Effects of Gas Composition in Producing Carbon Nanomaterials by Plasma Enhanced Chemical Vapor Deposition

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Abstract. Carbon nanomaterials are becoming new materials which can be used in many fields including transistors, sensors, displays, hydrogen storage, capacitors, catalyst supporters and so on. PECVD is an important method for producing carbon nanomaterials. However, it remains a challenge to control the final production of the PECVD process. This paper tries to figure out the gas factors influencing the growth of different carbon nanomaterials. This paper begins with a brief introduction of PECVD and the growth regime of carbon nanowalls and carbon nanotubes. It discusses how the Argon, carbon source, hydrogen and other gas affect the growth of CNMs. The paper ends with a discussion on the practical influence of confirming the function of each gas.

Keywords. PECVD, Plasma, Carbon nanomaterial, gas composition.

1. Introduction
Nowadays, carbon nanomaterials have become one of the hottest topics in the field of material. These carbon nanomaterials, including graphene, carbon nanowall(CNW), carbon nanotube(CNT) and so on, can be used in many different fields due to their properties, such as, flexible graphene transistors[1], graphene sensors, graphene displays, hydrogen storage by carbon nanotubes[2], super capacitors, catalyst supporters for fuel cells and superhydrophobic surfaces. To produce carbon materials, variety of methods have been developed, which contain liquid-phase exfoliation of graphite[3], synthesis on SiC, laser ablation technique and thermal chemical vapor deposition (T-CVD). Of all these ways for synthesizing carbon materials, T-CVD is one of the most common methods. T-CVD is first reported to be used to grow highly crystalline graphite films on Ni substrates in 1966[4]. T-CVD is popular for its easy setup in laboratories, low cost, successful use in long-term industry production. It is also the best approach for synthesizing other carbon nanomaterials. However, T-CVD requires high temperature, approximately 1000 °C, in its synthesizing progress, which makes this method improper to be applied in semiconducting industry[3]. Plasma enhances chemical vapor deposition (PECVD), It is based on CVD technique, which has become a best alternative of CVD now. The plasma bring a rich and active environment into the reaction system, including plenty of free radicals, energetic electrons, excited molecules and other active particles, which is provided by high temperature in thermal CVD. This highly active environment enables graphene growth at a much lower temperature than T-CVD and might lead to a faster growth rate [5, 6]. In this aspect, PECVD has become an important method for synthesizing different carbon nanomaterials. For example, high-quality and uniform graphene films is grown at 850°C by using RF-PECVD system, of which temperature is much lower than traditional T-
CVD even in this pioneering work[7]. And single wall carbon nanotubes can also be synthesized by PECVD. Avshish Kumar et al. successfully synthesized SWCNTs on Si substrate which had very high quality, high density and were vertically aligned[8]. Through RF-PECVD, Carbon nanowalls(also called vertically oriented graphene) with large surface area and sharp edge are synthesized[9]. Acosta Gentoiu et al. obtained carbon nanotubes (VA-CNTs), amorphous carbon nanoparticles (CNPs), and carbon nanowalls (CNWs) at different temperatures[10]. Despite using the same kind of plasma driven at radio frequency, the outcome of the process varies. According to previous research, its known to us that the gas composition including plasma sources and precursors would affect the final production of a PECVD progress

2. Gas effect in PECVD

There are various nano constructions in different carbon nanomaterials including carbon nanotubes and carbon nanowalls while most of these carbon materials are based on graphene. Carbon nanotubes (CNTs) are defined as tube shaped, hollow cylinders made of seamlessly rolled graphene sheets[11]. And carbon nanowalls (CNW) are based on 2D form graphene-like structure which are vertically oriented. Also for this reason, sometimes CNWs are also called vertical graphene(VG). This kind of nanostructure contains open boundaries, sharp edges, nonstacking morphology, large interlayer spacing, and a huge surface area.[12]

When synthesizing carbon nanomaterials with PECVD, there are huge differences in growth condition and mechanism compared to those of using thermal CVD. In the conventional thermal CVD procedure, heat provides energy to decompose hydrocarbon and other molecules, which creates active radicals. However, the PECVD reactor generates electromagnetic fields which ionizes hydrocarbon and other molecules. It also creates active radicals. [3]

