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Investigating the plasma chemistry for the synthesis of carbon nanotubes/nanofibers in an inductively coupled plasma enhanced CVD system: the effect of processing parameters

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Abstract.

A parameter study is carried out for an inductively coupled plasma used for the synthesis of carbon nanotubes or carbon nanofibers (CNTs/CNFs), by means of the Hybrid Plasma Equipment Model (HPEM). The influence of processing parameters including gas ratio for four different gas mixtures typically used for CNT/CNF growth (i.e., CH₄/H₂, CH₄/NH₃, C₂H₂/H₂ and C₂H₂/NH₃), ICP power (50~1000W), operating pressure (10mTorr~1Torr), bias power (0~1000W) and temperature of the substrate (0~1000 °C) on the plasma chemistry is investigated and the optimized conditions for CNT/CNF growth are analyzed. Summarized, our calculations suggest that a lower fraction of hydrocarbon gases (CH₄ or C₂H₂, i.e., below 20%) and hence a higher fraction of etchant gases (H₂ or NH₃) in the gas mixture result in more “clean” conditions for controlled CNT/CNF growth. The same applies to a higher ICP power, a moderate ICP gas pressure above 100 mTorr (at least for SWCNTs), a high bias power (for aligned CNTs), and an intermediate substrate temperature.

1. Introduction

In the past decades, carbon nanotubes and nanofibers (CNTs/CNFs) became the subject of many investigations, encouraged by their unique electronic and mechanical properties [1]. A large number of potential applications has been considered including nanoelectronics[2], hydrogen storage[3], and field emission devices[4]. Most of these applications are, however, still under development and no significant commercial product using CNTs/CNFs can be found on the market at present[5].

CNTs/CNFs can be synthesized by several methods, such as arc discharges, laser ablation, thermal chemical vapour deposition, and plasma enhanced chemical vapour deposition (PECVD). Compared to other growth techniques, PECVD has become a very promising method because vertically aligned CNTs/CNFs can be grown at relatively low temperature. Moreover the radius and length of the CNTs/CNFs can be controlled over a wide range[6].

A variety of plasma sources have been reported in the literature for CNT/CNF growth [7-24], such as direct current (dc) glow discharges [7-10], microwave discharges (MW)[11, 12], radio-frequency capacitively coupled plasmas (RF-CCP) [13-15]and RF inductively coupled plasmas (RF-ICP)[16-24]. A wide range of operating conditions was reported for the CNT/CNF growth by PECVD. However, for a specific PECVD system, CNTs/CNFs can only be synthesized in some particular conditions. In order to investigate and optimize the suitable growth conditions, some parametric studies have been performed in the past decades.

A series of systematic studies was performed by Milne and coworkers [7-9] on the CNT growth process conditions by dc-PECVD, using a C₂H₂/NH₃ gas mixture. The growth properties (such as growth rate, diameter, length and density of the CNTs) were studied as a function of the Ni catalyst layer thickness (0.5~9 nm), bias voltage (0~-600V), deposition temperature (550~900°C), C₂H₂:NH₃ ratio (where the molar fraction of C₂H₂ varied from 20% to 75%) and pressure (0.2~10Torr)[7]. They found that the diameter and length of the CNTs exhibited a linear dependence on the Ni initial thickness, while the density of the CNTs showed a maximum at 2 nm thickness of Ni. The electric field above the substrate

determined the alignment of the CNTs. It was found that CNTs were perfectly aligned with uniform diameter and length at electric field $\approx 0.15\text{V}/\mu\text{m}$ ($\sim 600\text{V}$). They also found that the length of the CNTs increased linearly with growth time and pressure, but showed a maximum at 30% C_2H_2 in the $\text{C}_2\text{H}_2:\text{NH}_3$ gas mixture. The study of deposition temperature showed that the growth rate initially increased with the substrate temperature and then decreased at temperatures above 700°C [7]. The plasma composition under the same conditions was also analyzed by mass spectrometry [8]. H_2 , N_2 and HCN were detected as the major neutral species beside NH_3 and C_2H_2 , and the dominant ions were NH_3^+ , C_2H_2^+ , NH_2^+ , NH_4^+ , HCN^+ and C_2H^+ . A variation of the fraction of C_2H_2 in the $\text{C}_2\text{H}_2:\text{NH}_3$ plasma was performed in order to find out the reason why optimal growth occurred at around 20% C_2H_2 . Their results show that H_2 was derived from NH_3 at low C_2H_2 fraction and from C_2H_2 at high C_2H_2 fraction, which resulted in a minimum in H_2 generation at around 23% C_2H_2 . The role of NH_3 was found to suppress C_2H_2 decomposition and encourage CNT formation. C_2H_2 was found the dominant precursor for CNT formation. Finally, four key factors determining the properties of CNTs by dc-PECVD were also investigated by this group, including the presence of plasma during deposition, the ratio of feedstock gas to etchant gas, the plasma power and the strength of the electric field [9]. They found that the presence of plasma during the deposition process enabled deposition to take place at lower temperatures, facilitating the use of substrates which would otherwise be damaged. The ratio of carbon feedstock gas to etchant gas was important for controlling the shape of the deposited CNTs. It was also shown that a higher plasma power resulted in a lower growth rate, whereas a higher electric field caused a higher amount of ionization in the plasma, which resulted in a higher growth rate.

Hash developed a one-dimensional model to investigate the plasma chemistry for the growth of CNTs/CNFs by dc-PECVD [10]. The effect of dc power was studied in the paper. Their results showed that the plasma played a significant role in determining the gas-phase species impinging on the catalyst. It was demonstrated that the feedstock gases ($\text{C}_2\text{H}_2/\text{NH}_3$ in the case under study) were efficiently dissociated at higher plasma power, which resulted in a decrease of the growth precursor (C_2H_2) and hence in a decreased growth rate.

The synthesis of CNTs/CNFs by MW-PECVD has been reported by several groups [11, 12]. Matthew *et al.* [11] carried out a parametric study of the synthesis conditions for high-quality single-walled carbon nanotubes (SWCNTs) in a MW-PECVD system. A H_2/CH_4 mixture and an MgO-supported bimetallic Mo/Co catalyst were used in this study. Reaction parameters including temperature ($580\sim 823^\circ\text{C}$), $\text{H}_2:\text{CH}_4$ ratio (50:2, 50:5, 50:10 and 30:10), plasma power (130~500W), and synthesis time (1~180 min) were examined to assess their influence on the SWCNT growth. Significant differences between the temperature of the catalytic surface and the heated susceptor were observed. The optimum temperature was found as 770°C at the catalytic surface. The volumetric flow rate of hydrogen to methane was found to be optimal at a ratio of 50:10. An enhancement of the SWCNT density was observed with higher plasma power. The authors concluded that the synthesis of SWCNTs could be better controlled by these synthesis parameters in the MW-PECVD system. Wang and co-workers [12] reported a study on growing few-walled CNTs in a MW-PECVD system, where a gas mixture of $\text{C}_2\text{H}_2/\text{NH}_3$ and catalyst of polystyrene-*block*-polyferrocenylethylmethylsilane were used. The effects of growth temperature ($600\sim 885^\circ\text{C}$), growth pressure (20~30 Torr), and precursor gas ratio (15~75/150) on the growth of CNTs were investigated. The study showed that the diameter of the CNTs increased when temperature decreased. Moreover, a higher growth pressure resulted in better CNT growth. Finally, it was shown that the longest CNTs with the highest density were observed for the smallest gas ratio of $\text{C}_2\text{H}_2/\text{NH}_3$ (15/150).

