cm² by the inner diameter of the cylindrical quartz tube.

The ASTex-type reactor consists of a cylindrical stainless steel chamber. The microwave (2.45 GHz) is coupled from the rectangular waveguide into the cavity via an axial antenna. A discharge called a “plasma ball” is generated above the substrate. The plasma ball provides the substrate heating. In this system, the CVD process would be operated at pressures of a few tens of Torr (~10³ Pa), and the reactor pressure and microwave power cannot be varied completely independently. At too high pressure or low microwave power, plasma cannot be sustained. On the other hand, if the microwave power is too high for a given pressure, the plasma becomes unstable and tends to jump to the quartz (fused silica) window, occasionally resulting in the destruction of the window by the heat.

Fig. 2.1 Schematic of microwave plasma-enhanced CVD systems. (a) NIRIM (National Institute of Research of Inorganic Materials) type, (b) ASTeX (Applied Science and Technology, Inc.) type
In the case of diamond growth, deposition is carried out in a mixture of CH₄ and H₂ at substrate temperatures of 700–800°C. Typical H₂/CH₄ flow rate ratio is about 100. The high H₂/CH₄ flow rate ratio for diamond growth is essential to remove unwanted non-diamond phase. In the case of the synthesis of carbon nanotubes or carbon nanowalls, on the other hand, deposition process is carried out at a low H₂/CH₄ flow rate ratio of 1–4.

Wu et al. reported the synthesis of carbon nanowalls on the catalyzed substrate using the NIRIM-type MWPCVD reactor [2, 16–18]. Although the growth of carbon nanowalls was found during the growth of carbon nanotubes at first, they successfully synthesized carbon nanowalls on various substrates using MWPCVD, and systematically investigated the effects of the gas flow rate ratio and electrical field on the formation of carbon nanowalls. They also reported the field emission and electron transport properties of carbon nanowalls. Typical carbon nanowalls were grown employing a mixture of CH₄ and H₂ at the H₂/CH₄ flow rate ratio of 4, total pressure of 1 Torr (133 Pa), and substrate temperatures of 650–700°C. Figure 2.2a–f show SEM images of carbon nanostructures grown at different

![SEM images of carbon grown at different H₂/CH₄ flow rate ratios: (a) 30, (b) 15, (c) 10, (d) 6, (e) 4, (f) 1. Scale bars: (a), (b), (d), and (f) 1 μm; (c) and (e) 100 nm. By courtesy of Prof. Wu [18] – reprinted with permission from The Royal Society of Chemistry](image)
H$_2$/CH$_4$ flow rate ratios [18]. The H$_2$/CH$_4$ flow rate ratio was found to cause drastic changes to the morphology of the nanocarbon films. Typical carbon nanowall film was grown at the H$_2$/CH$_4$ flow rate ratio of 4, as shown in Fig. 2.2e. Wu et al. have also demonstrated the use of carbon nanowalls as templates for the formation of other types of nano materials, which will be described in Chap. 7.

Chuang et al. reported the growth of carbon nanowalls in freestanding, three-dimensional aggregates by MWPCVD using ASTex-type reactor, and investigated their field emission property [4, 19]. Three-dimensional macroscopic carbon nanowall aggregates extruded from plasma sites on the copper growth stage. Ammonia and acetylene were used as a source mixture. The ammonia to acetylene gas flow rate ratio NH$_3$/C$_2$H$_2$ had a strong influence on the microstructures of carbon nanowalls, and the growth of carbon nanowall aggregates was observed for a NH$_3$/C$_2$H$_2$ gas flow rate ratio below 1. In their method, growth of carbon nanowalls was catalyst-free and unconstrained by substrate surfaces. Deposition was extremely efficient and produced centimeters-long superstructures in only 10 min. They also carried out Brunauer-Emmett-Teller (BET) measurements [20] in liquid nitrogen and reported that the BET surface area for nitrogen adsorption at 77 K is 37.3 m$^2$/g and the average pore width is 12.3 nm, for carbon nanowalls grown with a NH$_3$/C$_2$H$_2$ ratio of 0.4 [19].

