Low temperature growth and characterization of carbon nanostructures

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Low Temperature Growth and Characterization of Carbon Nanostructures

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School of Electrical & Electronic Engineering

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Summary

Carbon nanostructures, such as carbon onions and carbon nanotubes, have attracted tremendous research interest for the last decade due to their superior physical and chemical properties and promising applications. But most of the current fabrication processes require high temperature, which causes problems like long cycle time, non-cost effective and substrate melting temperature restriction. Therefore developing low temperature synthesis of carbon nanostructures is of great scientific and practical significance.

This report focuses on the low temperature fabrication and characterization of carbon nanostructures such as onion-like carbon and carbon nanotubes (CNTs). Onion-like carbons were grown on different substrates at room temperature using plasma enhanced chemical vapor deposition (PECVD). Aligned CNT forest was synthesized using a water-assisted PECVD process.

Onion-like polyhedral fullerenes (OLPFs) were synthesized on silicon substrates by PECVD using highly diluted acetylene in hydrogen and argon at room temperature (RT). The OLPF were grown uniformly on the substrates with diameters ranging from 200 to 400 nm and density of around 10^9 cm^{-2} . Transmission electron microscopy reveals that the OLPF consists of several concentric polyhedral carbon layers surrounding a hollow core with a inter shell distance of 0.346 nm. Raman spectra reveal that the OLPF prepared at RT are more defective than those samples synthesized at high temperature. The growth mechanism of the OLPF with and without metal catalyst core is discussed.

OLPF has also been grown on the substrate coated with diamond particles. Scanning electron microscopy image shows that there is a bright tip on each carbon onion. The bright tip has strong correlation with the diamond particle nucleation.

The carbon-onion samples were irradiated by electron in order to investigate the transformation of the structure. The shift of D band has been observed. Various reasons have been discussed, like graphite to diamond transition and defects induced by electron irradiation.

It is expected that atomic vacancies or nanometric cavities reduce the number of chemical bonds of nearby atoms and hence the strength of a voided solid. However, the hardness of a porous specimen does not always follow this simple picture of coordination counting. Nanoindentation measurement for carbon onions grown on the silicon substrate revealed higher hardness and young's modulus than the carbon film grown under similar condition. An introduction of a certain amount of atomic vacancies or nanocavities could, instead, enhance the mechanical strength of the porous specimen given. Understanding the mechanism behind the intriguing observations remains yet a big challenge. This work will show with analytical expressions that the shortened and strengthened bonds between the under-coordinated atoms and the associated local strain and energy trapping [Sun, *Prog Solid State Chem* 35, 1-159 (2007)] in the negatively curved surface skins dominate the observed nanocavity hardening. Agreement between predictions and the experimentally observed size-dependence of mechanical strength of some nanoporous materials evidences for the proposed mechanism.

Aligned high density CNT forest has been grown on nickel catalyst layer using water-assisted PECVD process at room temperature. It shows that water molecule can also increase both the activity and lifetime of the catalyst at low temperature, which was reported only at high temperature before. The field emission measurement of the CNT forest showed that due to screening effect the turn on field was around $9\text{V}/\mu\text{m}$. The superhydrophobicity of the CNTs was studied. The contact angle of the CNT forest was 152.6° and 156.5° for the samples grown with and without CF_4 in the plasma, respectively. The superhydrophobicity of the CNTs is durable and stable. The growth mechanism of the CNT forest is discussed.

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Chapter 1 Introduction

1.1 Motivation and objectives

The motivation of this thesis is to use the plasma enhanced chemical vapor deposition (PECVD) technique to grow carbon nanostructures - two of the most important fullerenes: carbon onions and carbon nanotubes, at low temperature and conduct characterizations. The objectives of this thesis are: (1) to develop an optimum process for growing carbon nanostructures at low temperature without deteriorating their properties; (2) to understand the influence of process conditions, such as type of substrates, gas precursor, flow rate and plasma power, on the carbon nanostructures; (3) to study the electron irradiation effects on the carbon nanostructures at low temperature; (4) to propose an analytical model, which could explain atomic vacancies or nanocavities could enhance the mechanical strength of the porous specimen, such as carbon onions; and (5) to investigate the impact of water molecule on the activity as well as lifetime of the catalyst for CNT growth at low temperature, and also the influence of surface roughness and surface energy on the wettability of aligned CNT trees.

Fullerenes have been found to exist in interstellar dust as well as in geological formations on earth. But they were almost unknown to us until 1980s[1]. In the last three decades, due to their unusual properties for carbon materials, large amount of research work has been carried out on exploring the physics, chemistry, and engineering potential of these materials. Different methods were also developed to synthesis the fullerenes, but most of them require high temperature, which greatly limited the fullerenes' applications due to

long cycle time, low throughput, substrate melting temperature limitation, non-cost effective. Therefore, finding ways to reduce the substrate temperature of the synthesis of carbon nanostructures is of great scientific and practical significance.

1.2 Major contribution of the thesis

A systematic study of carbon onions deposited at low temperature on different substrates using the PECVD technique was carried out. Low temperature electron irradiation effect on the carbon onions in a field emission system was also investigated. An analytical model has been proposed to explain the hardening effects of the atomic vacancies and nanocavities on the porous material, such as carbon onions. Finally water assisted growth of aligned carbon nanotube forests at low temperature was studied. The characterization of the samples includes: surface morphology, crystalline structure, electron emission, Raman spectroscopy, nanoindentation and water contact angle. The major contributions in this thesis are:

- The uniformly distributed carbon onions have been successively grown without any external heating. Comparing with those carbon onions grown at high temperature, they tended to be in polyhedral shape rather than in spherical and were more defective, which suggested the effect of the temperature variation on the carbon structures. The gas precursor flow rate and plasma power effect on the carbon onions growth were also examined.
- It was found that no catalyst was required for the growth of hollow core carbon onions.

- There is a strong correlation between the bright tips on the carbon onions and fibers/pillars, which are grown on the nanodiamond coating, with the diamond nanoparticle. To the author's best knowledge. This phenomenon has not been reported before. This may lead to a new growth mechanism of the carbon structures growth on the nanodiamond coating and future applications.
- Low temperature electron irradiation effect on the carbon onions in field emission system revealed a trend of transformation of graphite to diamond transition.
- The analytical expression shown in the thesis has very good agreement between predictions and the experimentally observed size-dependence of mechanical strength of some nanoporous materials, which are evidences for the proposed mechanism.
- Water assisted high density aligned carbon nanotubes growth, which was always demonstrated at high temperature previously, has been achieved at low temperature using PECVD. It was shown that water molecules could also increase both the activity and lifetime of the catalyst at low temperature. The simple process presented in this thesis could be easily adopted for large-scale, low cost and high density CNT production for various potential applications.

1.3 Organization of the thesis

- Chapter 2 contains a review of the relevant literature on carbon onions and carbon nanotubes, two of the most important fullerenes, and their growth methods. The electron/ion irradiation effects on the carbon onions, atomic vacancies and

nanocavity hardening effect on nanoporous materials, the anti-wetting on aligned carbon nanotubes and water assisted CNTs growth are also briefly introduced.

- Chapter 3 describes the two main experiment techniques used in this work, which are plasma enhanced CVD and electron field emission.
- Chapter 4 gives an overview of the various characterization techniques used to study the carbon nanostructures grown at low temperature, providing introductory information on the characterization equipment.
- Chapter 5 focuses on the low temperature growth and characterization of carbon onions on different substrates.
- Chapter 6 shows the results and discussion of low temperature electron irradiation effects on carbon onions in field emission system.
- Chapter 7 proposes an analytical model for the hardening effect of atomic vacancies and nanocavities on the nanoporous materials, such as carbon onions.
- Chapter 8 deals with the low temperature water assisted growth of aligned carbon nanotube forests and its superhydrophobic properties.
- Chapter 9 provides the conclusions and recommendations for future work.

Chapter 2 Literature Review and Technical Background

Carbon is one of the most versatile elements on the periodic table in terms of the number of compounds it may form. It may form virtually an infinite number of compounds. This is largely due to the types of bonds it can form and the number of different elements it can join in bonding.

Carbon's atomic number is 6. Its electronic structure is $1s^2 2s^2 2p^2$. Carbon can exist in sp^3 , sp^2 , and sp hybridizations (Figure 2.1 to Figure 2.3) and form several different types of bonds, such as single, double and triple bonds.

Figure 2.1 sp^3 hybridization

sp^3 hybridization, as shown in Figure 2.1, results from the combination of the s orbital and all three p orbitals in the second energy level of carbon. It results in four hybrid

orbitals and occurs when a carbon atom is bonded to four other atoms. The geometric arrangement of those four hybrid orbitals is called tetrahedral. The angle between the sp^3 hybrid orbitals is 109.5 degree.

Figure 2.2 Sp^2 hybridization

Another kind of hybridization shown in Figure 2.2 uses the s orbital and two of the p orbitals from the second energy level of carbon to form three hybrid orbitals. This kind of hybridization is called sp^2 hybridization. It has three hybrid orbitals and there is also an unchanged p orbital that is not shown here. The geometric arrangement of these three sp^2 hybrid orbitals is in a flat plane with 120 degree angles between them. The leftover p orbital lies at a 90 degree angle to the hybrid orbitals. This kind of hybridization occurs when a carbon atom is bonded to three other atoms.

Figure 2.3 sp hybridization

As shown in Figure 2.3, there is still a third type of hybridization, it is sp hybridization. In it the s orbital and one of the p orbitals from carbon's second energy level are combined together to make two hybrid orbitals. Those hybrid orbitals form a straight line. There is a 180 degree angle between one orbital and the other orbital. They are exactly opposite one another from the center of the carbon atom. Because this type of sp hybridization only uses one of the p orbitals, there are still two p orbitals left which the carbon can use. Those p orbitals are at right angles to one another and to the line formed by the hybrid orbitals. This kind of hybridization occurs when a carbon atom is bonded to two other atoms.

As the free element it forms allotropes from differing kinds of carbon-carbon bonds. As shown in Figure 2.4, in the three dimension there is diamond (sp^3), which is a semiconductor, in the two dimension, graphite (sp^2), and in the one dimension nanotubes (sp^2) exist which can be conductors of semi-conductors. Finally those in the zero dimension and have unusual properties, such as C_{60} (sp^2).

Figure 2.4 Allotropes of carbon

(a) Diamond

(b) Graphite

(c) Carbon nanotube

(d) C60

Carbon nanotube and C60 are both called fullerenes, which are molecules, composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from

being planar. Fullerenes are fascinating because they show unusual properties for carbon materials. They are the most exciting new set of chemical structures discovered in the last part of the 20th century. Tremendous effort has been made on exploring the physics, chemistry, and engineering potential of these materials. In this chapter, the history, structures, properties and synthesis methods of the two most important fullerenes, carbon onions and carbon nanotubes, will be introduced.

2.1 Carbon onions

The C₆₀ molecule, which is shown in Figure 2.4d was discovered in 1985 by Curl, Kroto and Smalley [2] in the course of their experiments to understand the absorption spectra of interstellar dust. It was named buckminsterfullerene, after the American architect Richard Buckminster Fuller (Figure 2.5a), who was renowned for his geodesic domes, which were based on hexagons and pentagons. It was also called buckyballs, since it contains 60 carbon atoms arranged in a sphere much like the vertices of a soccer ball (Figure 2.5b). The discovery of C₆₀, which won Curl, Kroto and Smalley the 1996 Nobel Prize in chemistry, has stimulated a large activity in chemistry. It opened up the new branch of Fullerene-Chemistry which studies the new families of molecules that are based on Fullerenes.

(a)

(b)

Figure 2.5 C₆₀ was named buckminsterfullerene, after the American architect Richard Buckminster Fuller [3] (a) and it was also called buckyballs (b)

In 1992, Ugarte [4] found that carbon soot, when subjected to intense high-energy beams of electrons, transformed into nested layers of concentric spheres and formed an onion like fullerene, which was firstly discovered by Iijima [1] in 1980. One example of TEM image for onion like fullerene is shown in Figure 2.6a.

Figure 2.6 TEM picture of a carbon onion [5] (a), and carbon onion model (b)

Carbon onions are also viewed as concentric big spherical fullerenes [6], as the model shown in Figure 2.6b. Theorists have asserted that graphite in a flat sheet of hexagons represents the most stable form of carbon. But that may hold true only for infinitely large graphite sheets. Sheets with a finite number of atoms have edges with dangling bonds: The carbon atoms along these borders need to attach to something else in order to become stable. Thus, when 60 to 600 carbon atoms link up, the dangling bonds encourage the formation of hollow fullerenes [4]. Ugarte's work shows that collections containing millions of carbon atoms also curled and seemed most stable in the form of multilayered spheres.

The onion like fullerene molecule is very stable, being able to withstand high temperatures and pressures. The exposed surface of the structure is able to react with

other species while maintaining the spherical geometry. The hollow structure is also able to entrap other smaller species such as helium, while at the same time not reacting with the fullerene molecule. In fact the interior of most buckyballs is so spacious. They can encase any element from the periodic table. Figure 2.7 shows the encapsulation of metal nanocrystals in the onion like fullerene. Buckyballs do not bond to one another. But they can stick together via Van der Waals forces. By doping fullerenes, they can be electrically insulating, conducting, semiconducting or even superconducting [7].

Figure 2.7 Encapsulation of metal nanocrystals in onion like fullerene [8]

Some other potential applications for fullerenes include: lubricants [9], drug delivery systems [10], pharmaceuticals and targeted cancer therapies [11], hydrogen storage for applications in fuel cells [12], optical devices [13], chemical sensors [14], photovoltaics [15], polymer electronics such as organic field effect transistors (OFETS) [16], antioxidants [17], polymer additives [18], cosmetics [19], where they “mop up” free radicals, single-molecule transistors [20], electromechanical amplifier [21] etc.