Okita and co-workers performed some studies on synthesizing CNTs in an RF-CCP system. A 1D-fluid model was used to reveal the plasma chemistry behind the CNT growth [13-15], for a CH_4/H_2 gas mixture with total flux of 30 sccm, a growth pressure of 1~10 Torr, an input power of 100 W, and the substrate heated to 650°C . The amount of carbon deposited on the substrate was calculated both from experimental results and 1D-fluid simulations and reasonable agreement was reached [13]. It was suggested that the positive ions, as well as CH_3 and C_2H_5 were the main species that fulfil the role of supplying carbon to the substrate. The effect of hydrogen on the CNT formation was investigated as well as the influence of the gas mixture ratio of CH_4/H_2 [14]. An optimal gas ratio of 27/3 (CH_4/H_2) was found for obtaining thin CNTs with a high number density. It was confirmed that MWCNTs were not etched by a H_2 plasma. The pressure dependence on the CNT growth was analyzed using a 1D-fluid model in [15]. It was found that

non-radical neutrals heavier than CH_4 were greatly generated, and their fluxes tended to increase with increasing gas pressure, while the fluxes of positive ions were decreasing. These results suggested that non-radical neutrals played an important role as CNT precursors as well as the radicals.

PECVD based on ICP systems became recently more and more attractive for the synthesis of CNTs/CNFs, because of their simple geometry, the independently controlled bias power and because they are widely used in the semiconductor industry. In order to scale up the growth conditions for CNTs/CNFs in ICP-PECVD, several parametric studies have been carried out by Meyyappan and coworkers [16-18] and by Tsai and coworkers [19-22] for different types of ICP reactors. A detailed parametric study varying inductive power (0~200W), pressure (0.5~20 Torr), temperature (700~800°C), gas composition (1~20% of CH_4), catalyst thickness (1~40nm), and power to substrate (0~120W) was undertaken in [16-18] for a planar-type ICP-PECVD system, with the RF-coil situated on top of the reactor. A CH_4/H_2 gas mixture and Al/Fe catalysts were used to grow CNTs. Emission spectroscopy and a global model were applied to characterize the plasma under study. The results showed that both MWCNTs and MWCNFs were synthesized, and the power applied on the substrate seemed to play the key role in the transition from MWCNTs to MWCNFs. Indeed, MWCNTs were grown in the lower capacitive power region (0~20W), while MWCNFs were predominantly grown in the higher capacitive region (more than 50W). The study on dilution of argon indicated that the reduction of H atoms in the plasma caused the transition from MWCNF growth to MWCNT growth. The 0-D model was shown to generate global scaling laws of plasma properties with process variables, which are the main characteristics of the bulk plasma. However, CNTs/CNFs are grown in the plasma sheath on the substrate surface, where the plasma properties are different from the plasma bulk; therefore a more detailed two-dimensional model will be of interest in order to describe the plasma in a more accurate way. Wei et al. [19-21] reported a parametric study on the growth of vertically aligned CNFs by a solenoid-type ICP-PECVD system. A mixture of C_2H_2 and H_2 was used, where C_2H_2 provided the carbon source for the CNF growth, and H_2 was applied to keep the Ni catalyst active. The influence of process parameters such as ICP source power (200~1800W), growth time (3~20 min), dc bias (-100~-600V), pressure (7.9~54 mTorr), substrate temperature (400~650°C) and gas mixture ratios ($\text{H}_2:\text{C}_2\text{H}_2$ varying from 1:2 to 4:2), on the CNF formation was analyzed. The plasma composition was detected by mass spectrometry. It was shown that the CNF density decreased with ICP power, dc bias, and growth time. It was proposed that the ion-assisted etching effect by atomic hydrogen resulted in the detachment of CNFs even with low electric field in the plasma sheath.

Yang[22] studied the influence of process parameters on the synthesis of SWCNTs in an ICP-PECVD system. The gas mixture of CH_4/H_2 with two different catalysts (Fe and Ni) was tested. The operating pressure was fixed as 1Torr. He found that CNTs can grow both with Fe and Ni catalyst for the conditions under study. The substrate heating temperature affected the carbon supply to the catalyst and the diffusion of carbon on the surface and in the bulk of the catalyst. A lower substrate heating temperature was found to suppress the excess of carbon supply. It was also observed that CH_4 decomposed more easily under higher ICP power to generate unsaturated hydrocarbon radicals; the latter can more easily resolve carbon for CNT growth. Therefore the author suggested that SWCNTs would be synthesized with lower ICP power.

From the literature review above, it appears that CNTs/CNFs could be synthesized under either moderate pressure (1~10 Torr) or low pressure (10s of mTorr) in a PECVD system. Both methane (CH_4) and acetylene (C_2H_2) are popular feedstock gases for the carbon source, whereas a dilution by H_2 and NH_3 is often used to obtain hydrogen-rich plasmas, in order to produce 'clean' CNTs/CNFs. Most of the above works focus on how to grow CNTs/CNFs in low-temperature PECVD, whereas the role of the plasma and the key precursors for CNT growth still remain a bit unclear.

In order to obtain a good insight in the plasmas used for CNT/CNF growth, some modelling efforts have been attempted in the past decades, for DC discharges [10], CCP discharges [15] (see also above) and for ICP systems [23-24]. Denysenko *et al.* [23] performed detailed numerical simulations with a global model for depositing vertically aligned carbon nanostructures in an ICP-PECVD system. A gas mixture of $\text{Ar}/\text{CH}_4/\text{H}_2$ was used in their study. The densities and fluxes of radicals and charged species as well as the effective electron temperature, and methane conversion factor were calculated under various conditions. Their results showed that the deposited cation fluxes generally exceed those of the radical neutrals. The conversion rates of methane and hydrogen were found very high (~99%) in their study.

Furthermore, Ostrikov *et al.*[24] reported a two-dimensional simulation of nanoassembly precursor species in an inductive Ar/H₂/C₂H₂ plasma. The number density and fluxes of the main building blocks and surface preparation species involved in the nanoassembly of carbon-based nanopatterns were calculated in their study. They showed that the nanopattern quality might be affected by the process parameters and the non-uniformity of the surface fluxes of each particular species.

Moreover, the growth kinetics of carbon nanotubes/nanofibers in hydrocarbon plasma have been studied by Ostrikov and coworkers[25-28]. The ion-induced dissociation of hydrocarbons, the interaction of adsorbed species with incoming hydrogen atoms, and the dissociation of hydrocarbon ions were included in the model[25-27]. They found that surface diffusion of carbon adatoms produced on the catalyst particle via ion-induced dissociation of a hydrocarbon precursor plays an important role in CNF growth at low process temperatures. The catalyst size effects on the growth of SWCNT were also analyzed in [28]. The results indicated that wide-sheath plasma systems feature growth rates up to two orders of magnitude higher than in neutral systems.

Some other models for the catalytic growth of carbon nanotubes were developed by Lysaght and Chiu(for CVD) [29-30] and by Naha and Puri[31]. The latter model is more detailed and generally applicable. It consists of several mechanisms including (a) impingement of carbon atoms from the predominant carbon-containing species in the ambient, (b) their adsorption and desorption at the catalyst-gaseous hydrocarbon interface, (c) surface and bulk diffusions, (d) nucleation and (e) separation of solid undissolved carbon in nanostructured form. Their results showed that an increase in either the temperature or feedstock partial pressure leads to an increasing CNT growth rate and terminal length. However, the plasma condition for CNT/CNF growth was not included in their model.

We have applied the 2D Hybrid Plasma Equipment Model (HPEM) [32-38] to investigate the plasma chemistry for a CNT-PECVD system. An ICP reactor, more specifically, a transformer coupled plasma (TCP) reactor [16, 39] is considered.