Hiramatsu et al. have grown a variety of carbon structures by MWPCVD using the ASTex-type reactor shown in Fig. 2.1b. Diamond films, carbon nanotubes, and carbon nanoflakes can be fabricated by changing the synthesis condition including gas flow rate ratio of hydrogen to hydrocarbon, process temperature, and substrate pre-treatment. Figure 2.3a–d show SEM images of carbon structures grown on Si
substrate by MWPCVD using the same ASTex-type reactor shown in Fig. 2.1b. As described before, diamond films were grown at the H₂/CH₄ flow rate ratio of 50–100, total pressures of 45–55 Torr (6–7 × 10² Pa), and substrate temperature of approximately 700°C on a scratched Si substrate (Fig. 2.3a), and nanodiamond films were grown at the H₂/CH₄ flow rate ratio of 10–30 [21, 22]. As shown in Fig. 2.3b, aligned single-walled and double-walled carbon nanotube films were grown at the H₂/CH₄ flow rate ratio of 1.4 on a Co-catalyzed Si substrate [23, 24]. On the other hand, carbon nanoflakes were fabricated at higher temperatures and higher pressures of source gases, as compared with the case of carbon nanotube growth. Figure 2.3c, d show SEM images of carbon nanoflakes grown for 5 min at the H₂/C₂H₂ flow rate ratio of 1, total pressures of 80 Torr (~10⁴ Pa), and substrate temperature of about 850°C on the Si substrate without catalyst.

2.2 Inductively Coupled Plasma Enhanced Chemical Vapor Deposition

Radio frequency (RF: 13.56 MHz) inductively coupled plasma (ICP) is one of high-density plasmas, and has been used to etch several materials including Si, SiOₓ, SiNₓ, and metal films in the LSI (large-scale integration) fabrication process. The ICP is operated at relatively low pressures below 100 mTorr (13.3 Pa). The plasma is contained inside a chamber, which is surrounded by an inductive coil antenna. There are two types of ICP geometries: planar and cylindrical. In the planar geometry, the electrode is a coil antenna of flat metal wound like a spiral, as shown in Fig. 2.4a. In cylindrical geometry, it is like a helical spring, as shown in Fig. 2.4b. The plasma density of ICP is approximately ten times higher than that in a capacitive mode at the same RF power input [25].

In the case of planar geometry, RF power is inductively coupled into the process chamber with a planar-coil antenna through a quartz (fused silica) window. When a time-varying electric current is passed through the RF coil antenna located on the quartz window, it creates a time varying magnetic field around it, which in turn induces azimuthal electric current in the gas inside the chamber, leading to breakdown and production of high-density plasma. Plasma density of ICP discharge is on the order of 10¹² cm⁻³.

![Fig. 2.4 Schematic of inductively coupled plasmas with (a) planar spiral antenna and (b) helical antenna](image-url)
Holloway’s group reported the synthesis of carbon nanosheets using RF-ICP [6, 26, 27]. They used CH$_4$ as a carbon source with a concentration of 40% in a H$_2$ atmosphere. Free-standing carbon nanosheets with thickness less than 1 nm, consisting of one to three graphene layers, were synthesized at total pressure of 90 mTorr (12 Pa), RF power of 900 W, and substrate temperature of 680°C on a variety of substrates including Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, SUS304 stainless steel, SiO$_2$, and Al$_2$O$_3$ without any catalyst or special substrate treatment. They also reported a series of researches on the field electron emission from carbon nanosheets [6, 28, 29]. Owing to the high enhancement factor from the atomically sharp edges, carbon nanosheets can be an ideal emitter material.