2.1.1 Growth methods

In the last 3 decades, several groups demonstrated different ways of synthesizing onion like fullerenes (OLFs), such as electric arc-discharge [22], high energy electron irradiation in a transmission electron microscopy (TEM) [4], annealing carbon soot [23] and ultra-dispersed diamond [24], implant carbon ions into high temperature silver/copper substrates [6], arc discharge between two graphite electrodes submerged in water [25], and catalytic synthesis of carbon onions [26]. Basically, there are two approaches (1) a “bottom up” process, in which fullerenes are built up from small precursors such as C atoms and C₂ units, and (2) a “top down” process, in which hot graphitic microparticles decompose into fullerenes or small carbon molecules by releasing energy. The latter decomposition mode may initiate a “bottom up” growth of the fragments, suggesting that “bottom up” and “top down” processes may occur together.

Most of the above processes required high temperature, which may have problem if the substrate’s melting temperature is low or complicated substrate catalyst layer preparation. Low productivity and poor size distribution are still the remaining issues on OLFs synthesis. Several groups have proposed catalyst related hollow core OLFs growth mechanisms on the catalyst layer [26, 27], but the growth mechanism is still not clear due to the lack of physical evidence. The current work is to prepare OLPFs on Si substrates with and without catalyst layer at room temperature using the biased-assisted chemical vapor deposition.

2.1.2 Electron / ion irradiation effects on the carbon onions

As mentioned earlier, carbon onions consist of an arrangement of closed concentrically nested graphitic shells. Figure 2.6a shows perfectly spherical carbon onions are generated under intense irradiation of carbonaceous precursors. A strong self-compression of carbon onions under irradiation occurs, seen as a decrease of the inter-shell spacing from about 0.29 nm at the surface of the onions down to values around 0.22 nm in the center.

In 1996, Banhart *et al.* found that under electron irradiation at temperatures above 600 °C, the cores of compressed carbon onions transform to diamond [5]. It is shown in Figure 2.8 that, if the irradiation is continued, the diamond cores grow at the expense of the surrounding graphite shells until the onions have wholly transformed to diamond.

Figure 2.8 Growth of a diamond crystal inside a carbon onion under sustained electron irradiation at $T = 700\text{ }^{\circ}\text{C}$ (a) after 2 h, (b) after 3 h of irradiation [5].

One year later, Wesolowski *et al.* reported that spherical carbon onions can also be generated by irradiating graphitic carbon soot with Ne^+ ions of 3 MeV energy, and

transformation of their cores to cubic diamond crystals is observed under continued irradiation. In comparison to the electron irradiation, the yield of diamond under ion irradiation is much higher. The increased diamond yield under ion irradiation is explained by the higher displacement cross-section, the higher energy transfer, and the higher total beam current on the specimen [28].

The mechanism of the transformation of graphite to diamond under electron or ion irradiation at high temperature is shown in Figure 2.9.

Figure 2.9 Transformation of graphitic nanoparticles to diamond under electron or ion irradiation at high temperature

Both the formation of carbon onions and electron or ion irradiation experiments on the carbon onions described above are carried out at high temperature. In this project, various

approaches were developed to synthesis carbon onions at low temperature. The carbon onions samples were also irradiated by electron generated by carbon nanotubes in a field emission system at room temperature. The Raman spectra were used to examine the low temperature electron irradiation effect on the carbon onions.

2.2 Carbon nanotubes

Carbon nanotube (CNT) is another very important carbon fullerene. Although who should really be given the credit for the discovery of carbon nanotubes is still a contentious issue [29]. It is undoubted that the field of carbon nanotube research was launched after the tremendous impact of the Iijima's paper in 1991 [30]. Since then the world envisioned a rapid growth of nanotube research.

A single-walled carbon nanotube (SWNT) can be imagined as rolled-up rectangular strips of hexagonal graphite monolayers (graphene) as shown in Figure 2.10.

Figure 2.10 Schematic models for single-wall carbon nanotubes: (a) an “armchair” (n,n) nanotube, (b) a “zig-zag” $(n,0)$ nanotube, and (c) a “chiral” (n,m) nanotube

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. It is well-known from tight-binding (TB) theory that, for a given (n,m) nanotube, a SWCNT is metallic when $(n - m)$ is a multiple of 3. Otherwise, it is semiconducting.

Depending on the synthesis procedures, SWCNTs may nest inside each other to form “Russian dolls”, known as multi-walled carbon nanotubes (MWCNTs).

Figure 2.11 Schematic models for multi-wall carbon nanotubes

Both theoretical and experimental investigations show that the unique structure gives carbon nanotubes remarkable mechanical, electronic, and optical properties. The strong covalent bonds between carbon atoms of CNTs lead to a high Young's modulus close to 1.25 TPa, about five times the value of steel. In contrast to ordinary materials, different types of SWNTs can be either metallic or semiconducting. The high aspect ratio qualifies CNTs as excellent field emission devices. Due to these amazing properties, CNTs have so many applications: field effect transistor [31], nanoelectromechanical systems [32], flat-panel display [33], chemical sensor [34], molecular channel [35], hydrogen fuel cell [36], light emitter [37] and etc.

2.2.1 Growth methods

A wide range of deposition techniques have been developed to grow CNTs, including arc-discharge [38], chemical vapor deposition [39] and laser ablation [40]. A short summary of these three most popular methods is shown in Table 2.1.

Table 2.1 A summary of the CNTs major production methods

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992 [38]	Endo, Shinshu University, Nagano, Japan [39]	Smalley, Rice, 1995 [40]
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of CNTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the CNTs form; try various conditions until hit on one that produces prodigious amounts of SWCNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWCNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWCNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWCNT synthesis is possible.
Advantages	Can easily produce SWCNT, MWCNTs. SWCNTs have few	Easiest to scale up to industrial production; long length, simple	Primarily SWCNTs, with good diameter control and few defects. The

	structural defects; MWCNTs without catalyst, not too expensive, open air synthesis possible	process, SWCNT diameter controllable, quite pure	reaction product is quite pure.
Disadvantages	Tubes tend to be short with random sizes and directions; often needs a lot of purification	CNTs are usually MWCNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

The way in which nanotubes are formed is not exactly known. The growth mechanism is still a subject of controversy, and more than one mechanism might be operative during the formation of CNTs. One of the mechanisms consists out of three steps. First a precursor to the formation of nanotubes and fullerenes, C_2 , is formed on the surface of the metal catalyst particle. From this metastable carbide particle, a rodlike carbon is formed rapidly. Secondly there is a slow graphitisation of its wall. This mechanism, which is shown in Figure 2.12a, is based on in-situ TEM observations [41].

Figure 2.12 Visualisation of a possible carbon nanotube growth mechanism

There are several theories on the exact growth mechanism for nanotubes. One theory [42] postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped, in which case the deposition will take place on only one half of the surface (this is the lower curvature side for the pear shaped particles). The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by "extrusion (also known as base growth)" in which the nanotube grows upwards from the metal particles that remain attached to the substrate, or the particles detach and move at the head of the growing nanotube, labelled "tip-growth" as shown in

Figure 2.12b. Depending on the size of the catalyst particles, SWCNT or MWCNT are grown. In arc discharge, if no catalyst is present in the graphite, MWCNT will be grown on the C_2 -particles that are formed in the plasma.

For most of the current CNTs growth methods long cycle time for high temperature process, complicated process for aligned CNT growth and low throughput are still remaining issues which needed to be solved for mass production. A low temperature process which is able to synthesis large quantity of aligned CNTs in short cycle time (less than one hour) will be presented in this report.

2.2.2 Water assisted growth of carbon nanotubes

Nowadays chemical vapor deposition (CVD) has become a standard technique for the synthesis of carbon nanotubes (CNTs). But it suffers a lot from low catalyst activity, which means only a few percent of the catalysts produce CNTs, while the majority of them remain inactive. It greatly limited the yield of CNTs, and also the inactivated catalysts remain in the as-grown CNTs as impurities necessitating further chemical purification. It was firstly reported by Hata et al. [43] that the addition of a small and controlled amount of water into a CVD growth could increase the activity for catalyst dramatically, which results in the massive growth of highly dense vertically aligned impurity-free SWNT forests. Hence the water assisted CNTs synthesis was called “Super-Growth CVD”. It was also found that the life time of the catalyst could be extended tremendously. Water, a weak oxidizer, is believed to be able to selectively remove the amorphous carbon coated on top of the catalyst, which in turn could produce

CNTs with millimeter-scale heights on substrates with catalyst densities even below one monolayer.

Considerable research work has been carried out on optimizing the water assisted CNT growth [44], understanding its growth mechanism [45, 46] and its applications [47]. But almost all the process conditions reported require high temperature ($> 600^{\circ}\text{C}$), in this work, low temperature water assisted CNTs growth will be studied using PECVD technique without any external heating provided.

2.2.3 Anti-wetting on aligned carbon nanotubes

The wetting behavior of solid surfaces by a liquid is a very important aspect of surface chemistry, which is normally characterized using contact angle (CA) measurement. Generally, the wettability of a solid surface is controlled by its chemical composition [48] (closely related to the surface energy) and geometrical structure [49] (closely related to the surface roughness) and is usually enhanced by surface. A very rough, heterogeneous surface allows air to be trapped more easily underneath the water droplet so the droplet essentially rests on a layer of air. A significantly higher surface area compared to the projected area in the case of a rough surface requires a greater energy barrier to create a liquid-solid interface [50]. Coupled to this, when the surface energy of the surface material is intrinsically low, the combined effect is that the surface will repel any water that comes into contact with it [51]. For a solid substrate, when the CA of water on it is larger than 150° , it is called superhydrophobic. A schematic illustration of water droplet resting a superhydrophobic surface is shown in Figure 2.13.

Figure 2.13 Schematic illustration of water droplet resting on a superhydrophobic surface

The wettability of Aligned CNTs (ACNT) is highly attractive and is promising for many applications [52-55], including bionic micro-machines, micro-fluid devices and as scaffolds for cell seeding and proliferation and etc. ACNT surface roughness and surface free energy can be controlled by varying the arrangement of CNTs on the substrate and by chemical modification, respectively, leading to different wetting behaviors [56]. In this work, a low temperature process for superhydrophobic aligned CNTs growth will be presented.

2.3 Nanocavity hardening

It has long been puzzling that atomic vacancies or point defects, like the hollow core in the carbon onion, can act as pinning centers inhibiting the motion of dislocations and hence enhancing the mechanical strength of a material [57]. For examples, the hardness of FeAlN is proportional to the square root of the concentration of nitrogen vacancies [58]. The hardness of tungsten aluminium carbon (WAlC) compounds increases monotonically up to a maximum at 35% C vacancies whereas the mass density decreases

[59]. Fracture measurement and modeling analysis indicated that a small number of atomic defects could improve the strength of WS₂ nanotubes [60]. A study using atomistic simulations and analytical continuum theory [61] on the influence of the vacancy concentration on the Young's modulus and tensile strength revealed the enormous impact of an atomic defect on the strength of the nanotubes. Moreover, presence of nanometer-sized cavities also enhance the mechanical properties of solid materials [62, 63]. For instance, the internal stress of an amorphous carbon film can be raised from 1 to 12 GPa by producing nanometric pores using noble gases (Ar, Kr, and Xe) bombardment during film deposition [64, 65].

Metal foams with excessive amount of discretely distributed nanocavities have formed a new class of materials, which offer a variety of applications in fields such as lightweight construction or crash energy management[66, 67]. Despite the geometrical shapes of the pores [68-70], the significance of the nanoporous foams is the large portion of under-coordinated atoms in the surface skins of various curvatures. The foams can be envisioned as a three-dimensional network of ultrahigh-strength nanowires or ligaments or spherical holes in the matrix. The foamed materials are expected stiffer at low temperatures and tougher at raised temperatures compared with bulk crystals. Stiffness measurement for the typical open cell Au foams of a ~30% relative density samples with different ligament sizes [71] demonstrates that the sample surface is stronger and the foams made of the smaller ligaments are even stronger.

Characterization [72] of the size-dependent mechanical properties of nanoporous Au using a combination of nanoindentation, column pillar micro compression, and molecular dynamics (MD) simulations suggested that nanoporous gold could be as strong as bulk Au, and that the ligaments in nanoporous gold approach the theoretical yield strength of bulk gold, or even harder [71]. At a relative density of 42%, porous Au manifests a sponge-like morphology of interconnecting ligaments on a length scale of ~ 100 nm. The material is polycrystalline with grain sizes of 10-60 nm. Microstructure characterization of residual indentation reveals a localized densification via ductile (plastic) deformation under compressive stress. A mean hardness of 145 MPa and a Young's modulus of 11.1 GPa has been derived from the analysis of the load-displacement curves. The hardness of the investigated nanoporous Au has a value some 10 times higher than the hardness predicted by the scaling laws for the open-cell foams [73]. The compacted nanocrystalline Au ligaments exhibit an average grain size of < 50 nm and hardness values ranging from 1.4 to 2.0 GPa, which are up to 4.5 times harder than the polycrystalline Au [74]. Using scaling laws for foamed materials, the yield strength of the 15 nm diameter ligaments is estimated to be 1.5 GPa, close to the theoretical strength of Au. This value agrees well with extrapolations of the yield strength in the Hall-Petch relation (HPR) at submicron scales [75]. Similarly, the strength of Al foams can be increased by 60–75% upon thermal treatment and age hardening after foaming [76]. It was also found that the hardness of the Al foam is twice as high as pure Al, and the hardness decreases with increasing temperature [77].

On the other hand, the porous structure is thermally less stable. MD simulations [78] of the size effect on melting in solids containing nanovoids revealed four typical stages in void melting that are different from the melting of bulk materials or nanoparticles. Melting in each of the stages is governed by the interplay among different thermodynamic mechanisms arising from the changes in the interfacial free energies, the curvature of the interface, and the elastic energy induced by the density change at melting. As a result, the local melting temperatures show a strong dependence on the void size. Despite these exciting prospects, the understanding of the mechanical and thermal behavior of metal foams at the nanoscale is still very much in its infancy [73, 79].

There have been several models regarding the cavity hardening of nanovoided systems. Quantize fracture mechanics in terms of the classical continuum medium mechanics and the thermodynamic Gibbs free energy considers that a discrete number of defects arising from a few missing atoms in a nanostructure could contribute to the mechanical strength [60, 80]. Another theoretical approach considers the electronic structure around the Fermi energy [81]. Theoretical calculations suggested that the presence of two unsaturated electronic bands near the Fermi level responding oppositely to shear stress enhances the hardness of the voided systems behaving in an unusual way as the number of electrons in a unit cell changes. This finding agrees with the bond-order-length-strength (BOLS) correlation mechanism [82] indicating that a given density of states will shift to lower energy because of the broken bond depressed potential well of trapping.