In a previous paper[40], the effects of different gas mixtures on the plasma chemistry for CNT/CNF growth have been studied. Four kinds of feedstock gas mixtures (i. e., CH₄/H₂, CH₄/NH₃, C₂H₂/H₂, and C₂H₂/NH₃) were considered for two different pressures: 50 mTorr and 1 Torr, corresponding to the low and moderate pressure range investigated in the experiments.

In the present work, a detailed parametric study is carried out to investigate the effect of gas mixture ratios, ICP power, operating pressure, bias power and substrate heating temperature. Our aim is to find out the influence of these processing parameters on the plasma characteristics, especially near the surface of the substrate, used for the synthesis of CNTs/CNFs.

2. Description of the model

The Hybrid Plasma Equipment Model (HPEM), which has been developed at the University of Illinois by Kushner and coworkers [32-38] is used in our study. It addresses the plasma physics and chemistry in a modular way. The main modules are the Electromagnetic Module (EMM), Electron Energy Transport Module (EETM), and Fluid Kinetics Module (FKM). The EMM calculates the electromagnetic fields within a given reactor volume by solving Maxwell equations. These fields are used as inputs in the EETM, where the electron density, electron temperature, electron energy distribution function and electron impact reaction rates are computed with a Monte Carlo procedure or with the Boltzmann equation. The electron impact reaction rates are used as input in the FKM where the densities and fluxes of the various plasma species (i.e. heavy particles and electrons) are computed with continuity equations, and the electrostatic field with Poisson's equation. This electrostatic field is used as input again in the EMM, and this cycle is iterated until convergence is reached.

Four different gas mixtures, i.e., CH₄/H₂, CH₄/NH₃, C₂H₂/H₂, and C₂H₂/NH₃ are investigated. In the CH₄/H₂ plasma, 33 species (electrons, ions, radicals and background neutrals) along with 58 electron impact reactions, 115 ion-neutral reactions, and 45 neutral-neutral reactions are taken into account in our model. For the C₂H₂/H₂ plasma, 48 different species are considered, which take part in 105 reactions involving 31 electron-impact reactions, 29 neutral-neutral reactions and 45 ion-neutral reactions. When NH₃ is used as dilution gas instead of H₂, an extra number of 22 species, 43 electron-impact reactions, 48 ion-neutral reactions and 67 neutral-neutral reactions were added to the model. All details about this plasma chemistry can be found in our previous paper[40].

Finally, a sticking model, where the deposition of species at the wall is described, is applied to treat the plasma–wall interactions. The sticking coefficients assumed for the different radicals can also be found in [40]. For the ions a sticking coefficient of 1 is assumed, because they will be neutralized. For the molecules, a sticking coefficient of 0 is used, as they are considered to be reflected at the walls.

It should be realized that this model does not yet provide a full description of the CNT growth, because it is limited to the plasma chemistry and does not include the actual growth processes of the CNT. Carbon drains to the CNT surface and generation of hydrogen and other fragments and their backflow are not considered. Only sticking coefficients of the various plasma species at the surface are taken into account. This might influence the plasma chemistry calculations to some extent. On the other hand, the plasma volume is much larger than the substrate surface, so that the effect on the overall plasma chemical composition is probably not so big. In a future work, we would like to include the effect of the surface processes to our plasma chemistry model, to obtain a more complete description of the PE-CVD growth process of CNTs.”

3. Results and discussion

3.1. Operating conditions

The standard calculations were performed for a gas mixture of CH_4/H_2 at a pressure of 50 mTorr, in a gas ratio of 20% CH_4 and 80% H_2 . Other operating conditions are: 100 sccm total gas flow rate, 300 W source power, 30W bias power at the substrate electrode and an operating frequency of 13.56 MHz applied to the coil and to the substrate electrode. The substrate is heated to 550 °C. These are typical

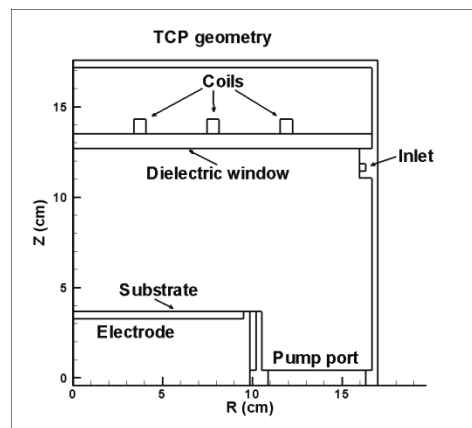


Figure 1: Two-dimensional TCP reactor geometry used in the model. The reactor is cylindrically symmetric, so only one half plane of the reactor is shown.

operating conditions for CNT growth under low pressures, as was illustrated in the introduction.

The parameter study focused on the effect of gas mixture ratios, ICP power, operating pressure, bias power and substrate heating temperature, on the plasma chemistry used for CNT/CNF growth. It should be noted that when one parameter is changed, the others are kept as the standard condition.

The reactor geometry under study is a TCP reactor, which is often used for CNT growth [11, 16, 39]. It is schematically illustrated in Figure 1.

3.2. Effect of gas mixture ratios

For this study, four different gas mixtures, i.e. CH_4/H_2 , CH_4/NH_3 , $\text{C}_2\text{H}_2/\text{H}_2$ and $\text{C}_2\text{H}_2/\text{NH}_3$, are taken into account, where CH_4 and C_2H_2 are the deposition gases and H_2 and NH_3 are the etchant gases. The fraction of deposition gas (CH_4 or C_2H_2) in the gas mixture is varied from 0 to 100. As it was discussed in the literature [5, 17], the carbon sources for CNT/CNF growth are determined by the species impinging on the substrate and the decomposition activity on the catalyst surface. Therefore the fluxes of different species arriving at the substrate surface were calculated at the different ratios of gas mixtures under study.

a. Methane-hydrogen plasma (CH₄/H₂)

The calculated fluxes of the various neutrals and ions bombarding the substrate in the CH₄/H₂ mixture, averaged over the radial position on the substrate, are plotted as a function of CH₄ gas fraction in figure 2. It is clear from figure 2(a) that C₂H₂, C₂H₄ and C₂H₆ are the dominant molecules regardless of the gas mixture ratios, besides the feedstock gases CH₄ and H₂. The fluxes of these molecules first increase quickly before the fraction of CH₄ reaches 20%, and then, more slightly when the fraction of CH₄ is further enhanced. The primary radicals are H and CH₃ at all mixture ratios. The H flux decreases gradually as the H₂ gas fraction decreases, while the CH₃ flux shows the same trend as the background gas CH₄. It is also clear that the fluxes of C and C₂ are the lowest of all radicals. These observations confirm that the carbon source for CNT/CNF growth mainly arises from the decomposition of hydrocarbon molecules on the surface of the catalyst[41].

Of course, this conclusion is only made based on the fluxes of the plasma species to the substrate, and does not take into account the surface processes, i.e., the reaction rate coefficients at the surface. Indeed, it could be that the small flux of C₂ is compensated by higher reaction rates at the surface. As mentioned above, we plan to include these processes in our future work.

It is observed from figure 2(b) that most ion fluxes show a rapid decrease as the CH₄ fraction increases except for C₂H_x⁺ (x=2, 3, 4, 5, 6). The C₂H₂⁺ and C₂H₃⁺ fluxes show a local maximum at 10% CH₄ gas fraction, while C₂H_x⁺ (x=4, 5, 6) rise with increasing CH₄ concentration. It is worth noting that the total ion flux decreases only slightly as a function of the CH₄ fraction in the gas mixture. Moreover, because the fluxes of the heavy ions, i.e. C₂H_x⁺ (x=2~6), rise upon increase of the CH₄ fraction, this may result in enhancement of physical sputtering and hence cause damage of the CNTs/CNFs.