Hishikawa et al. reported the growth of carbon nanowalls using RF-ICP employing a mixture of CH$_4$ and Ar [30]. Figure 2.5 shows a schematic of ICP reactor used for the growth of carbon nanowalls. The ICP chamber was 16 cm in diameter and 30 cm in height. A one-turn coil antenna with a diameter of 10 cm was set on a quartz window at the top of the chamber. RF (13.56 MHz) power was applied to the coil antenna and plasma was generated in the chamber. Si substrate was set on the middle of the substrate holder at 10 cm below the quartz window. Growth experiments were carried out at substrate temperatures of 700–850°C, RF power of 500 W, total gas pressure of 10–60 mTorr (1.3–8 Pa), and flow rates of CH$_4$ and Ar of 7 and 1.4 sccm (sccm denotes cubic centimeter per minute at STP), respectively.

Figure 2.6a, b show typical SEM images of carbon nanowalls grown by RF-ICP employing a mixture of CH$_4$ and Ar for 30 min [30]. Carbon nanowalls with relatively smooth surface were fabricated at a growth rate of approximately 50 nm/min. In the case of growth for more than 1 h, however, the morphology of carbon nanowalls changed to a highly branched surface. As shown in Fig. 2.6c,
a highly branched carbon nanowall film with high surface to volume ratio was fabricated in 4 h. These carbon nanowalls sometimes can be easily detached at the base, resulting in the formation of free standing carbon nanowall membrane, as shown in Fig. 2.6d.

In the case of plasma-enhanced CVD using RF-ICP, carbon nanowalls can be also synthesized employing CH\textsubscript{4} without dilution, CH\textsubscript{4}/H\textsubscript{2}, and CH\textsubscript{4}/N\textsubscript{2} mixtures. As shown in Fig. 2.6e, the average spacing between walls for the carbon nanowall film grown with CH\textsubscript{4}/H\textsubscript{2} mixture was slightly wide, compared with that grown with CH\textsubscript{4}/Ar mixture shown in Fig. 2.6b. On the other hand, carbon nanowall film grown with CH\textsubscript{4}/N\textsubscript{2} mixture seemed wavy, as shown in Fig. 2.6f.

RF-ICP CVD system has advantages of simple design and scalability to large area growth. In addition, the growth rate of carbon nanowalls using RF-ICP CVD with CH\textsubscript{4}/Ar mixture was rather high compared with other methods.
2.3 Capacitively Coupled Plasma Enhanced Chemical Vapor Deposition with Radical Injection

In the case of formation of carbon nanowalls using plasma-enhanced CVD with hydrocarbon/hydrogen system, it is thought that the combination of CH$_3$ radicals and H radicals is important. High-density plasmas such as microwave plasma and ICP are suitable for dissociating H$_2$ molecules to produce H atoms, as described before. In contrast, CH$_3$ radical density is higher in parallel-plate capacitively coupled plasma (CCP) employing CH$_4$ gas [31]. Figure 2.7 compares the features of CCP with ICP. The CCP might be useful to produce plenty of hydrocarbon radicals such as CH$_3$ radicals effectively, and also useful for large area deposition of the film. However, because of the shortage of H atoms [32], the CCP by itself is not suitable for the growth of carbon nanowalls.

In some cases, it is difficult to produce various kinds of species with different roles selectively and effectively at the same time using single plasma, although we have managed to control radical densities in the plasma by changing the mixing ratio of source gases and introducing pulse-time modulation of RF or microwave input power. To solve this situation, hydrocarbon or fluorocarbon gases are excited by a parallel-plate CCP, while the H atom density around the growing surface is augmented by the injection from high-density H$_2$ plasma as a remote H radical source. This is the idea of radical injection technique.

Previously, Hiramatsu et al. have demonstrated the formation of diamond crystals using a unique plasma-enhanced CVD system that consists of a parallel-plate radio frequency (RF) CCP assisted by H radical injection [33, 34]. Radical injection technique enables us to control multiple radicals individually. The successful formation of vertically aligned carbon nanowalls was demonstrated using fluorocarbon (typically, C$_2$F$_6$) plasma-enhanced CVD with H radical injection [7, 8].