According to the empirical models of foam plasticity [74, 83], the relationship between the yield strength (σ) and the relative density (ρ_f/ρ_b) of a foamed material follows the scaling laws,

$$\sigma_f = \sigma_b \times \begin{cases} (\rho_f/\rho_b)^{3/2} & \text{(Gibson \& Ashby)} \\ C_b(\rho_f/\rho_b)^{3/2} & \text{(Hodge, et al)} \end{cases}, \quad (1)$$

where the subscripts f and b denote foam and bulk properties, respectively. The $\rho_f = (V_{\text{total}} - V_{\text{void}})/V_{\text{total}}$. Substituting the Hall-Petch relation $\sigma_b = \sigma_0(1 + AK_j^{-0.5})$ for the σ_b in the modified scaling relation with a given porosity, Hodge et al [74] derived information of size dependence of ligament strength in Au foams, which follow the HPR relation with $C_b = 0.3$ as a factor of correction. K_j is the dimensionless form of solid size.

The Young's modulus of Pd and Cu foams varies with the porosity in the empirical relations, [84-86]

$$Y = Y_0 \times \begin{cases} 1 - 1.9p + 0.9p^2 & \text{(Wachtman \& MacKenzie)} \\ (1 - p/p_0)^n & \text{(Rice)} \end{cases} \quad (2)$$

with p the porosity being defined as $p = V_{\text{void}}/V_{\text{total}}$. The mass density is related to the porosity in the form of $\rho_f = 1 - p$. The p_0 is the value of p for which the porosity dependent properties go to zero [87]. The index n and p_0 are adjustable parameters. A linear fit with $n = 1$ to the measured data of various pores has been realized using this model. The decrease in Young's modulus and flow stress with density at larger pore sizes

follow exceedingly well the scaling laws attributing the observations to the existing pores that provide initiation sites for failure.

The theories given in eqs (1) and (2) have been successfully used to describe the deformation behavior of multiphase materials of larger pore sizes showing that the strength of foam materials always decreases when the porosity is increased. However, neither the effect of pore size nor the effect of bond nature of the matrix is involved in the models. Because the mechanical behavior of a surface is different from the bulk interior [88-90], it would be necessary to consider the effective elastic constants of a nanofoam in terms of a three-phase structure, i.e., the bulk matrix, the voids, and the interface skins [91]. In fact, mechanical measurements of nanofoams on a submicron scale [92, 93] revealed close resemblance of the nanosized ligaments in foams showing a dramatic increase in strength with decreasing ligament size [73, 75]. Therefore, the effects of pore size, bond nature, temperature and in particular the role of the large portion of the under-coordinated atoms should be considered in practice. In order to apply the scaling relations to nanoporous metal foams, the yield strength should be considered as a variable of the ligament or void size. Therefore, an atomistic analysis of the effective elastic modulus of the porous systems from the perspective of bond relaxation and the associated local strain and energy trapping is necessary and will be shown in this work.

Chapter 3 Experiment Technique

3.1 Plasma enhanced CVD System

The plasma enhanced chemical vapor deposition (PECVD) system used in this work is shown in Figure 3.1.

Figure 3.1 Schematic diagram of PECVD

As shown in Figure 3.1, the experiment apparatus for carbon onions and carbon nanotubes growth was a standard vertical quartz tube with gas inlet on top and exhaust at the bottom, two electrode plates were placed horizontally in the quartz tube and connected to the pulsed DC supply outside through the two vertical metal bars. Substrate was placed on the cathode, which was the lower electrode.

The flow rate of precursor gases were controlled by digital mass flow controls (MKS instruments). All the gases went through the gas mixer before entering the vertical quartz reaction tube, which was a cylinder cavity. It could make the precursor gases to mix well with each other and enhance the uniformity for the carbon nanostructures growth. The adjustable valve below quartz tube and in front of the rotary pump (ALCATEL) could be used to vary the pumping speed, which in turn would control the pressure during the growing process.

A commercial pulsed direct current (DC) power supply was used to generate the glow discharges between the two electrodes in the quartz tube for the plasma enhanced chemical vapor deposition (PECVD) process. They have the advantage of producing fewer arcs compared with pure direct current (DC) discharges and radio frequency (RF) discharge, and they cause less electromagnetic interference. Furthermore, it is possible to control the substrate temperature with the pulse duty cycle without changing the plasma parameters during the pulse-on times [94].

For the water-assisted carbon nanotubes growth the system was modified by connecting a water bubbler, as shown in Figure 3.2a, for introducing the water molecules into the process.

(a)

Figure 3.2 The PECVD system with water bubbler connected

- (a) Photo of PECVD system with water bubbler (lower left hand corner) connected
- (b) Schematic diagram of water bubbler

The water bubbler was a vacuum stainless steel cylinder with two viewing windows on each side on the body and two gas pipes on the top. One of the two pipes, which was longer inside the bubbler, served as carrier gas (Ar, N₂ and etc.) inlet. It brought the carrier gas below the water level and then bubbles were formed in the water. The other gas pipe, which was shorter inside the bubbler and above the water level, collected the gas carried with water molecules. A flow controller was connected on the gas outlet to control the amount of water molecules flowing into the reactor chamber with the carrier gas.

3.2 Field Emission System

When an electric field is directed towards a solid at room temperature, electrons that are emitted from the solid are called field emission. Energy diagram of field emission is

shown in Figure 3.3. An electron at an energy of E_i is free to move inside the solid. When it reaches the surface, it tries to move away and out of the surface. The solid then lacks a negative charge and the resulting Coulomb force attracts the electron back into the solid. The potential energy is Φ_s . If an electric field directed towards the emitting surface, the electron potential is bent as additional potential energy Φ_e . The total potential energy is Φ_t . The solid and vacuum is now separated by a triangle barrier. The tail of the electron wave function is able to penetrate to the vacuum and hence tunneling occurs.

Figure 3.3 Energy diagram of field emission.

In this work, an automatic field emission system has been used for measuring the field emission prosperities of the carbon nanostructures, grown at low temperature, under the

influence of an electric field and investigating the room temperature electron irradiation effects on the carbon onions. The system consists of four main components:

- i. Vacuum system
- ii. Power supply
- iii. Current measuring unit
- iv. Video camera

Figure 3.4 shows the setup of the electric field emission system. In the experiment set-up, the spacer of 100 μ m was used to separate the cathode (emitter) and anode (collector) to prevent both from electrically shorted. The area under emission test was a round opening in the center of the spacer with the radius of 1 to 2 mm. The sample was clamped firmly in the transparent glass chamber with the connection leads connected to the power supply. The chamber was pumped down to 10^{-4} Pa at room temperature. A voltage was applied between the anode and the cathode to supply an electric field sweeping from 100-2000V. The emission current was monitored by a Keithley 6517A electrometer. A CCD camera was used to record the spatial distribution of the emission sites.

Figure 3.4 Schematic illustration of the electron field emission system [95]

Chapter 4 Characterization Techniques

4.1 Scanning Electron Microscope

The scanning electron microscope (SEM) has unique capabilities for analyzing surfaces.

It is analogous to the reflected light microscope, which forms an image from light reflected from a sample surface with maximum resolution of ~ 1 micron. The SEM uses electrons for image formation with much higher resolution. The different wavelengths of these radiation sources result in different resolution levels: electrons have a much shorter wavelength than light photons, and shorter wavelengths are capable of generating high-resolution information.

In a typical SEM as shown in Figure 4.1, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from 50 keV to a few hundred eV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the

surface, The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation can be detected to produce an image.

Figure 4.1 Schematic illustration of a typical scanning electron microscope

The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. The electrons are detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a Digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the

activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, resolutions less than 1 nm are possible.

The combination of high resolution, an extensive magnification range, and high depth of focus makes the SEM uniquely suited for the study of surfaces. As such, it is an indispensable tool in materials science research and development. In this work, the surface morphology of the carbon nanostructure was studied by a hot filament scanning electron microscope (SEM) (JEOL JSM-5910LV), with the SEM operated at 15 keV.

4.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film (see electron microscope), or to be detected by a sensor such as a CCD camera.

The contrast in a TEM image is not like the contrast in a light microscope image. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption, although the intensity of the transmitted beam is still affected by the volume and density of the material through which it passes. The intensity of the diffraction

depends on the orientation of the planes of atoms in a crystal relative to the electron beam: at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern TEMs are often equipped with specimen holders that allow the user to tilt the specimen to a range of angles in order to obtain specific diffraction conditions, and apertures placed below the specimen allow the user to select electrons diffracted in a particular direction. Comparison of TEM with optical microscope and SEM is shown in Figure 4.2.

Figure 4.2 Comparison of transmission electron microscope with optical microscope and scanning electron microscope

A high contrast image can therefore be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure, and can be viewed on a fluorescent screen, or recorded on photographic film or captured electronically. In the most powerful diffraction contrast TEM instruments, crystal structure can also be investigated by High Resolution Transmission Electron Microscopy (HRTEM), also known as phase contrast imaging as the images are formed due to differences in phase of electron waves scattered through a thin specimen.

Resolution of the HRTEM is limited by spherical and chromatic aberration, but a new generation of aberration correctors has been able to overcome spherical aberration. Software correction of spherical aberration has allowed the production of images with sufficient resolution to show carbon atoms in diamond separated by only 0.89 Å and atoms in silicon at 0.78 Å at magnifications of 50 million times. Improved resolution has also allowed the imaging of lighter atoms that scatter electrons less efficiently — lithium atoms have been imaged in lithium battery materials. The ability to determine the positions of atoms within materials has made the HRTEM an indispensable tool for nanotechnology research and development in many fields, including heterogeneous catalysis and the development of semiconductor devices for electronics and photonics.

In this work, detailed studies of the carbon nanostructures were carried out using TEM (JEOL JEM-2010) operating at 200 kV. The TEM samples with carbon nanostructures

were scratched from the substrate and then dispersing the specimens onto carbon-coated copper grids.

4.3 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It yields information about crystal lattices and their stresses, impurities and free carriers. Raman spectroscopy relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible (e.g. 632nm red from a HeNe laser or 514.5nm green from an argon ion laser), near infrared (e.g. 785nm from a diode laser), or ultraviolet range (e.g. 325nm from a He:Cd laser). When light impinges upon a molecule and interacts with the electron cloud of the bonds of that molecule. A molecular polarizability change, or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the intensity, whereas the Raman shift is equal to the vibrational level that is involved. As shown in Figure 4.3, the incident photon (light quantum), excites one of the electrons into a virtual state. For the spontaneous Raman effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, and which generates Stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-Stokes Raman scattering.

Figure 4.3 Raman energy levels and Raman scatterings

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line (due to elastic Rayleigh scattering) are filtered out and those in a certain spectral window away from the laser line are dispersed onto a detector.

Raman spectroscopy is a fast, non-destructive method of characterising a variety of carbon nanostructures. Tuinstra and Koenig first took the Raman spectrum of graphite in 1970 [96]. They discovered that a single crystal of graphite produces a single peak at 1575cm^{-1} whereas in all other graphite materials (activated charcoal, carbon black etc.) a second feature appears at 1355cm^{-1} , as shown in Figure 4.4. The intensity of this second peak increases relative to the first peak as (a) the amount of "disorganised" carbon increases and (b) the graphite crystal size decreases. The 1575cm^{-1} peak (called the "G" peak, after crystalline graphite) is the only Raman active mode of the infinite lattice. The

other peak (the "D" peak from disordered graphite) is caused by breakdown of the solid-state Raman selection rules, which prevent its appearance in the spectrum of the perfect crystal.

Figure 4.4 514nm Raman spectrum of highly oriented pyrolytic graphite, with insert of nuclear displacement associated with each vibration.

In this work, room temperature Raman spectra were taken with Renishaw micro-Raman spectrometers, equipped with 514.5 nm laser line as the excitation source. The incident laser was focused on the sample through an optical microscope, and the resolution is 1 cm^{-1} .

4.4 Water Contact Angle Measurement

Water contact angle could determine the surface free energy of solid bodies and their components as well as for determining the surface and interface tension of liquids from the drop or lamella contour. The contact angle is the angle at which a liquid/vapor interface meets the solid surface. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface, as shown in Figure 4.5a.

(a)

(b)

Figure 4.5 Contact angle formation on a solid surface

- (a) Image from a video contact angle device (water drop on glass).
- (b) Schematic illustration of contact angle formation

The contact angle plays the role of a boundary condition. As shown in Figure 4.5b, σ_s and σ_l describe the surface tension components of the two phases; γ_{sl} represents the interfacial tension between the two phases, and θ stands for the contact angle corresponding to the angle between vectors σ_l and γ_{sl} . At equilibrium, the chemical potential in the three phases should be equal as expressed by Young-Dupré equation: $\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta$.

On extremely hydrophilic surfaces, a water droplet will completely spread (an effective contact angle of 0°). This occurs for surfaces that have a large affinity for water (including materials that absorb water). On many hydrophilic surfaces, water droplets will exhibit contact angles of 10° to 30° . On highly hydrophobic surfaces, which are incompatible with water, one observes a large contact angle (70° to 90°). Some surfaces have water contact angles as high as 150° or even nearly 180° . On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent. These surfaces are termed superhydrophobic and can be obtained on fluorinated surfaces (Teflon-like coatings) that have been appropriately micropatterned. These new surfaces are based on lotus plants' surface (which has little protuberances) and would be superhydrophobic even to honey. The contact angle thus directly provides information on the interaction energy between the surface and the liquid.

Contact angle is measured using a contact angle goniometer. In this work, hydrophobic property of aligned carbon nanotubes forest grown in water assisted low temperature process was measured by a video-supported contact angle measuring instrument (DataPhysics OCA 20) at room temperature, as shown in Figure 4.6.