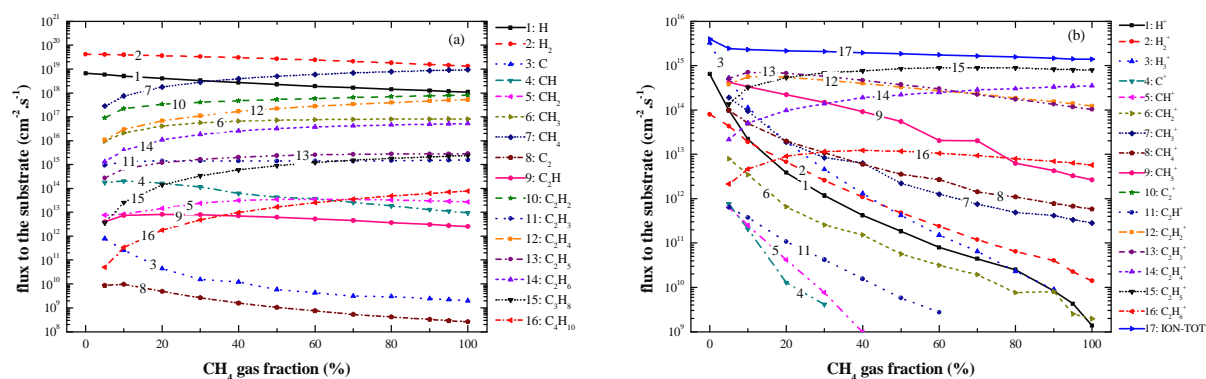


Figure 2 Calculated radially-averaged fluxes of (a) neutrals and (b) ions bombarding the substrate as a function of CH₄ fraction in a CH₄/ H₂ gas mixture at a pressure of 50 mTorr. The operating conditions are: 100 sccm total gas flow rate, 300W source power, 30W bias power at the substrate and 13.56 MHz operating frequency at the coil and at the substrate electrode. The substrate is heated to 550 °C.

It was reported that the unsaturated hydrocarbons such as C₂H₂ and C₂H₄, have a higher reactivity than CH₄ on the transition metal clusters[41]. Moreover C₂H₂ and C₂H₄ decompose more easily at the catalyst surface than CH₄ at lower temperature[41]. Furthermore, C₂H₂ [42]and C₂H₄ [43] have been reported as key precursors for the efficient growth of SWCNTs by CVD. Bell *et al.*[8] also confirmed that C₂H₂ was the dominant precursor for CNT formation in a C₂H₂/NH₃ plasma. Therefore it is well possible that C₂H₂ and C₂H₄ are the major precursors for CNT/CNF growth in the CH₄/H₂ plasma. The large amount of atomic hydrogen, on the other hand, plays a key role in the dehydrogenation of the adsorbed hydrocarbons, enhancing the surface diffusion of carbon, and etching amorphous carbon[41]. Finally, the CH₃ radicals are probably responsible for the amorphous carbon fraction in the CNTs[13].

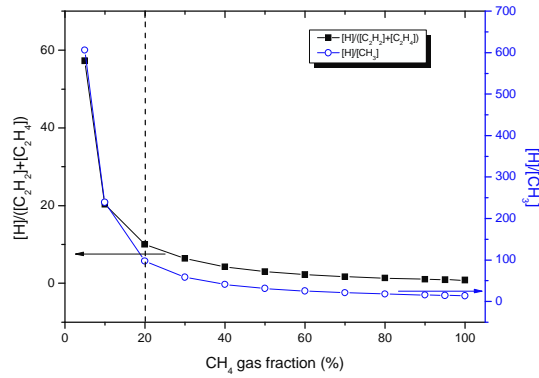


Figure 3 Ratio of etchant (H) to the most probable carbon source for CNTs ($C_2H_2 + C_2H_4$) (left axis) and to the most probable carbon source for an amorphous film (CH_3) (right axis) as a function of CH_4 gas fraction at the same operating conditions as in figure 2.

Therefore, the ratio of H fluxes (representing etchants) to the fluxes of $C_2H_2 + C_2H_4$ (representing the carbon supply for CNTs/CNFs) as well as the ratio of H fluxes to CH_3 fluxes (as a source for amorphous carbon) are plotted in figure 3, as a function of CH_4 gas fraction. Both ratios drop rapidly at a small fraction of CH_4 , until about 20% of CH_4 , and then they further decrease slightly at high CH_4 concentrations. In the left region to the dashed line, the fluxes of atomic hydrogen by far exceed the fluxes of the carbon source both for CNTs/CNFs as well as for an amorphous film. We expect that this will lead to “clean” conditions for CNT/CNF growth, as the amorphous phase, which might be present in the growing tube, will be etched away by the H-flux and moreover, the carbon supply for CNT/CNF growth is also well controlled. In [11] it was also concluded, albeit for a MW-PECVD system, that an optimal ratio of H_2/CH_4 was obtained at 50:10, hence corresponding to less than 20% CH_4 in the gas mixture.

b. Methane-ammonia plasma (CH_4/NH_3)

When NH_3 is applied as the dilution gas instead of H_2 , some new species appear in the plasma as was mentioned in section 2 (see [40] for all details). For the sake of clarity, we define the same species both in the CH_4/H_2 plasma and in the CH_4/NH_3 plasma as “original species”. The new species are called “extra species”. The fluxes of the original species exhibit the same trends as in the CH_4/H_2 plasma; therefore they are not shown here again. The fluxes of the new species are displayed in figure 4 for the neutrals (a) and the ions (b).

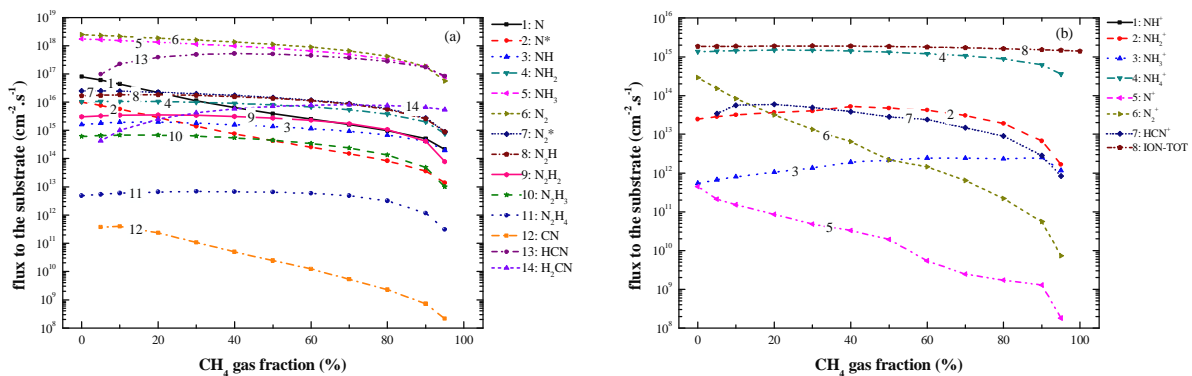


Figure 4 Calculated radially-averaged fluxes of (a) extra neutrals and (b) extra ions bombarding the substrate as a function of CH_4 fraction for a CH_4/NH_3 gas mixture. The other operating conditions are the same as in figure 2.