**Plasma generation methods**

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<tr>
<th>Capacitively coupled plasma (CCP)</th>
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<tr>
<td>Plasma density: ~10$^{10}$ cm$^{-3}$</td>
<td>Plasma density: ~10$^{12}$ cm$^{-3}$</td>
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<td>• Large area deposition</td>
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<td>• Effective to generate CH$_3$ radicals from methane plasma</td>
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![Comparison of capacitive plasma and inductive plasma](image)
2.3.1 RF Plasma-Enhanced CVD with H Radical Injection

Figure 2.8 shows a schematic of the RF capacitively coupled plasma (CCP)-enhanced CVD apparatus assisted by a remote radical source, which consists of a parallel-plate CCP region and a remote radical source that uses an inductively coupled H₂ plasma (H₂ ICP). The main reaction chamber was equipped with circular parallel-plate electrodes separated by 5 cm. RF (13.56 MHz) voltage was applied to the upper electrode and the lower electrode was grounded. Carbon source gas (e.g., C₂F₆, CH₄, CF₄, CHF₃, and C₄F₈) was introduced into the RF-CCP region. H₂ was fed through a quartz tube of 26 mm inner diameter and 20 cm length. A five-turn RF coil was mounted on the quartz tube. The RF coil was connected to the RF power generator operating at 13.56 MHz. The flow rates of carbon source gas and H₂ were kept at 15 and 30 sccm, respectively, and the total gas pressure was 100 mTorr (13.3 Pa). The typical RF powers of CCP and ICP were 100 and 400 W, respectively, and the substrate temperature was 500°C, which was the maximum temperature in the present system. The substrates used in this work include Si, SiO₂, Al₂O₃, Ni, and stainless steel without any catalyst.

Typical SEM images of the carbon nanowalls grown using a C₂F₆/H₂ system on Si (100) substrate for 3 h are shown in Fig. 2.9a, b. These pictures show that two-dimensional carbon sheets were grown vertically on the substrate. The thickness of carbon nanowalls was 10–30 nm, and their height was about 600 nm. In the case of the deposition without H₂ ICP, on the other hand, carbon nanowalls were not fabricated. Figure 2.9c shows an SEM image of deposits formed using C₂F₆/H₂ system for 3 h without ICP. Fluorocarbon polymer with a cauliflower shape was deposited.

Figure 2.9d–f show SEM images of carbon nanowalls grown for 15 min, 30 min, and 1 h, respectively. As shown in Fig. 2.9d, at the nucleation stage of growth, nano-islands with sizes of 3–10 nm were formed on the substrate, followed by the formation of disordered carbon nanoflakes of smaller sizes (Fig. 2.9e) and subsequent growth of isolated nanowalls with a semicircular shape standing vertically on the substrate in the next stage of growth as shown in Fig. 2.9f.

Fig. 2.8  Schematic of the RF capacitively coupled plasma-enhanced CVD apparatus, assisted by a remote H radical source used for the growth of carbon nanowalls [7] — reprinted with permission from American Institute of Physics
Growth rate curves for the nanowalls fabricated using C$_2$F$_6$/H$_2$ system were obtained by measuring the height and thickness of the nanowalls for differing amounts of growth time (0–8 h). The height of nanowalls increased linearly with the increase of growth time. On the other hand, the thickness of nanowalls increased gradually at first up to 3 h and thereafter became constant at about 50 nm. The spacing between nanowalls increased at first, and then became almost constant at about 200 nm. Gas phase and surface reactions of fluorocarbon radicals such as CF$_2$ in the fluorocarbon–hydrogen plasmas have been studied extensively by Fisher’s group [35, 36]. It was reported that with C$_2$F$_6$/H$_2$ and CF$_4$/H$_2$ plasmas, the film structure would vary from fluorocarbon polymer, through amorphous hydrogenated fluorinated carbon to diamond like carbon as the H$_2$ flow rate ratio increased. In the case of our deposition without H$_2$ ICP, a fluorocarbon polymer with a cauliflower shape was deposited as shown in Fig. 2.9c. Injected H radicals would react more effectively with fluorocarbon radicals in the gas phase as well as at the surface by F abstraction. H radicals would play an important role for producing $sp^2$-bonded carbons at the surface to form continuous $sp^2$ network, resulting in the formation of carbon nanowalls. The ratio of CF$_x$ ($x = 1$–3) radicals to H radicals would be an important factor to form carbon nanowalls. Measurement of H atom density in the plasma is described in Chaps. 4 and 5.