To be more exactly, the mechanism of growing CNTs and CNWs by PECVD is presented below. The growth regime for CNTs and CNWs are similar to some extent. Figure 1 shows a typical environment for synthesizing CNTs[3]. The substrate with catalyst included, which usually is pure metal including nickel or copper, is placed on a holder in the reactor. Hydrocarbon gases of different partial pressures and other often used precursors are introduced into the reactor before the plasma is generated. The plasma should cover the whole substrate. When plasma is turned on, the hydrocarbon gas and precursors are ionized into highly active radicals. Meanwhile, the plasma helps increase the temperature of the catalyst surface and offers more energy for the reaction. Electromagnetic field existing in the system accelerate the ions in the system and thus these ions will bombard the surface of the substrate, which creates nucleation sites for the growth of CNTs/CNWs. By the time hydrocarbon radicals come into contact with the surface of the substrate, they begin to form bonds and help form some small nanoislands which are the bases of CNTs/CNWs. And theses nanoislands then also form dangling bonds to attach more carbon radicals to them and become the nucleation centers which are essensial for growing nanomaterials. Under proper conditions, the plasma becomes stable and the deposition of carbon nanomaterials continues and happens at every place where the plasma is existing. At the same time, in order to remove the surplus hydrocarbon molecules and radicals, vacuum pumps are necessary in the system.
Figure 1. Schematic illustration of a PECVD growth environment (with carbon sources, precursors, hydrogen plasma and various radicals) for CNTs synthesis on a catalyzed substrate

Though CNWs and CNTs share the similar growth regime, it is not unnecessary to figure out what conditions may affect the final production of the PECVD process. It is already known that the temperatures have great effect on the final production, which is showed in figure 2[10].

![Figure 1](image1.png)

**Figure 2.** In-depth distribution of hydrogen amount by ERDA measurements of the CNT, CNP, and CNW produced at different $TD$.

2.1. Ar**gon**

Ar is widely used in PECVD process because significant function in the plasma generation and the growth of CNMs.

Due to the high excitation and ionization potential, there are only a few inelastic collisions among the interaction between electrons and Ar atoms. While, the loss of energy in the inelastic collisions between Ar atoms and electrons are the main energy transfer approach among the plasma environment,
which means that the energy transfer is significantly reduced. Such effect causes the electrons energy retained that the average electron temperature increase. Consequently, Ar helps produce a plasma available for elevated energy electrons and proper level of ionization rate. This feature enhances the PECVD process and may help improve the plasma stability[5].

Besides, Ar addition helps enhance the formation of some radicals which are significant for the growth of CNWs, including C2, H and ionic clusters of carbon (CnHx+). According to preview works, it is known that a higher concentration of Ar helps increase the fraction of C2 and H atoms which benefitting the high degree of graphitization on the substrate at a relative low temperature[14, 15]. In a particular case, the CNWs grow temperature reduces from 1000 to 650°C as the Ar concentration increases from 30% to 70%[16]. Regimes of such process is presented as below[17].

\[
\begin{align*}
C_2H_2 + Ar & \rightarrow C_2 + H_2 + Ar \\
C_2H_2 + Ar_{,m} & \rightarrow C_2H_2 + Ar \\
H_2 + Ar & \rightarrow ArH_2 + H \\
H_2 + Ar & \rightarrow Ar + H_2
\end{align*}
\]

Such subsequent reaction enhances the formation of high mass clusters which are supposed to be the basic constructions for CNWs.

Also, Ar benefits for the purity of the growing gas environment as it possesses high stability and has low reaction rate[5].

When it comes to the effect of Ar to modify the final state of PECVD growth, the situation becomes much more complex. Ar+ bombardment is an important factor affecting the final production of the PECVD process. Though the basic growth for CNWs and CNTs are similar, there are some differences existing.

CNTs are catalyst needed, which means that the characteristics of the catalyst significantly affect the final properties of the CNTs[18-20]. However, CNWs are quite the opposite. They have a defect-induced self-growth mechanism. That means catalyst are not necessary in the growth of CNWs[20, 21]. So in a growth process, there are competitions for carbon source between CNTs and CNWs.