We found that H_2 is again the most dominant species, in spite of the fact that it is now not one of the feedstock gases, and it drops slightly at high fraction of CH_4 . Apart from the hydrocarbons C_2H_2 , C_2H_4 and C_2H_6 , now also N_2 and HCN become predominant molecules beside the feedstock gases CH_4 and NH_3 . With respect to the radicals, atomic hydrogen (H) is again the most important species followed by CH_3 , N, N_2H , and NH_2 . It is interesting that H and H_2 follow the same trend as NH_3 , i.e., they drop when

the gas fraction of CH_4 increases. This indicates that H and H_2 are mainly generated by decomposition of NH_3 at the conditions under study. Also a lot of HCN is observed in our results, which first increases and then drops as a function of CH_4 fraction. We also found that HCN is mainly formed in the bulk plasma region, which is consistent with Hash's results[44].

It is shown in figure 4(b), that the total ion flux again remains almost constant as a function of CH_4 fraction. However, NH_4^+ now become the predominant ion when NH_3 is used as the additive. It is apparent that NH_4^+ , NH_3^+ , and NH_2^+ do not drop significantly, and even rise (in the case of NH_3^+) upon increase of CH_4 , or decrease of the NH_3 fraction. This indicates that NH_3 is more efficiently ionized at lower NH_3 fraction. The decomposition rates (DR) of the feedstock gas molecules as a function of CH_4 gas fraction in both CH_4/H_2 and CH_4/NH_3 are depicted in figure 5. Note that a DR of 1 indicates 100% decomposition.

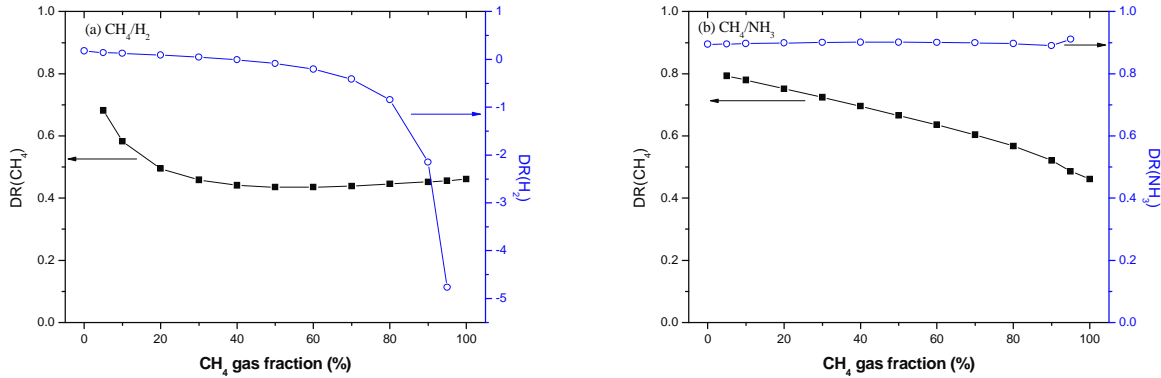


Figure 5 Decomposition rates (DR) of the background gas molecules, calculated for (a) CH_4/H_2 and (b) CH_4/NH_3 gas mixtures. The other operating conditions are the same as in figure 2. The negative values mean that more background gas species are formed instead of decomposed.

It is clear that CH_4 has a higher DR at small fraction of CH_4 in both gas mixtures, but it exhibits a different behavior upon increase of the CH_4 gas fraction for the two different dilution gases. When a small amount of H_2 is mixed into the CH_4 (corresponding to a high CH_4 gas fraction), the DR of CH_4 decreases slightly from 0.46 at 100% CH_4 to 0.43 at 50% CH_4 . For a lower fraction of CH_4 , and hence a higher fraction of H_2 , the DR of CH_4 is dramatically improved up to about 0.7 at 5% CH_4 . On the other hand, in the CH_4/NH_3 plasma, a linear increase is found for the DR of CH_4 with decreasing CH_4 gas fraction, from 0.46 at 100% CH_4 to about 0.8 at 5% CH_4 . In general, a high DR of CH_4 in the plasma at low CH_4 fraction in the gas mixture points again towards favorable conditions for CNT/CNF growth, as it is stated in literature [41] that CH_4 cannot decompose easily on the catalyst surface, in contrast to higher hydrocarbons.

The H_2 feedstock gas hardly decomposes in the CH_4/H_2 discharge, and even much more H_2 molecules are formed under CH_4 -rich conditions rather than decomposed. In contrast to the H_2 gas, NH_3 shows a very high and fairly constant DR of around 0.9, for all gas mixture ratios. This high DR of NH_3 has also been reported in the literature[10].

c. Acetylene-hydrogen plasma ($\text{C}_2\text{H}_2/\text{H}_2$)

In the $\text{C}_2\text{H}_2/\text{H}_2$ plasma, C_{2n}H_2 ($n=2, 3$), C_6H_4 and C_{2n}H_6 ($n=4, 5, 6$) become important molecules besides the background gases C_2H_2 and H_2 , as can be observed from figure 6 (a). The fluxes of C_{2n}H_2 ($n=2, 3$) follow the same increasing trend as C_2H_2 upon increasing C_2H_2 gas fraction, while the C_6H_4 and C_{2n}H_6 ($n=4, 5, 6$) fluxes are clearly less dependent on the C_2H_2 gas fraction. This can be explained because the C_{2n}H_2 molecules are mainly formed by C_2H insertion into $\text{C}_{2n-2}\text{H}_2$ ($n=2, 3$), which results in similar trends of the C_{2n}H_2 ($n=1, 2, 3$) fluxes. However, the C_6H_4 and C_{2n}H_6 ($n=4, 5, 6$) species are formed by neutralization of the corresponding ions on the wall, and they stay in the reactor much longer due to their heavy mass.

The primary radicals (see figure 6 (b)) are H and C_{2n}H_3 ($n=1, 2, 3$). The H flux drops linearly upon increase of the C_2H_2 fraction (and hence decrease of the H_2 fraction), while the fluxes of C_{2n}H_3 ($n=1, 2, 3$) species rise gradually with the C_2H_2 fraction and reach a maximum at around 40% C_2H_2 . When the C_2H_2 fraction further increases, the fluxes of C_{2n}H_3 ($n=1, 2, 3$) species begin to drop. This is because the

$C_{2n}H_3$ ($n=1, 2, 3$) radicals are mainly formed by H insertion into $C_{2n}H_2$ ($n=1, 2, 3$), and the significant decrease of the H radicals with increasing C_2H_2 fraction should be responsible for this.

From figure 6(c), it is clear that the total ion flux shows a steady downward trend with increase of C_2H_2 gas fraction. Indeed, a large number of heavy ions such as $C_{2n}H_6^+$ ($n=4, 5, 6$) are formed in the C_2H_2 plasma, which become predominant with increase of the C_2H_2 fraction. The lower mobility of these heavy ions compared to light ions results in the decrease of total ion flux bombarding the substrate. Similar to the CH_4/H_2 discharge, the lighter ions such as H^+ , H_2^+ , $C_2H_2^+$ and $C_2H_3^+$ are predominant under H_2 -rich conditions, while the heavier ions (i.e., $C_{10}H_6^+$ and $C_{12}H_6^+$) turn to be important under C_2H_2 -rich conditions. It is worth noting that a large flux of $C_4H_3^+$ (see figure 6(d)) was observed for all conditions. Therefore this ion is suggested to play an important role in the growth of CNTs/CNFs, for the conditions under study.