Fig. 2.9 SEM images of the carbon nanowalls grown on Si substrate using C$_2$F$_6$ RF-CCP assisted by H radical injection for 3 h; (a) top view and (b) closeup view. Inset in (a) is a cross-sectional view. (c) SEM image of deposits formed using the C$_2$F$_6$/H$_2$ system without ICP for 3 h. SEM images of carbon nanowalls grown for (d) 15 min, (e) 30 min, and (f) 1 h [7] - reprinted with permission from American Institute of Physics
2.3.2 VHF Plasma-Enhanced CVD with H Radical Injection

Figure 2.10 shows a schematic of the very high frequency (VHF) plasma-enhanced CVD system with H radical injection, which was developed with the aim of achieving large-area growth of carbon nanowalls with a reasonable growth rate [37]. This system consists of a parallel-plate VHF (100 MHz) capacitively coupled plasma (CCP) region and a surface wave microwave (2.45 GHz) excited H₂ plasma (H₂ SWP) as a radical source. A carbon source gas (C₂F₆) was introduced into the VHF CCP region. During the carbon nanowall growth, the Si substrate was heated using a carbon heater. The surface temperature of the growth substrate was 600°C, which was measured using an optical pyrometer. Using this system, the heated substrate was showered with fluorocarbon radicals as well as H atoms, in a controlled manner. The flow rates of C₂F₆ and H₂ were maintained at 50 and 100 sccm, respectively, and the total pressure was changed in the range from 0.1 to 1.2 Torr (13–160 Pa). Typical microwave and VHF powers were 250 and 300 W, respectively.

![Schematic illustration of the VHF plasma-enhanced CVD system with H radical injection](image)

**Fig. 2.10** Schematic illustration of the VHF plasma-enhanced CVD system with H radical injection [37] – reprinted with permission from American Vacuum Society

![SEM images of carbon nanowalls grown at pressures](image)

**Fig. 2.11** SEM images of carbon nanowalls grown at pressures of (a) 13.3, (b) 53.3, and (c) 80 Pa [38] – reprinted with permission from American Institute of Physics
Figure 2.11a–c show SEM top view images of carbon nanowalls grown using VHF plasma-enhanced CVD system with H radical injection on Si substrates at total pressures of 0.1, 0.4, and 0.6 Torr (13.3, 53.3, and 80 Pa), respectively [38]. At a low total pressure of 0.1 Torr, a carbon nanowall film with narrow interspaces was obtained (Fig. 2.11a). On the other hand, the carbon nanowall film grown at a total pressure of 0.6 Torr had wide interspaces of 30–40 nm (Fig. 2.11c). Here, the interspace is defined as the average distance between adjacent carbon nanowalls derived from SEM observation, by measuring diameters of more than 50 hollows selected randomly in the SEM top view image of carbon nanowall film. From the measurement of H and C radical densities in the CCP region, which is described in Chap. 5, the H/C radical density ratio was found to increase with the increase of total pressure [38]. As the H/C radical density ratio in the plasma increased, the growth rate of the carbon nanowalls decreased and the average interspaces between the walls became wider.

Figure 2.12a shows an SEM image of a typical carbon nanowall film grown on a Si substrate using a C_2F_6/H_2 mixture at a total pressure of 1.2 Torr (160 Pa). This image shows slightly branching two-dimensional carbon sheets standing almost vertically on the substrate. The growth rate of this carbon nanowall film was approximately 30 nm/min. Crystallinity of carbon nanowall is improved by adding a small amount of oxygen to the source mixture. Figure 2.12b shows an SEM image of carbon nanowalls grown with the addition of O_2 at a flow rate of 5 sccm. Branching can be suppressed and straight and large-size monolithic carbon nanosheet can be obtained by the addition of oxygen; however, the growth rate was reduced by approximately 33%. Carbon nanowall films grown with O_2 had larger plane sheets with wider interspaces than those grown without O_2.