Figure 4.6 Video-supported contact angle measuring instrument (DataPhysics OCA 20)

4.5 Nanoindentation

Nanoindentation is a powerful set of tools for investigating the mechanical properties of materials in small dimensions. It refers to depth-sensing indentation testing in the submicrometer range and has been made possible by the development of (1) machines that can make such tiny indentations while recording load and displacement with very high accuracy and precision, and (2) analysis models by which the load displacement data can be interpreted to obtain hardness, modulus, and other mechanical properties.

Once a nanoindentation machine has collected load-displacement data, like a typical curve shown in Figure 4.7, a number of different analyses can be used to determine the mechanical properties of the sample from the data. The results obtained depend on the analysis model chosen and can be very sensitive to the details of the analysis.

Figure 4.7 Load-displacement curve

- Modulus of elasticity

The slope of the curve, dP / dh , upon unloading is indicative of the stiffness S of the contact. This value generally includes a contribution from both the material being tested and the response of the test device itself. The stiffness of the contact can be used to calculate the *reduced modulus of elasticity* E_r as:

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A(h_c)}}$$

where $A(h_c)$ is the area of the indentation at the contact depth h_c (the depth of the residual indentation), and β is a geometrical constant on the order of unity. The reduced modulus E_r is related to the modulus of elasticity E_s of the test specimen through the following relationship from contact mechanics:

$$1/E_r = (1 - \nu_i^2)/E_i + (1 - \nu_s^2)/E_s$$

Here, the subscript i indicates a property of the indenter material and ν is Poisson's ratio. For a diamond indenter tip, E_i is 1140 GPa and ν_i is 0.07. Poisson's ratio varies between 0 and 0.5 for most materials (though it can be negative) and is typically around 0.3.

- Hardness

As in traditional indentation tests, the area of the residual indentation in the sample is measured and the hardness, H , is defined as the maximum load, P_{max} , divided by the residual indentation area, A_r , or

$$H = \frac{P_{max}}{A_r} .$$

An example indent image, from which the area may be determined, is shown in Figure 4.8. There is some controversy over the use of *area functions* to estimate the residual areas versus direct measurement. An area function $A(h)$ typically describes the projected area of an indent as a 2nd-order polynomial function of the indenter depth h . Exclusive application of an area function in the absence of adequate knowledge of material response can lead to misinterpretation of resulting data. Cross-checking of areas microscopically is usually needed.

Figure 4.8 An image of the residual indent left by a Berkovitch tip during a nanoindentation experiment

In this work, Nanoindentation experiments using a Hysitron triboscope with a Berkovich diamond tip was used.

Chapter 5 Low Temperature Growth of Carbon Onions

5.1 Carbon onions grown on ta-C:Ni film and silicon substrate

It has been reported that uniformly aligned carbon nanotubes (CNTs) with high-field emission current density could be grown at $\sim 600^\circ\text{C}$ on the tetrahedral amorphous carbon (ta-C) film with metal (Co, Fe, Ni) nanoparticles deposited using filtered cathodic vacuum arc (FCVA) technique [97, 98]. This chapter describes the work on carbon onion growth. The ta-C film with 5% at. Ni (ta-C:Ni) prepared by FCVA technique was used as the catalyst layer to grow the carbon onions at low temperature. Later it was found that catalyst layer is not necessary for the growth of hollow core carbon onions, bare silicon substrate was then used in the experiment to study the carbon onions' growth mechanism.

5.1.1 Experimental details

As mentioned, two kinds of substrates were employed. One is ta-C:Ni film deposited on silicon wafer by the FCVA [99] for 100 seconds, which is about 40 nm thick. The other is a bare n-type silicon (100) wafer with low resistivity ($0.02\ \Omega\text{cm}$). The distance between the anode and cathode is 1 cm. The pressure inside the vertical quartz tube is pumped down to around $1.5 \times 10^3\ \text{Pa}$. The duty cycle for the pulsed DC power supply was set to 0.83 ($25\mu\text{s}/30\mu\text{s}$, $T_{\text{on}}/T_{\text{on}}+T_{\text{off}}$). After the plasma ignited, the current of the plasma was set to a certain value (e.g. 0.1A) and the plasma was stabilized at around $\sim 200\ \text{V}$, which can sustain the desired current level. The flow rates of Ar, H_2 and C_2H_2 as well as the plasma power used for preparing the samples are tabulated in Table 5.1. No external heating was applied during the growth, except the heat generated by the plasma itself. The growth

time was 3 hours. Temperature increase due to the heating effect by pulsed DC plasma is a function of bias voltage and substrate current[100], which were both kept within relatively low levels in this work. Therefore an estimation of up to 200°C temperature increase is made for the heating effect of pulsed DC plasma used.

Table 5.1 Deposition parameters for the growth of OLFs on two different substrates

Figure 5.x	Catalyst	Flow rate (sccm)			Plasma power (W)
		Ar	H ₂	C ₂ H ₂	
1a-d	ta-C: Ni	60	40	0.5	20
2a, 2b	no catalyst	60	40	0.5	20

5.1.2 Results and Discussion

Figure 5.1 shows the OLFs grown on the ta-C: Ni film under the growth conditions given in Table 5.1. As shown in Figure 5.1a, the diameter of the OLFs are around 200 to 400 nm, and distributed across the sample surface. Transmission electron microscopy (TEM) images were also taken. The sample surface was scratched by a metal tweezers and the carbon onions were deposited onto copper grid for TEM observation. Both the OLFs with metal cores (Figure 5.1b & Figure 5.1c) and without metal cores (Figure 5.1d) have been observed, which is similar to the experiment results reported in [26, 27]. The measured inter graphite shell distance is 0.346 nm, which is quite close to the d_{002} of the graphite, which is 0.34 nm. The larger inter planar distance of the OLF than graphite may be

caused by the curvature of the graphitic plane and also the defects created in the low temperature process.

Figure 5.1 Carbon onions grown on the ta-C:Ni film.

- (a) SEM picture of carbon onions grown on the ta-C:Ni film
- (b) and (c) TEM picture of metal core carbon onions grown on the ta-C:Ni film.
- (d) TEM picture of hollow core carbon onions grown on the ta-C:Ni film.

In order to understand why the metal core and the hollow OLFs coexisted in the sample, the OLFs were also prepared on bare silicon substrate under the same deposition conditions. As shown in Figure 5.2a and Figure 5.2b, OLFs with similar size and density as those grown on the ta-C:Ni substrate have also been observed.

Figure 5.2 Carbon onions grown on bare silicon substrate

Figure 5.3 shows the high resolution TEM image of the OLFs grown on the bare silicon wafer. The similar onion-like polyhedral fullerenes structure was observed. It is shown in Figure 5.3 (a) that the OLF has several concentric carbon layers surrounding a hollow core, which attaches to a non spherical outer shell. The inter shell distance is 0.346 nm as shown in Figure 5.3 (b), which is very close to that of the OLFs grown on the ta-C:Ni substrate.

Figure 5.3 TEM picture of the carbon onion grown on silicon substrate

(a) TEM picture of the carbon onion grown on silicon substrate

(b) Inter plane distance measured for hollow core carbon onion grown on silicon substrate

The biasing condition has been varied to examine its influence on the carbon onions growth on silicon wafer. 20 W is almost the lowest power that can maintain stable plasma. Higher biasing condition, which leads to higher power of the plasma, has been investigated. Figure 5.4 (a) to (d) show the SEM images of the carbon onions grown under the plasma power of 20 W, 35 W, 45 W and 60 W, respectively, while all the other process conditions remain unchanged. It is observed that as the power of the plasma increases from 20 W to 60 W, the density of the OLFs drops from 10^9 to 10^7 cm⁻², and

the average diameter increases from 300 nm to 1 μm . The reduction of OLFs density could be attributed to the enhanced electric field around the OLFs, which make the etching effect of hydrogen and sputtering effect of argon more severe. At the same time, higher power will increase the substrate temperature due to the radiation, which transfers the energy from plasma to the substrate. The temperature increase could be up to 200° C depending on the bias voltage and substrate current as discussed in Chapter 5.1.1. Higher temperature may cause the smaller OLFs to coalesce into bigger OLFs. The diameter and density for the OLFs grown as functions of the plasma power are shown in Figure 5.5.

Figure 5.4 SEM picture of carbon onions grown on bare Silicon wafer under different plasma power of (a) 20 W, (b) 35 W, (c) 45 W and (d) 60 W.

Figure 5.5 Carbon onion size and density vs. plasma power

The argon and hydrogen flow rates were also varied while maintaining the plasma's power to 20 W. **Figure 5.6** (a) to (d) indicate that if the flow rate of argon is decreased and the flow rate for hydrogen is increased, while keeping the total flow rate to be 100 sccm, the density of the OLFs drops from 10^9 to 1.5×10^8 cm⁻² and the average diameter decreases from 300 nm to 150 nm, which is shown in Figure 5.7. The reason may be due to the competition between the carbon source decomposition, which is enhanced by the argon concentration, and the etching effect induced by the hydrogen.

Figure 5.6 SEM pictures of carbon onions grown on bare silicon wafer, while the plasma power is maintained at 20 W, at the H_2/Ar flow rate (sccm) of: (a) 40/60, (b) 45/55, (c) 50/50 and (d) 60/40.

Figure 5.7 Carbon onion size and density vs. gas flow rate

It should be mentioned that the shape of the carbon onions observed by SEM is more conical, rather than spherical as the TEM images shown in Figure 2.6 and Figure 2.7. It is because of the difference in deposition rate caused by the non-uniform electric field. The electric field at the onion tip is the highest, which attracts more carbon ions to be deposited. As the onion grows bigger, the difference in electric field strength also increases. Then the carbon onion's shape tends to be more conical than spherical.

The systematical experimental results indicate that the process parameter for Figure 5.2 is the optimum condition to grow carbon onions, which is 60 sccm for the flow rate of argon, 40 sccm for hydrogen with the plasma power of 20 W.

Raman spectra of OLFs are shown in Figure 5.8. G and D peaks are located at around 1609 cm^{-1} and 1337 cm^{-1} , respectively. The peak appears around 1000 cm^{-1} is the silicon second order peak. One of the reasons for the up shift of the G peak as compared with that of highly oriented pyrolytic graphite (HOPG) at around 1582 cm^{-1} , may be due to the increased graphite fraction in the $sp^2:sp^3$ composite material [101], where the tetrahedral sp^3 sites try to force the layers to be nonplanar while the sp^2 sites oppose the puckering of the layers. But it might not be true in this case, since the disorder induced D peak is quite strong and broad for our carbon onions, what's more, other research groups [102-104] found that, the G peak for sphere carbon onions after high temperature $1700\text{-}2100^\circ\text{C}$ annealing actually downshift a little bit ($1569\text{-}1577\text{ cm}^{-1}$) than the HOPG, which may be due to tensile strain in the graphene planes induced by the curvature [102]. Although the G peak for the as-grown carbon onion by electric arc method will shift up around 6 cm^{-1}

[104], the up shift of the G peak for our onion is much larger (more than 25 cm^{-1}), most likely it is due to the defect-induced D' peak though it is normally rather weak for carbon onions synthesized at high temperature. The D' peak located at around 1620 cm^{-1} and overlap with the G peak. Since our onions are grown in low power plasma and no external heating was provided, they may be more defective than those synthesized at high temperature. Because the weaker G peak and the stronger D' peak stand side by side, the overlapping leads to one bigger peak that shifts up by 25 cm^{-1} more than the G peak of the HOPG.

Figure 5.8 Raman shift of carbon onions grown at the optimum condition on Si.

Ugarte [105] has proposed a outside-to-inside growth mechanism for the polyhedral and spherical OLF, since for high energy electron irradiation, the energy is transferred from outside to inside of the onion. For low temperature catalyst carbon onion growth it should be from inside to outside (or bottom up) due to the growth sequence. Both Kovalevski et

el. [27] and He et al. [106] reported a comparable quantity of hollow onions coexisting with the onions encapsulated metal core. They attempted to correlate the hollow onion growth with the catalyst. Kovalevski suggested that the catalyst might escape from the defect on the inner carbon sphere to form another onion next to it. Another growth mechanism he proposed was that the catalyst moving rate was higher than the rate for carbon growth rate caused the carbon onion to burst. But the force, which causes the catalyst to escape from the core, is still unclear, and their experiments do not have biasing. If it is the solubility of carbon cause catalyst to move, a carbon nanotube should be formed on the catalyst escape root connecting to another carbon onion core. Unfortunately, no evidence was given to confirm this mechanism in their articles. He et al. [82] tried to explain the process of the growth of hollow carbon onions by a vapor liquid mechanism. They suggested that the catalyst may vaporize after the onion being formed. It is true that the melting temperature will drop for metallic catalyst nanoparticle, but the problem still remains on the extent of the melting temperature drop. If the drop is insignificant, the catalysts cannot evaporate.

Figure 5.1 and Figure 5.2 show the carbon onions grown on the substrate coated with nickel nano particles and grown on the substrate without catalyst. TEM showed that there is no much difference between the carbon onions grown on substrate with and without metal core. This observation may be indicative that the growth of hollow carbon onions does not relate to the catalyst at all. In our experiment, the argon ion bombardment after the plasma ignition will create uniform defect sites on the substrate. Carbon dissociated from acetylene in the plasma will form various clusters on these sites. The clusters, where

carbon atoms form a polyhedral closed surface, have minimum dangling bonds, hence most stable. They have less probability to be etched away by hydrogen than those with less stable structures. The electric field will be enhanced locally since they form a bump on the surface. It will attract more carbon atoms to deposit onto the surface. The etching effect by hydrogen will ensure the crystallization of the polyhedral carbon onion, while argon will increase the gas ionization ratio for the plasma and enhance the dissociation of the hydrocarbon. In our opinion the only difference between the metal cored and the hollow OLFs is the first one or two innermost layers of the graphite sphere. For the metal cored OLFs, it may relate to the catalyst particle, whereas it is the self assembly process for the hollow OLFs.