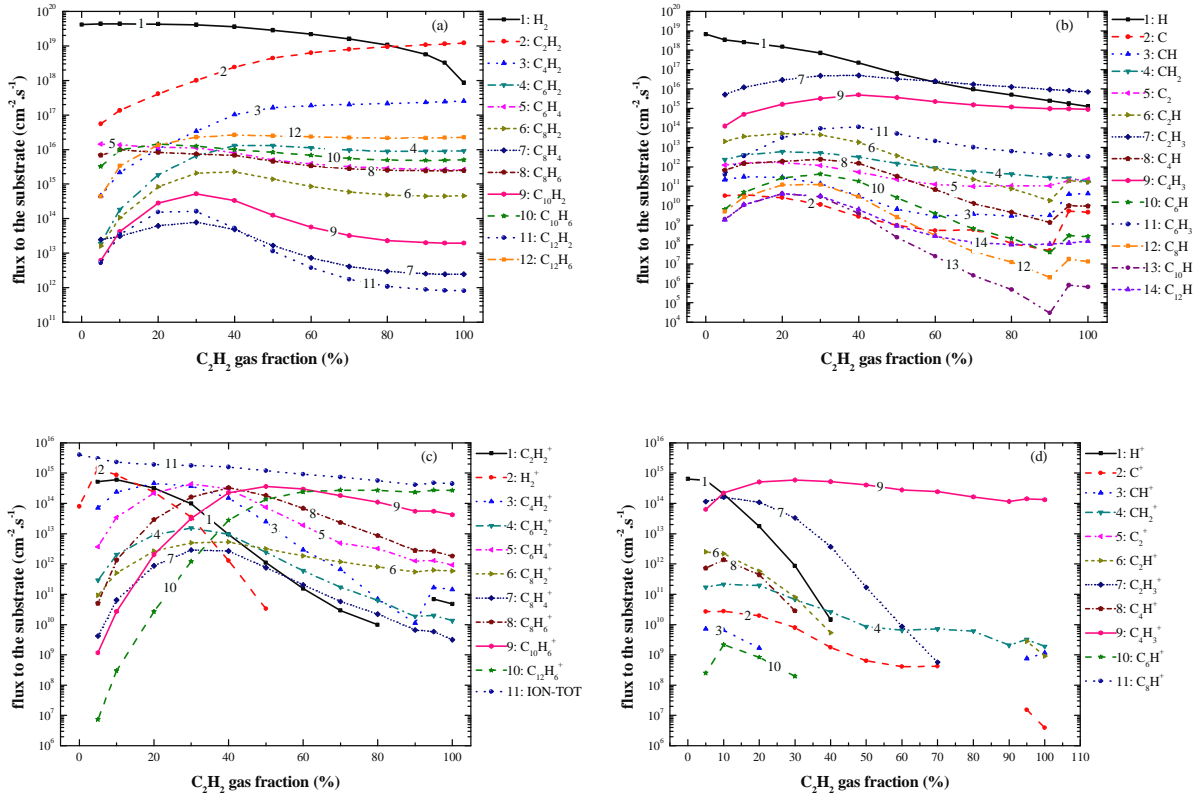


Figure 6 Calculated radially-averaged fluxes of (a, b) neutrals and (c, d) ions bombarding the substrate as a function of C_2H_2 gas fraction for a C_2H_2/H_2 gas mixture. The other operating conditions are the same as in figure 2.

It is stated that hydrocarbon ions play a key role in the formation of amorphous carbon films[45]. At conditions with low C_2H_2 fraction, most hydrocarbon ions show a relatively low flux as is clear from figure 6 (c, d), which would efficiently suppress the amorphous carbon growth. This could explain why “clean” CNTs/CNFs are typically grown under H_2 -rich conditions[8, 20]. Indeed, it was observed that the CNF growth rate decreased while the amorphous carbon film deposition increased with rising C_2H_2 fraction, both in a C_2H_2/H_2 mixture[20] and in a C_2H_2/NH_3 mixture[8].

d. Acetylene-ammonia plasma (C_2H_2/NH_3)

When NH_3 is used as the dilution gas (see figure 7), N_2 , N_2H_2 and NH_4^+ are found to be dominant neutrals and ions, respectively, similar to the CH_4/NH_3 plasma. Similar observations were made in [8]. The species N_2H and NH_2 become very important (see figure 7 (a)). However, unlike in the CH_4/NH_3 plasma, the flux of HCN is not significant at all. This is because HCN is generated from the reaction between CH_x ($x=2, 3, 4$) and N atoms, and the lower density of CH_x ($x=2, 3, 4$) in the C_2H_2 plasma leads to a lower formation of HCN. It was reported[46] that the presence of N_2 can enhance carbon diffusion into the catalysts. Indeed, the bombardment energy of ions in a nitrogen plasma is greater than

in a hydrogen plasma, which can keep the front catalyst surface clean and actively prolong surface passivation to enhance carbon bulk diffusion[46]. Our results show that the N_2 flux is predominant beside the NH_3 flux, especially for a low C_2H_2 fraction (less than 20%). Hence, this might explain why in many papers [7-9, 12] the C_2H_2/NH_3 mixture is used for CNT/CNF growth rather than the C_2H_2/H_2 plasma.

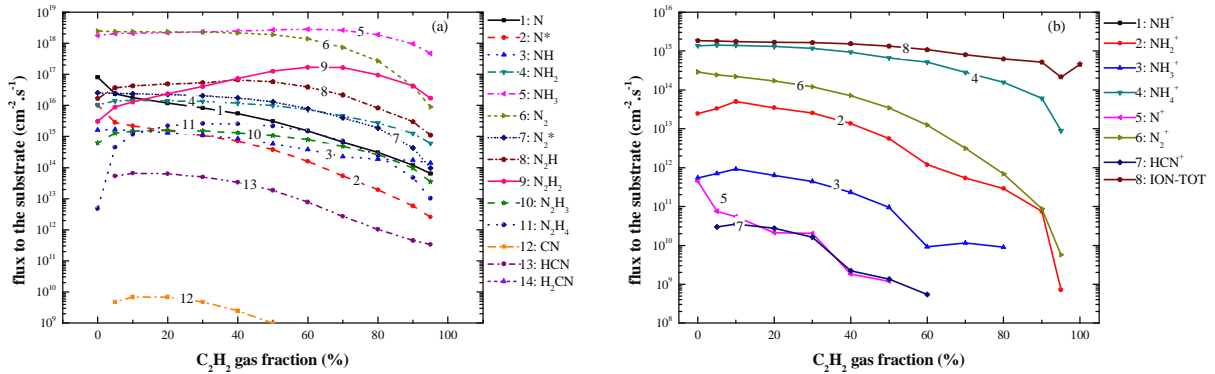


Figure 7 Calculated radially-averaged fluxes of (a) extra neutrals and (b) extra ions bombarding the substrate as a function of C_2H_2 gas fraction for a C_2H_2/NH_3 gas mixture. The other operating conditions are the same as in figure 2.

The DRs of the background gas molecules in the C_2H_2 -containing plasmas are displayed in figure 8 (a) for the C_2H_2/H_2 plasma and in figure 8(b) for the C_2H_2/NH_3 plasma. It is clear that C_2H_2 has a quite high DR (more than 0.75) when the gas fraction of C_2H_2 in the mixture is less than 30%. Such high DR of C_2H_2 leads to the reduction of C_2H_2 in the bulk plasma, and hence lowers the C_2H_2 flux arriving at the substrate. This might result in a relatively low growth rate of CNTs/CNFs, which was indeed observed in [7, 21], because the C_2H_2 species are believed to be the main precursors for CNT/CNF formation in a PECVD system [8, 47]. When the gas fraction of C_2H_2 is in the range of 30% to 70%, a rapid drop is observed for the DR of C_2H_2 (from 0.75 to around 0.2). In this region, the carbon supply for CNT/CNF growth rapidly becomes greater for two reasons: (i) the percentage of C_2H_2 in the mixture increases and (ii) the DR of C_2H_2 decreases. When the gas fraction of C_2H_2 is further increased, the C_2H_2 gas molecules are hardly decomposed in the plasma.