2.4 Electron-Beam-Excited Plasma Enhanced Chemical Vapor Deposition

An electron beam excited plasma (EBEP) is a high-density plasma directly introduced by a high-current and low-energy electron beam [39, 40]. The electron-beam energy and the electron current can be controlled independently by changing the
accelerating voltage and discharge current, respectively. By setting the electron-beam energy close to the energy corresponding to the maximum electron impact ionization cross-section of source gases, highly ionized and dissociated plasmas can be produced even at low pressures.

Carbon nanowalls were fabricated using an EBEP-CVD system shown in Fig. 2.13. The EBEP-CVD system consists of three parts: (a) a DC discharge plasma region, (b) an electron acceleration region, where extracted electrons are accelerated into the EBEP region, and (c) an EBEP region, which is high-density and low-temperature plasma at low pressures. The DC discharge plasma is sustained by electrons emitted from a cathode made of a LaB₆ disk. The electron beam is extracted from the DC discharge plasma and is accelerated by a pair of multi-hole grids into the EBEP region. Since the electron beam provides sufficient energy for the ionization and dissociation of the gas molecules, the plasma can be reliably produced even under low-pressure conditions. The mixtures of process gases (CH₄/H₂) were introduced into the deposition chamber. Growth experiments were carried out on an electrically floating substrate for 10–90 min at an electron-beam current of 2 A and an electron-acceleration voltage of 60–100 V, a total pressure of 10–30 mTorr (1.3–4 Pa), and the heater temperature of 570°C. Substrates used in this study were mirror-polished Si (100) without any catalyst.

Figure 2.14a shows the SEM image of carbon nanowall film grown for 10 min at an electron-acceleration voltage of 100 V, a total pressure of 20 mTorr (2.6 Pa), and a substrate temperature of 570°C. Figure 2.14b shows a magnified SEM image of carbon nanowalls. Carbon nanowalls grown here were very thin, and their thickness was approximately 3 nm. Figure 2.14c, d show the typical SEM images of carbon nanowall film grown for 90 min. In this case, the electron-acceleration voltage was set at 60 V to prevent the increase of substrate temperature during the growth.
experiment. These images show that two-dimensional carbon sheets were grown vertically on the substrate. The growth rate of carbon nanowall film using EBEP with CH$_4$/H$_2$ mixture was approximately 22 nm/min. Vertically standing aligned carbon nanowalls were considerably definite, forming a unique nanostructure similar to a maze with high aspect ratio.

Growth rate curves for the nanowalls fabricated using EBEP CVD with CH$_4$/H$_2$ system were obtained by measuring the height and thickness of the nanowalls for differing amounts of growth time (0–90 min). The height of carbon nanowalls linearly increased with the increase of growth time, while the thickness of carbon nanowalls was almost constant at a few nm. The average spacing between adjacent nanowalls increased at first, and then became almost constant at approximately 200 nm.

Morphology and growth rate of carbon nanowall film depended on the pressure during the fabrication process using the EBEP-CVD system. With the increase of the total gas pressure, the density of carbon nanowalls decreased. The average interspaces were controllable in the range of 50–200 nm by changing the total gas pressure. Moreover, the growth rate of carbon nanowall film increased with the increase of total gas pressure. At a total pressure of 30 mTorr (4 Pa), carbon nanowall growth rate as high as approximately 32 nm/min was obtained. In addition, it was found that wall spacing and density depended on the substrate temperature as well, while the thickness of carbon nanowall was almost constant. As the substrate temperature increased, the growth rate of carbon nanowall film increased up to 35 nm/min. In the case of fabricating carbon nanowalls at high temperature of 650°C, the density of carbon nanowalls was high and vertical.