5.2 Carbon onions/fibers grown on nanodiamond coating

It has been demonstrated that nanocrystalline diamond film could be grown at relative low temperatures (~ 200 to 400°C) by microwave plasma CVD technique with or without magnetic field assistance [107, 108]. The nanodiamond nucleation can effectively reduce the growth temperature, enhance the film uniformity, decreasing the activation energy for nanodiamond film growth and increasing the growth rate without deteriorating the diamond quality. In this chapter silicon substrate coated with nanodiamond has been employed in the low temperature PECVD process, the sample was characterized to examine the effect of nanodiamond nucleation on the nanostructure grown.

5.2.1 Experimental Details

The experiment apparatus is the same as the one shown in Figure 3.1. Nanocrystalline diamond of 1/15 μm diameter was coated onto the substrate. The distance between the anode and the cathode was 1.5 cm. The quartz tube as the chamber of growth was evacuated to around 1.5×10^3 Pa. The duty cycle of the pulsed DC power supply was set to 0.5. After the plasma ignition, the current of the plasma was set to 0.2 A and the plasma stabilized around a voltage of 300 V, which could sustain the desired current level. Therefore the power of the plasma was 60 W. The flow rates of N_2 , H_2 and C_2H_2 were 20, 40 and 2 sccm, respectively. No external heating was used during the growth, except the heat generated by the low power plasma itself, which could approximately raise the temperature by up to 200°C as discussed in Chapter 5.1.1. The growth time was 4 hours.

5.2.2 Results and Discussion

Figure 5.9 shows the SEM images of the carbon onions. Their diameters are in the range of 1 to 2 μm , and the density is around $1 - 2 \times 10^8 \text{ cm}^{-2}$. Most of the carbon onions are distributed near the edges of the substrate. From the SEM images it is observed that there is a bright tip on top of each carbon onion. The difference in contrast indicates that the tip has different physical or chemical properties comparing with the carbon onion, such as work function, crystalline structures etc. Since only the carbon related structures can be grown on the sample, the bright tips could relate to the nanodiamond coating on the sample.

Figure 5.9 Carbon onions with diamond tip.

Figure 5.10a and Figure 5.10b show a diamond particle at the tip of each carbon fiber. The diameter of the carbon fibers is about the same as the carbon onions, which are shown in Figure 5.9. Their heights are in the range of 1.5 to 3 μm. It is shown in Figure 5.10c and Figure 5.10d that, when the growth time was increased to 6 hours, both the diameter and the length of the carbon fibers increased significantly. The bright tips on top of each carbon fiber also become apparent and sharper.

For Figure 5.9 and Figure 5.10, the difference in growth resulting in onion and fiber are the electric field and growth time. Higher electric field causes higher carbon ionization rate and more carbon ions are deposited resulting fiber growth. Longer time can also cause fiber to grow with larger diameter and more apparent tip.

Figure 5.10 Carbon fibers with diamond tip. (a) and (b) Carbon fibers in the center of the sample; (c) and (d) Carbon fibers grown after 6 hours.

Carbon onions/fibers have been grown on the bare silicon wafer under the same process condition, similar structures were observed, but without the bright tip. It indicates that the bright tips have strong correlation with the diamond coating. Both TEM and Raman have been performed to characterize the tip. But unfortunately, due to challenges in TEM sample preparation; and very small quantity of reflected laser signal for Raman to collect and difficulties in focusing laser onto the tip, so far no obvious evidence has been found to prove it was diamond. Author hopes that further investigation could be carried out base on the current findings and finally potential applications could be developed.

From the experiment results shown in Figure 5.4, Figure 5.6, Figure 5.9 and Figure 5.10, the main factors which dominated the morphology of the carbon nanostructures are summarized in Table 5.2.

Table 5.2 Main factors that dominates the morphology of the carbon nanostructures

	Size (or diameter)	Density
H ₂ /Ar ratio increases	Decreases	decreases
Bias voltage increases	increases	decreases
Growth time increases	increases	decreases

The field emission property of the carbon fiber has been characterized by sweeping the voltage several times from 0 to 2000 V. The turn on voltage was measured to be around 10 V/ μm , as shown in Figure 5.11, which is rather high as compared to carbon nanotubes.

Figure 5.11 Field emission property of carbon fibers grown on nanodiamond coating

Figure 5.12 shows the SEM images of the carbon fibers after the field emission experiment. It is observed that the broken fiber with hollow core cylindrical structures. The phenomenon of the hollow core carbon fibers grown without any catalyst or with assistance of the diamond particle, to the author's knowledge, has not been reported before.

Figure 5.12 SEM pictures of carbon fibers after the field emission experiment.

It is worthwhile to explain the missing tip in the field emission experiment here. Due to the edge effect, electric arc will occur around the edge of spacer opening, which is 100µm thick with a 0.2 cm² round hole and being used to separate the (collector) anode and (emitter) cathode in the field emission experiment. The edge effect is easily to be

observed if transparent ITO glass is used on the anode. The very high current of electric arc can easily damage the specimen under test. The tip on the carbon fiber is believed to be burnt / damaged by the electric arcs and the missing tips cannot be found under SEM.

Chapter 6 Electron Irradiation Effects on Carbon Onions

As introduced in Chapter 2.1.2, carbon onions could be transformed into diamond in a transmission electron microscope (TEM) system under a few hours' high energy electron irradiation with intense current density at high temperature. The transformation only took place at the spot on which the electron beam focuses, and the high temperature process also greatly limits the substrate's melting point. It makes this technique almost impractical for the current diamond industry. In this chapter, low temperature electron irradiation effect on the carbon onions in a field emission system has been investigated. Carbon nanotubes (CNTs), which have been found to be very efficient and stable emitters [109], were used as the electron source. Raman spectra were used to characterize the carbon onions before and after the electron irradiation.

6.1 Experimental details

The carbon nanotubes, which were used as electron source for the electron irradiation, were grown by hot filament chemical vapor deposition. The catalyst layer was tetrahedral amorphous carbon (TAC) with 5% at. Ni deposited on silicon wafer by the filtered cathodic vacuum arc (FCVA) technique [99] for 100 seconds, which was about 40 nm thick. The substrate was placed on the substrate holder in a vertical quartz tube, which is similar to the apparatus shown in Figure 3.1, and it was heated up by hot filament to 650°C in hydrogen environment. Acetylene was used as the carbon source with a flow rate of 7 sccm. Growth pressure was 10^3 Pa and growth time was 15 mins. After the growth, the system was cooled down to room temperature in the hydrogen environment.

The electron irradiation was carried out in a high vacuum field emission system for 48 hours. Carbon onions grown on the bare silicon substrate under the process condition described in Chapter 3 were connected to the anode. They were facing to the CNTs, which were connected to the cathode. In between, the spacer's thickness was 100 μm with a 0.2 cm^2 round opening, and the applied voltage was 1500V. The system was pumped down to 10^{-4} Pa.

6.2 Results and discussion

Figure 6.1a-c show the SEM images of the CNTs, which are about 50 nm in diameter and 2 μm long with nickel catalyst particle on the tip. The field emission property of the CNTs is shown in Figure 6.1d, which indicates the turn on field is about 7V/ μm .

Figure 6.1 (a), (b) and (c) SEM image of carbon nanotubes and (d) its field emission property.

Figure 6.2 shows the current density as a function of the irradiation time. It is observed that in the first 3 hours, the current density decayed from 6 to 1 mA/cm², and stabilized around 1 mA/cm² for the rest of the time until a sudden rise in the current density in the end, which might attribute to certain structure (like electric field induced epitaxy) grown between the anode and cathode and eventually caused short circuit.

Figure 6.2 Current density vs. time for the electron irradiation on the onion like carbon

The Raman spectra of the carbon onions sample were measured before and after the electron irradiation as shown in Figure 6.3 with fitted with 3 bands. The D peak has shifted from 1360 cm⁻¹ to 1348⁻¹ after the electron irradiation, which could be an indication of the transition from graphite to diamond. But the electron irradiation energy

level and current density were much lower than those reported in [4, 5], which were in several MeV and in terms of A/cm^2 , respectively. Longer irradiation time (e.g. in terms of weeks) may be needed for diamond nucleation. The shift of D peak may also due to the defects induced by electron irradiation. It is also observed that the G peak has shifted from 1583 to 1590 cm^{-1} , which may be caused by more defects that were created during the 48 hours' electron irradiation.

Figure 6.3 Raman spectra of the carbon onions sample before and after the electron irradiation.

Chapter 7 Nanocavity hardening: impact of broken bonds at the negatively curved surfaces

The hardness and young's modulus for carbon onions grown on the silicon substrate, which were shown in Chapter 5, have been measured by nanoindentation. For the purpose of comparison, nanoindentation has also been done on a carbon film, which was grown under the similar condition, except that the flow rate of the hydrocarbon gas precursor was increased. The load vs. displacement curves for carbon onions and carbon film with different maximum load conditions are shown in Figure 7.1.

Figure 7.1 Load displacement curve for carbon onions and carbon film grown under similar condition on silicon substrate

It has been mentioned in Chapter 5 that the carbon onions grown on the silicon substrate had hollow cores in the center. Cross section SEM image revealed the carbon film was

uniform and continuous. From Figure 7.1 we can see that the carbon onions exhibit higher hardness and young's modulus than the carbon film. And the deformation for the carbon onions is much larger than that for the carbon film after indentation. It can be served as another evidence for the presence and absence of the nanocavities in the two carbon materials. In order to understand the reason why the carbon onions were harder than the carbon film grown under similar condition, their Raman spectra were also taken and found to be very similar, which means the contribution to the hardness from the sp^2 , sp^3 content in the two carbon material are very close. Therefore the hardening effect caused by nanocavities should be responsible for the difference in the hardness. In this chapter, an analytical expression will be derived based on Bond Order Length Strength (BOLS) theory to predict and compare with the experiment result reported for some nanoporous materials with much more mature fabrication process for controlling the porosity and nanocavity size.

7.1 Theory

7.1.1 Extended BOLS correlation

The core idea of the broken bond rule and the BOLS correlation mechanism [82, 88] is that the broken bonds cause the remaining bonds of the under-coordinated atoms to contract spontaneously associated with bond strength gain compared with the bulk cases as standard. The shortened and strengthened bonds and the associated energy trapping dictate the unusual behavior of a mesoscopic system.

Naturally, the under-coordinated atoms surrounding atomic vacancies, point defects, nanocavities, and voids in nanofoams perform exactly the same to the under-coordinated atoms at the positively curved surfaces of nanostructures or at a flat surface despite the slight difference in the coordinating environment. The extent of mechanical enhancement or thermal stability depression is determined by the portion of the under-coordinated atoms. Therefore, we can apply directly the BOLS correlation to the negatively curved surfaces of porous structures.

7.1.2 Analytical expressions

(A) Surface to volume ratio

Figure 7.2 Schematic illustration of the surface-to-volume ratio of a sphere with $4\pi n^3/3+1$ cavities and the three phase structures, i.e., voids, skins, and the matrix. Only atoms in the dark skins contribute to the property change yet atoms in the core region remain as they are in the bulk.

Considering a sphere of K_j radius with n spherical cavities of L_j radius lined along the K_j radius, as illustrated in Figure 7.2, the entire volume V_0 occupied by atoms, the sum of the skins of the voids and the sphere surface, V_i , the porosity p and mass density ρ_f are calculated as,

$$\begin{cases} V_0 &= \frac{4\pi}{3} \left[K_j^3 - \left(n^3 + \frac{3}{4\pi} \right) \frac{4\pi}{3} L_j^3 \right] & (\text{occupied - volume}) \\ V_i &= 4\pi \left[K_j^2 C_{io} + \frac{4\pi}{3} \left(n^3 + \frac{3}{4\pi} \right) L_j^2 C_{ii} \right] & (\text{Skin - volume}) \\ p &= \frac{4\pi}{3} \left(n^3 + 3/4\pi \right) \left(L_j / K_j \right)^3 = 1 - \rho_f & (\text{porosity - density}) \\ C_{ii} &= 2 / \{ 1 + \exp[(12 - z_{ii}) / (8z_{ii})] \} & (\text{bond - contraction}) \end{cases} \quad (3)$$

where C_{ii} and C_{io} represent the bond contraction coefficient for atoms in the inner negatively curved skins of the cavities and for atoms at the outer positively curved surface of the sphere, respectively. For the curvature dependent atomic coordination, we may extend the positive-curvature dependent coordination number to a case cover both positively (-) and negatively (+) curved surfaces:

$$z_1 = 4(1 \pm 0.75/K_j), \quad z_2 = z_1 + 1, \quad \text{and} \quad z_{i \geq 3} = 12. \quad (4)$$

The ratio between the volume sum of the skins and the volume entirely occupied by atoms can be derived as,

$$\begin{aligned} r_{ij}(n, L_j, K_j) &= \frac{V_i}{V_0} = \frac{3}{K_j} \frac{C_{io} + 4\pi/3(n^3 + 3/4\pi)(L_j/K_j)^2 C_{ii}}{1 - 4\pi/3(n^3 + 3/4\pi)(L_j/K_j)^3} = (\gamma_{io}, \gamma_{ii}) \\ &= \frac{3}{K_j} \begin{cases} C_{io} & (\text{Solid - sphere : } L_i = 0) \\ \frac{C_{io} + (L_j/K_j)^2 C_{ii}}{1 - (L_j/K_j)^3} = (\gamma_{io}, \gamma_{ii})_h & (\text{Hollow - sphere : } n = 0) \\ \frac{3C_{io} + 4\pi(n^3 + 3/4\pi)(L_j/K_j)^2 C_{ii}}{3 - 4\pi(n^3 + 3/4\pi)(L_j/K_j)^3} = (\gamma_{io}, \gamma_{ii})_p & (\text{Porous - sphere}) \end{cases} \end{aligned} \quad (5)$$

The $r_{ij} = (\gamma_{io}, \gamma_{ii})$ can be expressed in a vector form because of the coordination environment difference between the inner and the outer surfaces. The parameters n , L_j and K_j are constrained by the relation: $(2n+1)(L_j+2) \leq K_j-2$ because a limited number of cavities can be lined along the radius K_j . This expression covers situations of a solid sphere, a hollow sphere, and a sphere with uniformly distributed cavities of the same size. This relation can be extended to a solid rod, a hollow tube, and a porous nanowire as well.