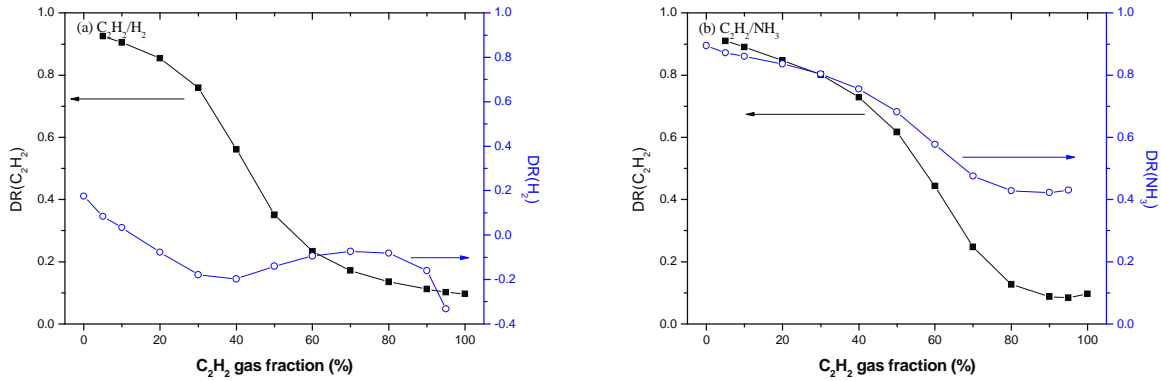


Figure 8 Decomposition rates (DR) of the background gas molecules, calculated for (a) C_2H_2/H_2 and (b) C_2H_2/NH_3 gas mixtures. The other operating conditions are the same as in figure 2. The negative values mean that more background gas species are formed instead of decomposed.

It is also observed that H_2 shows a very low DR at high fraction of H_2 in the mixture (see figure 8(a)). Furthermore, negative values of the DR are observed at C_2H_2 -rich conditions. Different from the H_2 gas additive, the DR of NH_3 shows a similar trend as the C_2H_2 DR. Indeed, the DR of NH_3 decreases with increasing C_2H_2 gas fraction, which leads to a decline of the atomic hydrogen at high fraction of C_2H_2 . Moreover, the excess of heavy hydrocarbon ions is also found in this region. Therefore, we expect that an amorphous carbon film will be formed, which cannot easily be etched away because of the low amount of etching H atoms, and this will suppress the growth of CNTs/CNFs. Indeed, most experiments in the literature were performed at C_2H_2 fraction below 20% [7, 12]. The influence of the $C_2H_2:NH_3$ ratio on the structure of CNTs synthesized by dc-PECVD has been reported by Chowalla et al. [7]. They found that

CNTs could be formed for C_2H_2 fraction from 5% to 30%. Above 30% C_2H_2 , the CNTs became obelisk-like and then turned to a tip structure with even higher C_2H_2 fraction. Also in [12] for a MW-PECVD system, the longest CNTs with the highest density were obtained for the smallest C_2H_2/NH_3 gas ratio (15/150), corresponding to around 10% of C_2H_2 .

In the following sections, the effects of ICP power, operating pressure, bias power and substrate heating temperature on the plasma chemistry for CNT/CNF growth will be analyzed, considering only the CH_4/H_2 gas mixture.

3.3. Effect of ICP power

The fluxes of species on the substrate as a function of ICP power are plotted in figure 9(a) for the neutrals and in figure 9(b) for the ions. A higher ICP power will give rise to increased dissociation and ionization of the molecules, which results in a decreasing flux of the molecules (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , and C_4H_{10}), and an increase in the fluxes of lighter radicals (H , CH , C , and C_2) and ions. Consequently the drop of C_2H_2 and CH_3 will result in a reduction of carbon supply for the growth of CNTs/CNFs, on the one hand, and amorphous carbon film, on the other hand. In addition, the increase of H radicals will enhance the removal of amorphous carbon film.

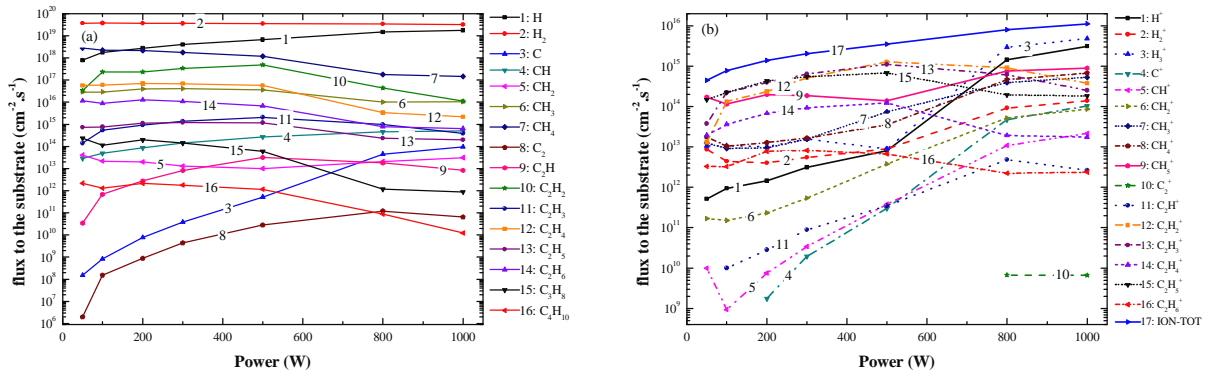


Figure 9 Calculated radially-averaged fluxes of (a) neutrals and (b) ions bombarding the substrate as a function of ICP power for a CH_4/H_2 gas mixture at a pressure of 50 mTorr with gas ratio of 20:80. The other operating conditions are the same as in figure 2.

It is indeed observed from figure 10 that the ratio of etchant (H) to depositing carbon sources both for CNTs ($C_2H_2 + C_2H_4$) and for an amorphous carbon film (CH_3) increases drastically when the ICP power is enhanced from 500W to 1000W. This indicates that the etching effect by atomic hydrogen is significant in the high ICP power region. Therefore, this suggests that a relatively “clean” condition for the formation of CNTs/CNFs could be achieved at higher ICP power, which is indeed reported by Lin *et al.* [20]. Indeed, they found that more amorphous carbon film was deposited on the surface of the CNFs and the substrate for 250W ICP power than in the 750W case [20].

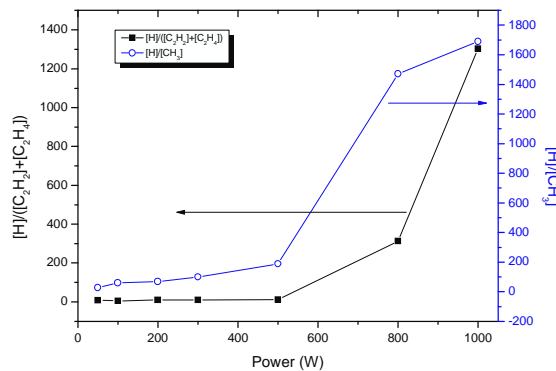


Figure 10 Ratio of etchant (H) to the carbon source for CNTs ($C_2H_2 + C_2H_4$) and for an amorphous carbon film (CH_3) as a function of ICP power for the CH_4/H_2 mixture at the same operating conditions as in figure 9.