![Fig. 2.14](image-url) (a) SEM top view image and (b) magnified SEM image of carbon nanowall film fabricated by EBEP-CVD employing CH$_4$/H$_2$ mixture for 10 min. (c) SEM side view image and (d) top view image of carbon nanowall film fabricated for 90 min [11] – reprinted with permission from Elsevier
alignment of carbon nanowalls was poor. On the other hand, definite and vertically aligned carbon nanowalls were successfully fabricated at relatively low temperature of 550°C.

Carbon nanowalls fabricated by the EBEP-CVD employing CH₄/H₂ can be easily detached from the substrate. Figure 2.15a shows an SEM image of carbon nanowall ribbons detached from the substrate. Isolated free-standing carbon nanowalls would be applied to the novel electronic devices. Figure 2.15b–d show SEM images of carbon nanowall mat scratched out from substrate, which implies that free-standing aligned carbon nanowall mat or filter will be fabricated using the present CVD system.

2.5 Hot Filament Chemical Vapor Deposition

The hot filament chemical vapor deposition (HFCVD) technique is an old but widely studied method to grow diamond films. The HFCVD method can be applied to synthesize carbon nanotubes and carbon nanowalls. A simplified schematic of HFCVD system is shown in Fig. 2.16. Single or multiple tungsten (W) filaments, which are heated to 2,000–2,200°C, are used to decompose a mixture of hydrocarbon and hydrogen gases. The deposition is carried out at pressures of 1–100 Torr and substrate temperature of 600–800°C, and a substrate is placed within a small distance (typically 5 mm) from a filament (Fig. 2.16).

Shang et al. [3] have reported the synthesis of carbon nanoflakes using HFCVD technique employing a mixture of C₂H₂ and H₂ gases without using catalysts or surface pretreatment. Two parallel W filaments were heated to 2,100°C. The carbon
nanoflakes deposited at 400–600°C had a thickness of less than about 10–20 nm. As the temperature increased in this temperature range, the size of nanoflakes decreased, while the density increased. In addition to the substrate temperature, the acetylene concentration also had a significant effect on the deposited films. As acetylene concentration increased, the nanoflake films became more disordered. They also measured the field emission property of carbon nanoflake film, showing a turn-on field of about 17 V/μm.

Itoh et al. [41] have prepared carbon nanowall films employing only CH$_4$ gas at relatively low substrate temperature of 500°C on the Ni-catalyzed quartz substrate, and measured the field emission property of carbon nanowall film, showing a turn-on field of about 2.6 V/μm. However, later this group have prepared carbon nanowalls employing a mixture of CH$_4$ and H$_2$ gases, and investigated the hydrogen dilution effect on the preparation of carbon nanowalls [42]. From their results, it is understood that the role of hydrogen radical is important in the growth of carbon nanowalls and hydrogen dilution is available for controlling the structure of carbon nanowalls with suitable hydrogen dilution ratio, while too large amount of hydrogen radicals would etch away not only disordered components but also ordered ones such as sp$^2$ networks.

Giorgi et al. [43] have synthesized carbon nanowalls using bias-assisted HFCVD method employing a mixture of He and CH$_4$ gases (typically He:CH$_4$ = 100:2) at the substrate temperature of 800°C on the Si substrate. Platinum particles were prepared on the carbon nanowalls by galvanostatic electrodeposition to investigate their electrocatalytic performance for methanol oxidation, and comparison between carbon powder and carbon nanowalls was carried out.

The carbon nanowalls fabricated by HFCVD method seem less aligned compared with those fabricated by plasma-enhanced CVD method using microwave plasma and inductively coupled plasma, which may suggest that the electrical field and/or ionic species contribute to the growth of carbon nanowalls.

The HFCVD method is relatively cheap in construction and easy to operate. However, the filament is sensitive to oxidizing gases, resulting in the limitation for
using a variety of gas mixtures. Furthermore, it is also difficult to avoid contamination of synthesized carbon structures with filament materials.