With the derived surface to volume ratio, $r_{ij}(n, L_j, K_j)$, and the given expressions for the quantity, $q_i(z_i, d_i, E_i)$, one can readily predict the size, cavity density, and temperature dependence of a detectable quantity Q of a system with large portion of under-coordinated atoms. The q_i is the density of Q at the specific i th atomic site.

(B) Thermal stability and elasticity

With the given q_i relations of $T_{mi} \propto z_i E_i$, and $Y_i \propto E_i/d_i^3$ [82], we can estimate the relative change for the melting point and elastic modulus of a nanofoam to that of the bulk,

$$\frac{\Delta T_m(m, n, K_j, L_j)}{T_m(m, 0, \infty, 0)} = \sum_{i \leq 3} (r_{io}, r_{ii}) \begin{pmatrix} z_{i0b} C_{io}^{-m} - 1 \\ z_{iib} C_{ii}^{-m} - 1 \end{pmatrix}$$

$$\frac{\Delta Y(T, m, n, K_j, L_j)}{Y(0, m, 0, \infty, 0)} = \frac{1}{(1 + \alpha T)^3} \sum_{i \leq 3} (r_{io}, r_{ii}) \left(\begin{array}{c} C_{io}^{-(3+m)} \left(1 - \frac{\int_0^T \eta_1(t) dt}{z_{io} C_{io}^{-m} E_b(0)} \right) - 1 \\ C_{ii}^{-(3+m)} \left(1 - \frac{\int_0^T \eta_1(t) dt}{z_{ii} C_{ii}^{-m} E_b(0)} \right) - 1 \end{array} \right) \quad (6)$$

where m is the bond nature indicator and $E_b(0)$ is the bond energy at 0 K. The $z_{iib} = z_{ii}/z_b$ and $z_b = 12$ is the bulk standard of atomic coordination number. $\eta_1(t)$ is the specific heat per bond, which follows Debye approximation [88, 90]. The integration $\int_0^T \eta_1(t) dt$ is the internal energy of the specific bond. The calculation sums over the skin of two atomic layers.

(C) Inverse Hall-Petch relationship (IHPR)

The mechanical strengthening with grain refinement in the size range of 100 nm or larger has traditionally been rationalized with the so-called T-independent HPR that can be simplified in a dimensionless form normalized by the bulk strength, $\sigma(\infty)$, measured at the same temperature and under the same conditions:

$$\sigma(K_j)/\sigma(\infty) = 1 + AK_j^{-0.5} \quad (7)$$

The slope A is an adjustable parameter for experimental data fitting, which represents both the intrinsic properties and the extrinsic artifacts such as defects, the pile-up of dislocations, shapes of indentation tips, strain rates, load scales and directions in the test.

As the crystal is refined from the micrometer regime into the nanometer regime, the classical HPR process invariably breaks down and the yield strength versus grain size relationship departs markedly from that seen at larger grain sizes - IHPR occurs. With further grain refinement, the yield stress peaks in many cases at a mean grain size in the order of 10 nm or so. A further decrease in grain size can cause softening of the solid, instead, and then the HPR slope turns from positive to negative at a critical size, or so-called the strongest grain size [110]. The IHPR is expressed as [111],

$$\frac{\sigma(K_j, T)}{\sigma(\infty, T)} = \left(1 + A' \times \exp \left[\frac{T_m(K_j)}{T} \right] \times K_j^{-1/2} \right) \times \left[\frac{d(K_j)}{d} \right]^{-3} \times \left[\frac{T_m(K_j) - T}{T_m} \right] \quad (8)$$

where A' is a prefactor and the $T_m(K_j)$ represents for the $T_m(m, n, K_j, L_j)$. The reduced bond length is given as, $d(K_j)/d = 1 + \sum_{i \leq 3} (r_{io}, r_{ii}) (C_{io} - 1, C_{ii} - 1)^*$.

Eq (8) represents that the IHPR originates from the intrinsic competition between the temperature-dependent energy-density-gain ($\propto [T_m(K_j) - T]/d^3(K_j)$) in the surface skin and the residual cohesive-energy ($\propto T_m(K_j)$) of the under-coordinated surface atoms and the extrinsic competition between activation ($\propto T_m(K_j)/T$) and prohibition ($\propto K_j^{-1/2}$) of atomic dislocations. The activation energy is proportional to the atomic cohesion which drops with solid size whereas the prohibition of atomic dislocation arises from dislocation accumulation and strain gradient work hardening which increases with the indentation depth. As the solid size is decreased, a transition from dominance of energy-density-gain to dominance of residual cohesive-energy occurs at the IHPR critical size because of the

increased portion of the under-coordinated atoms. During the transition, contributions from both processes are competitive.

7.2 Results and discussion

I. Critical porous size

Assuming a hollow sphere of L_j radius with a shell of $L_j - [L_j - (C_1 + C_2)]$ thick, we have the total energy stored in the shell skin in comparison to that in an ideal sphere without the surface effect,

$$\begin{aligned} \frac{E_{shell}}{E_{sphere}} &= \frac{\int_{L_j - C_1}^{L_j} 4\pi R^2 dR C_1^{-(m+3)} + \int_{L_j - C_1 - C_2}^{L_j - C_1} 4\pi R^2 dR C_2^{-(m+3)}}{\int_0^{L_j} 4\pi R^2 dR} \\ &= \left[1 - \left(1 - C_1/L_j \right)^3 \right] C_1^{-(m+3)} + \left[\left(1 - C_1/L_j \right)^3 - \left(1 - (C_1 + C_2)/L_j \right)^3 \right] C_2^{-(m+3)} \end{aligned} \quad (9)$$

Calculations were conducted based on the given $C_i(z_i)$ and the curvature dependent z_i values in eqs (3) and (4). From the results shown in Figure 7.3, we can find the critical size below which the total energy stored in the shell of the hollow sphere is greater than that in the ideal bulk of the same volume without considering the temperature effects. The estimation indicates that the critical size is bond nature dependent. The critical size is 6, 8, and 11.5 for $m = 1$ (metal), 3(carbon, 2.56), and 5 (Si, 4.88), respectively. The elasticity of the shell is always higher than the bulk because the elasticity is proportional to the energy density. However, in plastic deformation, the hollow sphere could be stronger than the ideal bulk because of the long range effect in the indentation deformation test. On the other hand, the thermal stability of the hollow nanosphere is

always lower than the solid sphere. Therefore, a hollow nanosphere should be tougher than the ideal solid sphere.

Figure 7.3 Bond nature dependence of the critical pore size below which the total energy stored in the shell of the hollow sphere is greater than the energy stored in an ideal bulk of the same size.

II. Correlation between porosity and pore size

In Figure 7.4, it can be seen that the smaller the cavities larger values of the surface to volume ratio. The properties of the porous structure are more dominated by the surface atoms for smaller cavities.

Figure 7.4 Relationship between number of cavities and porosity (a), porosity and surface to volume ratio (b) for different pore sizes of a $K_j = 600$ specimen

III. Predictions of porosity dependence of T_m and Y

Calculations of the Y and T_m were conducted by using a fixed value of sphere radius $K_j = 600$ with different L_j and n values and fixed $m = 1$ for metals. Figure 7.5 shows that the T_m drops when the porosity is increased; at the same porosity, the specimen with smaller pore size is less stable than the ones with larger pores. The Young's modulus increases with the porosity and the Young's modulus of the specimen with smaller pores increases faster. The predicted trends of thermal stability and strength agree well with the experiment observations for the size-dependent mechanical properties of nanoporous Au [74, 112]. It is important to note that there exists porosity limit for the specimens with small pore sizes due to constrain. For the relative T_m consideration, the surface-to-volume ratio should refer to the bulk volume excluding the volume of pores as given in eq (5); for the relative elasticity consideration, the surface-to-volume ratio should refer to the volume of the entire sphere of K_j radius.

Figure 7.5 Prediction of the porosity dependence of (a) T_m and (b) Y of porous Au foams with different pore sizes of a $K_j = 600$ specimen.

IV. Plastic deformation: Inverse Hall-Petch relation (IHPR)

In dealing with the plastic deformation using IHPR, we may use the following relation to find the effective volume by excluding the pore volume in the specimen:

$$\frac{4\pi}{3} K_j'^3 = \frac{4\pi}{3} \left[K_j^3 - \left(n^3 + \frac{3}{4\pi} \right) \frac{4\pi}{3} L_j^3 \right]$$

$$x = K_j'^{-0.5}$$
(10)

Figure 7.6 (a) shows the predicted IHPR as a function of L_j for $10 < K_j < 600$ specimens. Compared with the situation of single nanoparticle, the strongest size is significantly reduced for the foams. Figure 7.6(b) compares the predicted IHPR of Au with experimental results. The ligament size $x(K_j^{-1/2})$ is derived from Au foams with the modified scaling relation of (1), as shown in Chapter 2.3. In the figure, HPR is the classical Hall-Petch relation. IHPR 2 and IHPR 1 are the IHPR with and without involving the intrinsic competition of energy density and atomic cohesive energy as discussed for the nanoparticles. The scattered data for Au ligaments smaller than 5 nm deviates from the expected IHPR. One possibility is the surface chemical passivation effect because the higher chemical reactivity of small particles. Chemical passivation alters the bond nature of the surface bond that will enhance the strength of the bonds. A combination of the present IHPR with the scaling relation of (1) in Chapter 2.3 may describe the observed trends at larger porosities, and further investigation is in progress.

Figure 7.6 Prediction of (a) the IHPR for nanoporous Au sphere with $10 < K_j < 600$ and different pore sizes L_j and pore numbers n . (b) Comparison of the predicted IHPR of Au with measurement, Data 1 [72], Data 2 [71], Data 3 [73], and data 4 [75]. The ligament

size $x(K_j^{-1/2})$ is derived from Au foams with the modified scaling relation of Ashby. HPR is the classical Hall-Petch relation. IHPR 2 and IHPR 1 are the inverse HPR with and without involving the intrinsic competition as discussed for the nanoparticles.

According to the currently developed understanding, the magnitude of $T_m - T$, or the ratio T/T_m , plays a key role in determining the relative strength. The T_m of Al (933.5 K) is lower than that of Au (1337 K), which explains why the relative strength of Al foam to Al bulk is lower than that of Au.

V. Further evidence

The fact that the enhancement of the internal stress of a-C films by changing the sizes of nanopores through the bombardment of noble gases (Ar, Kr, and Xe) [64, 65] could provide further evidence for the proposed mechanism for nanocavity hardening. The voided amorphous carbon films have an uniquely intrinsic stress (~ 12 GPa) which is almost one order in magnitude higher than those found in other amorphous materials such as a-Si, a-Ge, or metals (< 1 GPa) [113]. Using extended near-edge XAFS and XPS, Lacerda et al [64] investigated the effect of the trapping of noble gases in the a-C matrix on the internal stress of the a-C films and the energy states of the trapped gases. They found that the internal stress could be raised from 1 to 11 GPa by controlling the sizes of the pores within which noble gases are trapped. Meanwhile, they found an approximate ~ 1 eV lowering (smaller in magnitude) of the core level binding energy of the entrapped gases associated with 0.03-0.05 nm expansion of the atomic distance of the trapped noble gases. The measured core-level shift is of the same order as those measured for noble

gases implanted in Ge [114], Al [115], and Cu, Ag, and Au [116, 117] and Xe implanted in Pd hosts [118]. The interatomic separation of Ar (Xe) increases from 0.24 (0.29) nm to 0.29 (0.32) nm when the stress of the host a-C is increased from 1 to 11 GPa [119].

Comparatively, an external hydrostatic pressure around 11 GPa could suppress the interplanar distance of microcrystalline graphite by $\sim 15\%$ [120], gathering the core/valence electrons of carbon atoms closer together. The resistivity of a-C films decreases when the external hydrostatic pressure is increased [121]. These results are in agreement with the recent work of Umemoto et al [122] who proposed a dense, metallic, and rigid form of graphitic carbon with similar characteristics. The effect of hydrostatic pressure is very much the same as the pore-induced internal stress using noble gas sputtering and implanting.

The binding energy weakening and atomic distance expansion of the entrapped gases indicate clearly that the gas-entrapped pores expand in size and the interfacial C-C bonds contract because of the bond order loss of the interfacial C atoms, which contribute to the extraordinary mechanical strength of the entire a-C films. The pore-induced excessive stress is expected to play the same role as the external hydrostatic pressure causing densification, metallization, and strengthening of the graphite by lattice compression.

Chapter 8 Water Assisted Growth of Aligned Carbon Nanotube Forests

It was reported in [43] that water could increase the activity, extend the lifetime of the catalyst and could also purify the single wall carbon nanotube by removing the amorphous carbon coated on the catalyst nanoparticles without oxidizing the CNTs at growth temperature. Therefore, comparing with the conventional growth method, water assisted process could improve the productivity significantly and less complicated purifications are needed, which can greatly accelerate the pace of developing processes for cost effective mass production for the CNTs. In this chapter further investigation on the water-assisted low temperature synthesis of carbon nanotubes is carried out.

8.1 Experimental details

Experiment apparatus setup was very similar to the one shown in Figure 3.1, except that a bubbler was used to introduce water vapor into the chamber. The substrate was coated with 100 nm nickel by electron beam evaporator. Flow rate of the acetylene, hydrogen and argon were 3 sccm, 50 sccm and 50 sccm respectively. Argon also served as the carrier gas for carrying water vapor into the chamber with a flow rate of 1 SCFH through the bubble. Distance between the anode and cathode was 1 cm. Pulsed DC power supply with duty cycle was set to 0.5 with the biasing voltage around 360-370 V. Plasma current was stabilized around 0.22-0.25 A, therefore the power of the plasma was 80 W. The whole system was pumped down to 1.5×10^3 Pa, and the growth time was 30 mins. No external heating was provided.

8.2 Results and discussion

Figure 8.1a shows the SEM picture of the carbon nanotubes grown by the water-assisted PECVD at low temperature. The CNTs are well aligned and uniformly self assembled into bundles with high density. The average diameter of the CNT bundles is around 1 μm , and the height is about 10 μm . The CNTs look like trees/forest in the low magnification image. The high magnification SEM picture indicates that the diameter of each CNT is very uniform. For the standard high temperature CNTs growth without biasing, the obtained CNTs are shown in Figure 8.1b, which are not aligned and the diameter is non-uniform with low density.