Thanks to Y Liu et.al team, some final behavior of the PECVD process are revealed through their experiment researching CNMs growth on catalyst or non-catalyst surface with different strength of Ar+ ion bombardment. On the catalyst surface, which in this case is Co, CNTs tend to grow better than CNWs. However, on the catalyst grow the small CNTs, which are too thin to suffer the Ar+ bombardment. And in the non-bombardment area, the small CNTs can grown with a high density with the help of catalyst. For the large CNTs, they can endure moderate ion bombardment as they possess thick and hard carbon nano structures. Redundant carbon layers are removed by Ar+ ion bombardment from the exterior of large catalyst particles. Thus, large CNTs with uniformness and thickness are grown on the surface with catalyst and bombardment.

However, Ar+ ion bombardment is insufficient in activating those over size Co catalyst particles. Such bombardment can only create a large number of defects on the surface of the graphite layers including the top of the large CNTs mentioned before. During the PECVD process, only a few part of the C sources are used in the formation of CNTs, and the rest of C radicals may help CNWs begin to nucleate from the large number of defects which formed by bombardment. Thus, an amount of graphene sheet grow outside the large CNTs with defects. Consequently, under a moderate bombardment condition, a nanostructure containing large CNTs and graphene sheets are obtained.

Under strong bombardment conditions, both large and small CNTs are destroyed by the bombardment, and thus the Co cannot act as catalyst in the process. It is worth mentioning that even with proper catalyst, CNTs cannot grow in the area without any bombardment. Before figuring out the explanation for such phenomenon, how the catalyst works need explanations. As we all know, the S-CNTs are grown in the modes of base-growth, and the L-CNTs are generated in tip-growth modes, which quite match the conclusion drawn by Tessonnier and Su [22]. When there is no Ar+ bombardment, which also means no carbon will be removed, large and over-large catalyst particles are
covered by these thick carbon layers and they are not able to function properly in the process of tip-growth. Thus L-CNTs are not able to grow under this condition.

As mentioned before, a higher accumulation of defects on the outside of carbon layers increases with the rise of the strength of Ar+ ion bombardment. Ar+ ion bombardment provides an efficient method of enhancing the nucleation of CNWs, and benefits for CNWs growth. The CNWs suffering strong bombardment on the catalyst surface become thicker and taller than that with restrained Ar+ ion bombardment.

Figure 3. The growth model of NCM under different Ar+ ion bombardment conditions
(a) the separation of catalyst layer and the substrate
(b) the formation of catalyst particles, the growth process of NCMs under the condition
(c)–(d) moderate bombardment
(e)–(f) strong bombardment

Base on all the results, competition does exist between the growth of CNTs and CNWs. For CNTs, the Ar+ ion bombardment can either benefits or hinders their growth. The shape, size and microstructure of CNTs depend on the specific situation of Ar+ ion bombardment. With little bombardment, it tends to form small CNTs, while in moderate bombardment condition, large CNTs with graphene sheets attached on the top tend to grow. Ar+ ion bombardment is critical in the growing process of CNWs because the growth increases as the intensity of the bombardment increases.

Therefore, it is possible to control the final production in PECVD process by only adjusting ion bombardment through plasma parameters. A subsubsection.

2.2. Precursor
Carbon source is another key factor in the PECVD process. Hydrocarbon including CH4 and C2H2 are commonly used in PECVD process. Some may also use fluorocarbon such as CF4 and CHF3. Carbon source significantly affects the final nanostructure of the CNWs. An specific example is shown as figure 4[13].
Figure 4. SEM images of VG grown for 8 hours using (a) the CH4/H2 system, (b) the CF4/H2 system, (c) the CHF3/H2 system, and (d) the C2F6/H2 system. (e) VG growth height as a function of growth time for different systems.

When growing carbon nanowalls, the CH4/H2 system and the fluorocarbon/H2 system share the similar micro structure as shown in figure 4(a)(b)(c)(d). However, there are some differences in these different environment though they share the same hydrogen environment. The interlayer space with CF4 is larger than CH4, while the growth rate of CH4 is higher than CF4. At the same time, different carbon source including C2F6 and CHF3 are also listed in the graph.