### 2.6 Atmospheric Pressure Plasma

Previously, a microwave-excited non-equilibrium atmospheric pressure plasma source with high electron density of $\sim 10^{15} \text{ cm}^{-3}$ and low electron temperature of $\sim 1 \text{ eV}$ was applied to the synthesis of carbon nanotubes [44]. This type of plasma has a great potential for realizing the new material processing because the larger amount of radicals is estimated by a few orders of magnitude compared with the conventional low-pressure and high-density plasmas and the complicated vacuum equipments are not required. Recently, this microwave-excited non-equilibrium atmospheric pressure plasma-enhanced CVD was applied to the synthesis of carbon nanowalls [45].

A schematic of non-equilibrium atmospheric pressure plasma-enhanced CVD system is shown in Fig. 2.17. The microwave (2.45 GHz) propagates from the top of the deposition chamber to the micro-slit electrode. The micro-slit electrode width is 0.2 mm and the distance between substrate and the micro-slit is 5 mm. A source gas mixture (He/H₂/CH₄) is introduced from the upper part of the micro-gap and pumped out from the lower part of the deposition chamber, such that the chamber pressure is kept at atmospheric pressure. Growth experiments were carried out for 30 min at a microwave power of 350 W, a total pressure of 1 atm and a heater temperature of $680^\circ \text{C}$. The flow rates of He, CH₄, and H₂ were 1,000, 25, and 25 sccm, respectively. Prior to the carbon nanowall growth, Ti nanoparticles were formed on the Si substrate using pulsed arc plasma deposition.

![Fig. 2.17 Schematic of non-equilibrium atmospheric pressure plasma-enhanced CVD system](image-url)
Figure 2.18 shows an SEM image of carbon nanowall film grown on the Ti-coated Si substrate by non-equilibrium atmospheric pressure plasma-enhanced CVD system employing CH₄/H₂/He mixture for 30 min. Height of the carbon nanowall film grown for 30 min was about 70 nm. On the other hand, aligned carbon nanotubes can be also grown on the Co-catalyzed Si substrate under identical plasma conditions. Figure 2.18b shows an SEM image of aligned carbon nanotube film grown for 5 min for comparison. In the case of carbon nanowall fabrication using atmospheric pressure plasma-enhanced CVD, the growth rate should be substantially improved for the practical application of carbon nanowalls.

2.7 Sputtering

Kusano’s group has reported the synthesis of vertically standing carbon nanoflakes by RF sputtering of glassy carbon target with the addition of CH₄ [14]. Figure 2.19 shows a schematic of a load lock-type sputtering machine. A glassy carbon disk was used as a sputtering target. The RF (13.56 MHz) power of 100 W was applied to the target. The mixture of Ar and CH₄ was used as a discharge gas, and their flow rates were 14 and 28 sccm, respectively. The total pressure was approximately 14.5 Pa. The Si substrate was heated to 670°C.

Figure 2.20 shows an SEM top view image of vertically standing carbon nanoflakes grown by sputtering for 3 h. A typical size of the nanoflakes grown for 3 h is a length of 1 μm, a width of 600 nm, and a thickness of 30 nm. Figure 2.21a–d show SEM images of carbon nanoflakes grown on Si substrates at 670°C for various discharge durations. As shown in Fig. 2.21a, at the early stage of growth, randomly oriented flakes of small sizes were formed densely, followed by the formation of
isolated nanoflakes with a semicircular shape (Fig. 2.21b) and subsequent growth of vertically well-aligned nanoflakes as shown in Fig. 2.21c, d.

It was reported that carbon nanoflakes were not grown in pure Ar atmosphere by sputtering using a glassy carbon target, and a high CH$_4$ partial pressure of more than 44.3 Pa was necessary to obtain carbon nanoflakes by sputtering with a glassy carbon target [14]. In this point, the present process might be regarded as sputtering-CVD combined growth. Therefore, carbon-containing radicals such as CH$_3$
generated from CH₄ molecules would be precursors for the growth of carbon nanoflakes. However, from the fact that there has been no report on the successful growth of carbon nanowalls by commonly used RF capacitively coupled plasma (without H radical injection) so far, it appears certain that sputtered C atoms would play important role in the synthesis of carbon nanoflakes, e.g., formation of the nucleation sites of nanoflakes at the very early stage of growth.

References

References

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