The results show that the water molecules could also assist the CNTs growth at low temperature. For the aligned CNT growth, argon ions bombardment may play a key role in catalyst nanoparticles formation. After the plasma ignition, argon ions were accelerated to the substrate which roughened the catalyst surface and formed the nickel nanoparticles on top. When sufficient heat was transferred from the plasma to the substrate, most of the catalysts were activated by assistance of the water. Then CNTs started to grow. Water also played an additional role in controlling the diameter, etching the amorphous carbon to purify the CNTs and extending the lifetime of the catalyst. Experiment has been carried out to grow CNTs without water vapor, while all the other process parameters remain the same as shown in Chapter 8.1. But instead of CNTs, one layer of amorphous carbon film was grown. It was another evidence of showing that water vapor could remove the amorphous carbon during the CNT growth. It is not clear yet why the CNTs could self assembled into bundles, but the CNTs grown on a thinner

catalyst layer (e.g. 10 nm) tended to stand alone rather than bundle together, which indicated the formation of CNTs bundle may relate to the catalyst layer thickness. Since on the thicker catalyst layer, the coalescence of the catalyst nanoparticles might be more severe.

(a)

(b)

Figure 8.1 SEM images for the CNTs grown on 100 nm e-beam evaporated nickel catalyst layer. (a) SEM images taken at 3 different magnifications for the aligned CNT forest grown in a low temperature water assisted process; (b) CNTs grown in the standard high temperature process

The field emission property of the aligned CNT forest has been characterized by sweeping the voltage several times from 0 to 1500 V as shown in **Figure 8.2**. The turn on field was measured to be about 9 V/ μm , which was higher than that of CNTs as shown in **Figure 6.1**. The screening effect might cause the relative high turn on field. Since the CNTs were bundled together, although each of them has high aspect ratio, self assembly into CNT trees could weaken the field around them, as a consequence the turn on field increased. It was also observed that the field emission property of the CNT trees were very stable and repeatable as shown in **Figure 8.2**.

Figure 8.2 Field emission property of aligned carbon nanotube grown in low temperature water assisted process

Figure 8.3 TEM image of aligned carbon nanotube grown in low temperature water assisted process. (a) TEM image for the CNT bundles; (b) TEM image for an individual CNT outside the bundle

High resolution TEM pictures have been taken for the aligned CNT trees as shown in Figure 8.3. Multi-wall CNTs were grown with catalyst tip. The tip's average diameter is about 100 nm, close to the e-beam evaporated catalyst layer thickness.

The water contact angle has been measured for the aligned CNT forest. As mentioned in the introduction, there are mainly two factors affecting a surface's water contact angle, i.e., the roughness and surface energy. Aligned CNT forest contributes to the roughness of the surface, which can trap the air under the water droplet to prevent it to spread into the CNTs. In addition, when the surface energy of the surface material is intrinsically low, the combined effect is a surface that will repel any water that comes into contact with it. It was demonstrated in Ref [123] that the surface contact angle increases with increasing the fluorine to carbon ratio. Therefore CF_4 was used to further increase the contact angle. It is shown in Figure 8.4 that the contact angle of the CNT forest is 152.6° , and it increased to 156.5° when CF_4 is incorporated into the plasma.

Figure 8.4 Water contact angle measurement for the aligned CNT forest

- (a) The contact angle is 152.6° without CF_4 in the plasma
- (b) The contact angle is 156.5° with CF_4 in the plasma

Superhydrophobicity refers to a surface with water contact angle greater than 150° . Stability of the water contact angle was also measured as shown in Figure 8.5. The superhydrophobicity of the aligned CNT trees is durable and stable.

Figure 8.5 Stability of water contact angle for the CNT forest with and without CF_4 in the plasma.

Chapter 9 Conclusions and Recommendations

9.1 Conclusions

Dense and uniform onion-like polyhedral fullerenes (OLFs) have been grown on silicon substrates by the PECVD at room temperature. The sizes of onions varied from 200-400 nm and the density was around 10^9 cm^{-2} . The processing parameters were systematically adjusted to study the influence of the plasma power and flow rate of argon and hydrogen on OLFs growth. The OLF consisted several concentric polyhedral carbon layers with about 0.346 nm inter shell distance. Raman spectroscopy of the OLFs reveals a weaker G peak and a stronger D' peak than those synthesized at high temperature, which indicates onions grown at low temperature are more defective.

Diamond tip were grown on carbon fibers prepared using substrate coated with diamond particles. Physical evidence shows that the diamond-tip has strong correlations with the diamond coatings. D band shift has been observed for electron irradiated carbon onions at room temperature, various reasons like graphite to diamond transition and defects induced by electron irradiation has been discussed.

Nanoindentation revealed that carbon onions grown on the silicon substrate had higher hardness and young's modulus than the carbon film grown under similar condition, which was dominated by the nanocavities hardening effect. An analytical model was proposed based on BOLS theory. It is concluded that the under-coordinated atoms in the negatively curved surfaces of atomic vacancies, point defects, nanocavities, and the

syntactic foams are responsible for the strain hardening and thermal stability depression of the negatively curved systems, being the same by nature to those positively curved systems such as nanorods, nanograins and flat surfaces. Numerically, the negatively curved systems differ from the zero- or the positively- curved systems only by the fraction of the under-coordinated atoms and the coordination environment that determines the extent of BOLS induced property change. Therefore, all derivatives and conclusions for the flat surface and the positively curved surface apply to the negatively curved ones without needing any modifications though quantitative information is to be obtained both experimentally and theoretically. It is also concluded that the pores play dual roles in mechanical strength. The smaller pores act as pinning centers because of the strain and the surface trapping; the larger pores provide sites for initiating structure failure under indentation test.

Aligned high density multi-wall CNT forest, which exhibited durable and stable superhydrophobicity, has been grown at low temperature using water-assisted process, which means, other than high temperature, water can also increase the activity and extend the lifetime for the catalyst at low temperature. It was found that CF_4 incorporation in the plasma could further increase the contact angle of CNT forest by 5 degrees.

9.2 Recommendations for Future Research

A more mature process is required to be developed for growing the carbon onions at low temperature, which can have better control over the nanocavity size and porosity. After that systematical nanoindentation study on the carbon onions should be carried out to further verify and fine tune the analytical nanocavity hardening model.

Further characterization is needed to study the crystalline structure of diamond tip on the carbon fiber and the phase transition in between, which should be helpful for studying its growth mechanism.

Catalyst layer thickness, growth time and water vapor concentration could be varied to investigate their influences on the density and length of the aligned CNT tree grown at low temperature and the difference in its wettability.

Bibliography

1. Iijima, S., *Direct Observation of the Tetrahedral Bonding in Graphitized Carbon-Black by High-Resolution Electron-Microscopy*. Journal of Crystal Growth, 1980. **50**(3): p. 675-683.
2. Kroto, H.W., et al., *C-60 - Buckminsterfullerene*. Nature, 1985. **318**(6042): p. 162-163.
3. *Cover of Time Magazine*. January 10, 1964.
4. Ugarte, D., *Curling and Closure of Graphitic Networks under Electron-Beam Irradiation*. Nature, 1992. **359**(6397): p. 707-709.
5. Banhart, F. and P.M. Ajayan, *Carbon onions as nanoscopic pressure cells for diamond formation*. Nature, 1996. **382**(6590): p. 433-435.
6. Cabioch, T., et al., *Carbon onions formation by high-dose carbon ion implantation into copper and silver*. Surface and Coatings Technology, 2000. **128**: p. 43-50.
7. Hebard, A.F., *Superconductivity in Doped Fullerenes*. Physics Today, 1992. **45**(11): p. 26-32.
8. Banhart, F., P. Redlich, and P.M. Ajayan, *The migration of metal atoms through carbon onions*. Chemical Physics Letters, 1998. **292**(4-6): p. 554-60.
9. Golan, Y., et al., *Microtribology and direct force measurement of WS₂ nested fullerene-like nanostructures*. Advanced Materials, 1999. **11**(11): p. 934-7.
10. Venkatesan, N., et al., *Liquid filled nanoparticles as a drug delivery tool for protein therapeutics*. Biomaterials, 2005. **26**(34): p. 7154-63.

11. Davydenko, M.O., et al., *Sensibilization of fullerene C60 immobilized at silica nanoparticles for cancer photodynamic therapy*. Journal of Molecular Liquids, 2006. **127**(1-3): p. 145-147.
12. Yufeng, Z., et al., *Hydrogen storage in novel organometallic buckyballs*. Physical Review Letters, 2005. **94**(15): p. 155504-1.
13. Fucheng, L., et al., *Optical limitation and bistability in fullerene*. Journal of Applied Physics, 1993. **74**(3): p. 2140-2.
14. Jeng-Shong, S., et al. *Piezoelectric crystal membrane chemical sensors based on fullerene C60*. 2001. Basel, Switzerland: Elsevier.
15. Segura, J.L., et al., *Design, synthesis and photovoltaic properties of [60]fullerene based molecular materials*. Materials Science & Engineering C, Biomimetic and Supramolecular Systems, 2005. **25**(5-8): p. 835-42.
16. Anthopoulos, T.D., et al., *High performance n-channel organic field-effect transistors and ring oscillators based on C₆₀ fullerene films*. Applied Physics Letters, 2006. **89**(21): p. 213504-1.
17. Gharbi, N., et al., *[60]fullerene is a powerful antioxidant in vivo with no acute or subacute toxicity*. Nano Letters, 2005. **5**(12): p. 8 pp.
18. Ginzburg, B.M., et al., *Thermal degradation of fullerene-containing polymer systems and formation of tribopolymer films*. Vysokomolekularnye Soedineniya. Ser.A Ser.B Ser.C - Kratkie Soobshcheniya, 2005. **47**(2): p. 314.
19. Halford, B., *Fullerene for the face*. Chemical and Engineering News, 2006. **84**(13): p. 47.

20. Park, H., et al., *Nanomechanical oscillations in a single-C-60 transistor*. Nature, 2000. **407**(6800): p. 57-60.
21. Joachim, C., J.K. Gimzewski, and A. Aviram, *Electronics using hybrid-molecular and mono-molecular devices*. Nature, 2000. **408**(6812): p. 541-548.
22. Kratschmer, W., et al., *Solid C-60 - a New Form of Carbon*. Nature, 1990. **347**(6291): p. 354-358.
23. Ugarte, D., *High-Temperature Behavior of Fullerene Black*. Carbon, 1994. **32**(7): p. 1245-1248.
24. Kuznetsov, V.L., et al., *Onion-Like Carbon from Ultra-Disperse Diamond*. Chemical Physics Letters, 1994. **222**(4): p. 343-348.
25. Sano, N., et al., *Nanotechnology - Synthesis of carbon 'onions' in water*. Nature, 2001. **414**(6863): p. 506-507.
26. He, C.N., et al., *Low-temperature synthesis of carbon onions by chemical vapor deposition using a nickel catalyst supported on aluminum*. Scripta Materialia, 2006. **54**(4): p. 689-693.
27. Kovalevski, V.V. and A.N. Safronov, *Pyrolysis of hollow carbons on melted catalyst*. Carbon, 1998. **36**(7-8): p. 963-968.
28. Wesolowski, P., et al., *Formation of diamond in carbon onions under MeV ion irradiation*. Applied Physics Letters, 1997. **71**(14): p. 1948-50.
29. Monthieux, M. and V.L. Kuznetsov, *Who should be given the credit for the discovery of carbon nanotubes?* Carbon, 2006. **44**(9): p. 1621-1623.
30. Iijima, S., *Helical microtubules of graphitic carbon*. Nature, 1991. **354**(6348): p. 56-8.

31. Tans, S.J., A.R.M. Verschueren, and C. Dekker, *Room-temperature transistor based on a single carbon nanotube*. Nature, 1998. **393**(6680): p. 49-52.
32. Meyer, J.C., et al., *Progress in single-walled carbon nanotube based nanoelectromechanical systems*. Physica Status Solidi B, 2006. **243**(13): p. 3500-4.
33. Wang, Q.H., M. Yan, and R.P.H. Chang, *Flat panel display prototype using gated carbon nanotube field emitters*. Applied Physics Letters, 2001. **78**(9): p. 1294-6.
34. Kong, J., et al., *Nanotube molecular wires as chemical sensors*. Science, 2000. **287**(5453): p. 622-625.
35. Wei, Z., et al., *Molecular dynamics study of a low energy carbon ion moving in a single-wall carbon nanotube*. Nanotechnology, 2005. **16**(11): p. 2681-4.
36. Dillon, A.C., et al., *Storage of hydrogen in single-walled carbon nanotubes*. Nature, 1997. **386**(6623): p. 377-9.
37. Misewich, J.A., et al., *Electrically induced optical emission from a carbon nanotube FET*. Science, 2003. **300**(5620): p. 783-786.
38. Ebbesen, T.W. and P.M. Ajayan, *Large-Scale Synthesis of Carbon Nanotubes*. Nature, 1992. **358**(6383): p. 220-222.
39. Endo, M., et al., *The production and structure of pyrolytic carbon nanotubes (PCNTs)*. Journal of the Physics and Chemistry of Solids, 1993. **54**(12): p. 1841-8.
40. Guo, T., et al., *Catalytic Growth of Single-Walled Nanotubes by Laser Vaporization*. Chemical Physics Letters, 1995. **243**(1-2): p. 49-54.