In the PECVD growth process, the existence of reactive carbon dimers (C2) plays a essential role. C2 and other CH radicals appear at areas near the substrate. They help critical nuclei transfer into CNWs as they insert into the acetylene-like C=C bond for the process of producing a carbene structure[23].

Different carbon source have different pathways to form C2 radicals. For C2H2, it produces C2 directly through dissociation because it has strong C---C bond. However, for CH4, it needs a much longer dissociation. It is easily transformed into CHx(x=1-3) radicals and then these CHx radicals produce C2 by recombination and subsequent dissociation. This explains the diamonds’ absence in the deposits when using C2H2. A higher C2 radical density benefits the organization of non-diamond carbon components which contain microcrystals of graphite, carbides and amorphous carbon[16]. What is more, the growth rate of CNWs is higher when using C2H2 than using CH4, and at the same time, the CNWs grown in C2H2 shows vertical orientation with more organization and more uniform sheet height distribution[24, 25].
2.3. Hydrogen
Hydrogen is another important gas in the PECVD process. It can be used not only in the synthesizing process but also before or after the growth as a functional gas. First, it can be used as pretreatment. The H2 plasma pretreatment plays a role of controlling the final diameter of CNTs. To be more specific, on Ni catalyst layers, different grain sizes of CNTs are obtained when using various plasma pretreating time.[26]

In the plasma environment, H2 will deposit into H+ ions. Just like the function of Ar+ ion, H2 can also be used as an etchant gas. With the bombardment of H+, amorous carbon can be removed from the substrate and catalyst surface. Zhang et al conducted the research of the synthesis of CNTs and they found that reactive hydrogen species are able to etch away deposited CNTs and thus were threatening the CNTs growth[27].

Though without H2, CH4 self can provide enough H for the graphene growth on Cu by PECVD. With a higher H2 flow rate, the graphene grows much better.[28]

2.4. Other gas
Other gas can also help or affect the growth of carbon nanomaterials in PECVD process such as oxygen and nitrogen.

Zhang et al also found that adding 1% oxygen to methane in the PECVD growth process could provide highly reproducible growth of densely packed SWCNTs[27].

N2 can perform as an efficient a-C etchant in the PECVD systems for CNWs growth. Soin et al. and Shang et al. conduct research of synthesizing CNWs by a TM-MW plasma reactor with the feedstock gas of CH4/N2 mixture. Both studies indicated that there are obvious advantages of using N2 instead of H2 in the removal of excess a-C[29, 30].

3. Conclusion
PECVD is an important method of producing carbon nanomaterials including carbon nanowalls, carbon nanotubes and graphene.

Ar+ bombardment figures prominently in selecting the terminal product of the PECVD growth. With little bombardment, it tends to form small CNTs, while in moderate bombardment condition, large CNTs with graphene sheets attached on the top tend to grow. For CNWs, Ar+ ion bombardment is an key asset and stronger Ar+ ion bombardment results in the growth of CNWs increasing. Different carbon sources lead to various speed of growth and final product with different nanostructures. These carbon sources provide C2 radicals in various paths. With a rich range of concentration of C2 radical, a higher C2 radical density benefits the growth of non-diamond carbon components. Also, carbon sources significantly affect the growth rate in PECVD process.

Hydrogen can have an effect on the size of the product and it helps increase the growth rate in some situations.

While the exact growth mechanical of these materials are not definitely clear, it is possible to base on these theories of growth and practical experiments to figure out the influence of the different gas concentrations in the PECVD process.

There are still many other kinds of gases which might be used in the PECVD process while their function in the reaction are no clear at the moment. Convincingly, the influence of each gas helps improve the technique of PECVD and provides guidance for optimum growth conditions. With more accurate control of reaction gas, the fast mass production of specific high-quality carbon nanomaterials might become possible in the future.

In the future, it is possible to control the gas proportions in order to grow one specific carbon nanomaterial with more purity and more homogeneity. And the research about adding other gases into the PECVD process may contribute to developing new techniques for producing new materials and enhance the growth rate further.

Further understanding of significant factors on growing nanomaterials is necessary for mass, fast and selected production of carbon nanomaterials.
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