41. Yasuda, A., N. Kawase, and W. Mizutani, *Carbon-nanotube formation mechanism based on in situ TEM observations*. Journal of Physical Chemistry B, 2002. **106**(51): p. 13294-8.
42. Sinnott, S.B., et al., *Model of carbon nanotube growth through chemical vapor deposition*. Chemical Physics Letters, 1999. **315**(1-2): p. 25-30.
43. Hata, K., et al., *Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes*. Science, 2004. **306**(5700): p. 1362-1364.
44. Yun, Y., et al., *Growth mechanism of long aligned multiwall carbon nanotube arrays by water-assisted chemical vapor deposition*. Journal of Physical Chemistry B, 2006. **110**(47): p. 23920-23925.
45. Futaba, D.N., et al., *84% Catalyst activity of water-assisted growth of single walled carbon nanotube forest characterization by a statistical and macroscopic approach*. Journal of Physical Chemistry B, 2006. **110**(15): p. 8035-8.
46. Futaba, D.N., et al., *Kinetics of water-assisted single-walled carbon nanotube synthesis revealed by a time-evolution analysis*. Physical Review Letters, 2005. **95**(5): p. 1-4.
47. Liu, J., X. Li, and L. Dai, *Water-assisted growth of aligned carbon nanotube-ZnO heterojunction arrays*. Advanced Materials, 2006. **18**(13): p. 1740-1744.
48. Woodward, J.T., H. Gwin, and D.K. Schwartz, *Contact angles on surfaces with mesoscopic chemical heterogeneity*. Langmuir, 2000. **16**(6): p. 2957-2961.
49. Adamson, A.W., *Physical Chemistry of Surfaces; Chapter X. Section 4*. 1990, Wiley: New York.

50. Lau, K.K.S., et al., *Superhydrophobic carbon nanotube forests*. Nano Letters, 2003. **3**(12): p. 1701-5.
51. Bico, J., C. Marzolin, and D. Quere, *Pearl drops*. Europhysics Letters, 1999. **47**(2): p. 220-226.
52. Ajayan, P.M., et al., *Carbon Nanotubes as Removable Templates for Metal-Oxide Nanocomposites and Nanostructures*. Nature, 1995. **375**(6532): p. 564-567.
53. Ebbesen, T.W., et al., *Decoration of carbon nanotubes*. Advanced Materials, 1996. **8**(2): p. 155-&.
54. Kim, P. and C.M. Lieber, *Nanotube nanotweezers*. Science, 1999. **286**(5447): p. 2148-2150.
55. Correa-Duarte, M.A., et al., *Fabrication and biocompatibility of carbon nanotube-based 3D networks as scaffolds for cell seeding and growth*. Nano Letters, 2004. **4**(11): p. 2233-2236.
56. Huan, L., Z. Jin, and J. Lei, *Wetting and anti-wetting on aligned carbon nanotube films*. Soft Matter, 2006. **2**(10): p. 811-21.
57. Kettle, C., *Introduction to Solid State Physics*. 6th ed. 1986, New York Wiley.
58. Chang, Y.A., et al., *Correlation of the Hardness and Vacancy Concentration in Feal*. Intermetallics, 1993. **1**(2): p. 107-115.
59. Yan, J.M., et al., *Crystal structure and carbon vacancy hardening of $(W_{0.5}Al_{0.5})Cl_{1-x}$ prepared by a solid-state reaction*. Chemphyschem, 2005. **6**(10): p. 2099-2103.
60. Kaplan-Ashiri, I., et al., *On the mechanical behavior of WS_2 nanotubes under axial tension and compression*. PNAS, 2006. **103**(3): p. 523-528.

61. Sammalkorpi, M., et al., *Mechanical properties of carbon nanotubes with vacancies and related defects*. Physical Review B (Condensed Matter and Materials Physics), 2004. **70**(24): p. 245416.
62. Shin, C.S., et al., *Vacancy hardening in single-crystal TiN_x (001) layers*. Journal of Applied Physics, 2003. **93**(10 1): p. 6025-6028.
63. Luk, V.K. and D.E. Amos, *Dynamic Cylindrical Cavity Expansion of Compressible Strain-Hardening Materials*. Journal of Applied Mechanics-Transactions of the Asme, 1991. **58**(2): p. 334-340.
64. Lacerda, R.G., et al., *Pressure-induced physical changes of noble gases implanted in highly stressed amorphous carbon films*. Physical Review B, 2003. **68**(5).
65. Poa, C.H., et al., *Stress-induced electron emission from nanocomposite amorphous carbon thin films*. Applied Physics Letters, 2002. **81**(5): p. 853-855.
66. Dai, C.S., et al., *Review of metal foam electrode material* Rare Metal Materials and Engineering 2004. **33**(6): p. 1-5 Suppl. 1.
67. Dunand, D.C., *Processing of titanium foams*. Advanced Engineering Materials, 2004. **6**(6): p. 369-376.
68. Korner, C. and R.F. Singer, *Processing of metal foams - Challenges and opportunities*. Advanced Engineering Materials, 2000. **2**(4): p. 159-165.
69. Hurysz, K.M., et al. *Steel and titanium hollow sphere foams*. 1998. San Francisco, CA, USA: MRS, Warrendale, PA, USA.
70. <http://en.wikipedia.org/wiki/Porosity>.
71. Hodge, A.M., et al., *Scaling equation for yield strength of nanoporous open-cell foams*. Acta Materialia, 2007. **55**(4): p. 1343-9.

72. Biener, J., et al., *Size effects on the mechanical behavior of nanoporous Au*. Nano Letters, 2006. **6**(10): p. 2379-2382.
73. Biener, J., et al., *Nanoporous Au: A high yield strength material*. Journal of Applied Physics, 2005. **97**(2).
74. Hodge, A.M., et al., *Monolithic nanocrystalline Au fabricated by the compaction of nanoscale foam*. Journal of Materials Research, 2005. **20**(3): p. 554-557.
75. Volkert, C.A., et al., *Approaching the theoretical strength in nanoporous Au*. Applied Physics Letters, 2006. **89**(6).
76. Lehmhus, D. and J. Banhart, *Properties of heat-treated aluminium foams*. Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing), 2003. **A349**(1-2): p. 98-110.
77. Kraft, O., et al., *The effect of temperature and strain rate on the hardness of Al and Al-based foams as measured by nanoindentation*. Zeitschrift fur Metallkunde, 2001. **92**(9): p. 1068-73.
78. Bai, X.-M. and M. Li, *Nucleation and melting from nanovoids*. Nano Letters, 2006. **6**(10): p. 2284-2289.
79. Biener, J., A.M. Hodge, and A.V. Hamza, *Microscopic failure behavior of nanoporous gold*. Applied Physics Letters, 2005. **87**(12): p. 121908-1.
80. Pugno, N.M. and R.S. Ruoff, *Quantized fracture mechanics*. Philosophical Magazine, 2004. **84**(27): p. 2829-45.
81. Seung-Hoon, J., et al., *Electronic mechanism of hardness enhancement in transition-metal carbonitrides*. Nature, 1999. **399**(6732): p. 132-4.

82. Sun, C.Q., *Size dependence of nanostructures: Impact of bond order deficiency*. Progress in Solid State Chemistry, 2007. **35**(1): p. 1-159.
83. L. J. Gibson, M.F.A., *Cellular Solids: Structure and Properties*. 2nd ed. 1997: Cambridge University Press: Cambridge, U.K.
84. Fu, H.H., D.J. Benson, and M.A. Meyers, *Analytical and computational description of effect of grain size on yield stress of metals*. Acta Materialia, 2001. **49**(13): p. 2567-82.
85. Wachtman, J.B., *Elastic deformation of ceramics and other refractory materials*, in *Mechanical and Thermal Properties of Ceramics*. 1969, NBS Special Publication. p. 139.
86. Mackenzie, J.K., *The elastic constants of a solid containing spherical holes*. Proceedings of the Physical Society. Section B, 1950. **63**: p. 1-11.
87. Rice, R.W., *Use of normalized porosity in models for the porosity dependence of mechanical properties*. Journal of Materials Science, 2005. **40**(4): p. 983-989.
88. Ming, Z., et al., *Atomistic origin, temperature dependence, and responsibilities of surface energetics: An extended broken-bond rule*. Physical Review B (Condensed Matter and Materials Physics), 2007. **75**(8): p. 085427.
89. Sader, J.E., *Surface stress induced deflections of cantilever plates with applications to the atomic force microscope: V-shaped plates*. Journal of Applied Physics, 2002. **91**(11): p. 9354-61.
90. Gu, M.X., et al., *Size, temperature, and bond nature dependence of elasticity and its derivatives on extensibility, Debye temperature, and heat capacity of*

- nanostructures*. Physical Review B (Condensed Matter and Materials Physics), 2007. **75**(12): p. 125403.
91. Pan, L.K., Q.S. Chang, and C.M. Li, *Estimating the extent of surface oxidation by measuring the porosity dependent dielectrics of oxygenated porous silicon*. Applied Surface Science, 2005. **240**(1-4): p. 19-23.
92. Wu, B., A. Heidelberg, and J.J. Boland, *Mechanical properties of ultrahigh-strength gold nanowires*. Nature Materials, 2005. **4**(7): p. 525-529.
93. Uchic, M.D., et al., *Sample dimensions influence strength and crystal plasticity*. Science, 2004. **305**(5686): p. 986-989.
94. Beer, T.A., et al. *Study of a pulsed DC glow-discharge used for plasma-CVD with an ultrafast videosystem and a Langmuir-probe*. 1998. Regensburg, Germany: Trans Tech Publications.
95. Wang, S.G., et al. *Electron field emission properties of nano-, submicro- and micro-diamond films*. 2002. Diepenbeek-Hassels, Belgium: Wiley-VCH Verlag.
96. Tuinstra, F. and J.L. Koenig, *Raman spectrum of graphite*. Journal of Chemical Physics, 1970. **53**(3): p. 1126-30.
97. Li, Y.J., et al., *Carbon nanotube films prepared by thermal chemical vapor deposition at low temperature for field emission applications*. Applied Physics Letters, 2001. **79**(11): p. 1670-1672.
98. Zhang, Y.B., S.P. Lau, and H.F. Li, *Field emission from nanoforest carbon nanotubes grown on cobalt-containing amorphous carbon composite films*. Journal of Applied Physics, 2007. **101**(3): p. 033524.

99. Shi, X., et al., *Properties of carbon ion deposited tetrahedral amorphous carbon films as a function of ion energy*. Journal of Applied Physics, 1996. **79**(9): p. 7234-40.
100. Kelly, P.J., et al., *Substrate effects during mid-frequency pulsed DC biasing*. Surface and Coatings Technology, 2001. **142-144**: p. 635-641.
101. Prasad, B.L.V., et al., *Heat-treatment effect on the nanosized graphite π -electron system during diamond to graphite conversion*. Physical Review B (Condensed Matter), 2000. **62**(16): p. 11209-18.
102. Roy, D., et al., *Characterisation of carbon nano-onions using Raman spectroscopy*. Chemical Physics Letters, 2003. **373**(1-2): p. 52-6.
103. Obraztsova, E.D., et al. *Raman identification of onion-like carbon*. 1998. Strasbourg, France: Elsevier.
104. Bacsá, W.S., et al., *Raman spectroscopy of closed-shell carbon particles*. Chemical Physics Letters, 1993. **211**(4-5): p. 346-52.
105. Ugarte, D., *Onion-like graphitic particles*. Carbon, 1995. **33**(7): p. 989-93.
106. He, C., et al., *Carbon nanotubes and onions from methane decomposition using Ni/Al catalysts*. Materials Chemistry and Physics, 2006. **97**(1): p. 109-115.
107. Xiao, X., et al., *Low temperature growth of ultrananocrystalline diamond*. Journal of Applied Physics, 2004. **96**(4): p. 2232-9.
108. Hiraki, A. *Low-temperature (200 degree C) growth of diamond on nano-seeded substrates*. 2000. Aix en Provence, France: Elsevier.
109. Lau, S.P., et al., *Carbon nanotubes grown on cobalt-containing amorphous carbon composite films*. Diamond and Related Materials, 2006. **15**(1): p. 171-5.

110. Schiotz, J., F.D. Di Tolla, and K.W. Jacobsen, *Softening of nanocrystalline metals at very small grain sizes*. Nature, 1998. **391**(6667): p. 561-563.
111. Sun, C.Q., S. Li, and C.M. Li, *Impact of bond order loss on surface and nanosolid mechanics*. Journal of Physical Chemistry B, 2005. **109**(1): p. 415-423.
112. Anant, M. and E. Jonah, *Size dependence of effective Young's modulus of nanoporous gold*. Applied Physics Letters, 2007. **90**(6): p. 061910.
113. Poa, C.H.P., et al., *Effects of stress on electron emission from nanostructured carbon materials*. Journal of Vacuum Science & Technology B, 2003. **21**(4): p. 1710-1714.
114. Wacławski, B.J., J.W. Gadzuk, and J.F. Herbst, *UV photoemission for rare gases implanted in Ge*. Physical Review Letters, 1978. **41**(8): p. 583-6.
115. Biswas, C., et al., *Argon nanobubbles in Al(111): A photoemission study*. Physical Review Letters, 2004. **92**(11).
116. Citrin, P.H. and D.R. Hamann, *Measurement and calculation of polarization and potential energy effects on core-electron binding energies in solids: X-ray photoemission of rare gases implanted in noble metals*. Physical Review B (Solid State), 1974. **10**(12): p. 4948-63.
117. Watson, R.E., J.F. Herbst, and J.W. Wilkins, *Core level shifts of rare-gas atoms implanted in the noble metals*. Physical Review B (Solid State), 1976. **14**(1): p. 18-25.
118. Kaindl, G., et al., *Distance-Dependent Relaxation Shifts of Photoemission and Auger Energies for Xe on Pd(001)*. Physical Review Letters, 1980. **45**(22): p. 1808-1811.

119. Lacerda, R.G., et al. *EXAFS study of noble gases implanted in highly stressed amorphous carbon films*. 2002. Nice, France: Elsevier.
120. Lynch, R.W. and H.G. Drickamer, *Effect of high pressure on the lattice parameters of diamond, graphite and hexagonal boron nitride*. Journal of Chemical Physics, 1966. **44**(1): p. 181-184.
121. Bhattacharyya, S. and S.V. Subramanyam, *Metallic conductivity of amorphous carbon films under high pressure*. Applied Physics Letters, 1997. **71**(5): p. 632-634.
122. Umemoto, K., et al., *Carbon foam: Spanning the phase space between graphite and diamond*. Physical Review B, 2001. **64**(19).
123. Chien-Te, H., et al., *Influence of fluorine/carbon atomic ratio on superhydrophobic behavior of carbon nanofiber arrays*. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures, 2006. **24**(1): p. 113-117.