The influence of ICP power on the DR of the background gas molecules is displayed in figure 11. Both DRs rise nearly linearly with ICP power for the reason explained above. The DR of CH₄ is around 0.2 at 50W and increases to almost 0.96 at 1000W. Again, this suggests that a higher ICP power is beneficial for CNT/CNF growth, as the CH₄ molecules do not efficiently decompose at the catalyst surface; therefore the decomposition needs to take place already in the plasma. The DR of H₂ is only 0.05 at 50W and increases to 0.22 at 1000W. Although the DR of H₂ becomes higher at 1000W, almost no change was observed for the flux of H₂ on the substrate, because the loss of H₂ caused by decomposition is compensated by new H₂ created by decomposition of CH₄.

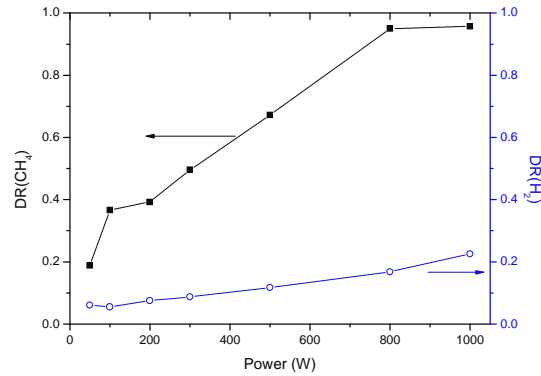


Figure 11 Decomposition rates (DR) of the background gas molecules, calculated for the CH₄/H₂ gas mixture as a function of the ICP power. The other operating conditions are the same as in figure 9.

3.4. Effect of gas pressure

The fluxes of the different neutral species to the substrate as a function of pressure are plotted in figure 12. It is found that the feedstock gases H₂ and CH₄ increase with pressure as expected, while the radicals C, CH, CH₂, C₂, C₂H and C₂H₃ decrease at higher pressure. The other neutrals remain virtually unchanged. As was illustrated in [40], most of the ion fluxes drop at increasing pressure; hence the total ion flux also shows a decreasing trend as a function of pressure. This is because the electrons lose their energy faster at higher pressure, which leads to a decrease of ionization, and hence results in a drop of the ion fluxes with increasing pressure.

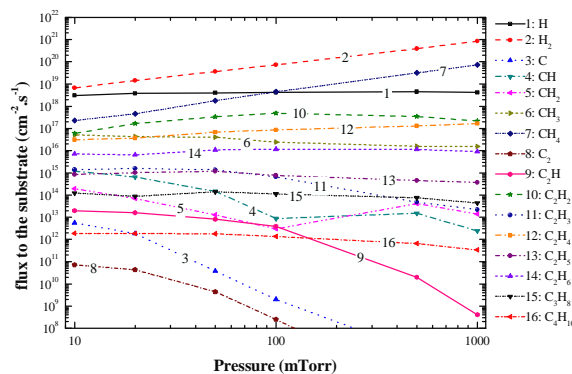


Figure 12 Calculated radially-averaged fluxes of the various neutrals bombarding the substrate as a function of gas pressure for a CH₄/H₂ gas mixture with gas ratio of 20:80. The other operating conditions are the same as in figure 2.

The ratios of etching species (H) to the carbon source for CNTs (C₂H₂ + C₂H₄) and to the carbon source for an amorphous carbon film (CH₃) are plotted in figure 13. It is clear that a larger ratio of H flux to CH₃ flux is found at high pressure, while the ratio of H flux to C₂H₂ and C₂H₄ drops dramatically first and then levels off at 100 mTorr. This indicates that CNTs/CNFs could be synthesized with less amorphous carbon pollution at higher pressure. In addition, the lower DR of CH₄ at higher pressure, as illustrated in figure 14, implies that the carbon supply for CNTs/CNFs could be limited at higher pressure. This could explain why SWCNTs are always synthesized at higher pressures (i.e., in the order of 1 Torr) by an ICP-PECVD system, as reported in[22], where the carbon source for growth can be well controlled.

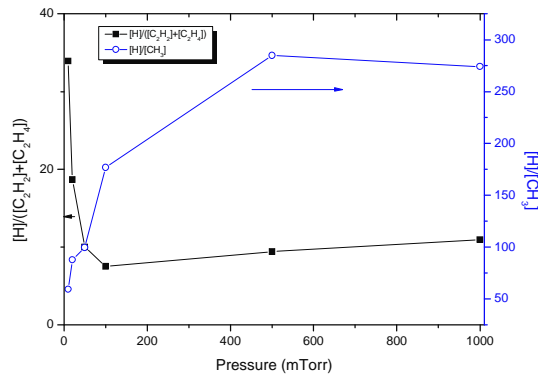


Figure 13 Ratio of etchant species (H) to the carbon source for CNTs ($C_2H_2 + C_2H_4$) and to the carbon source for an amorphous film (CH_3) as a function of gas pressure at the same operating conditions as in figure 12.

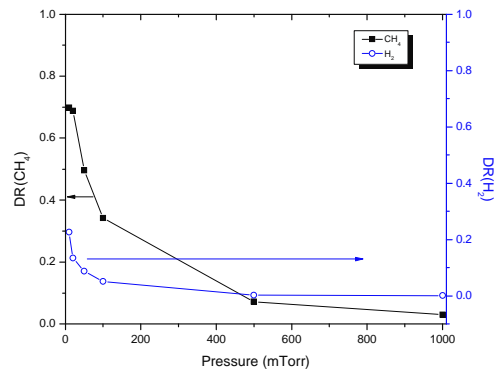


Figure 14 Decomposition rates (DR) of the background gas molecules, calculated for the CH_4/H_2 gas mixtures as a function of gas pressure. The other operating conditions are the same as in figure 12.

3.5. Effect of bias power

In the ICP, the power is mainly deposited in the region below the quartz windows, and it decomposes the feedstock gases to create a large number of radicals and ions. Therefore the fluxes of the various species to the substrate are mainly determined by the ICP power, gas pressure, and gas mixture ratios. The bias power is often applied on the substrate in order to grow aligned CNTs/CNTs [7, 16, 44, 48]. Indeed, it was found that local electric fields are built up near the substrate surface, and control the growth direction of CNTs/CNFs [7, 16, 44, 48]. Therefore, it is of interest to look in more detail at the DC bias voltage formed in front of the substrate, as well as to the sheath electric field which arises from this DC bias voltage.

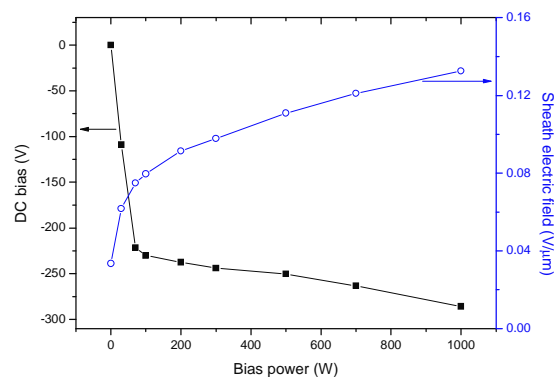


Figure 15 Variation of DC bias (left axis) and sheath electric field (right axis) on the substrate vs. bias power, for a CH_4/H_2 gas mixture at a pressure of 50 mTorr with a gas ratio of 20:80. The other operating conditions are the same as in figure 2.

The DC bias voltage and sheath electric field in front of the substrate surface are plotted as a function of bias power in figure 15. The bias voltage sharply decreases from 0 to -230V when the bias power changes from 0 to 100W. When the power is further increased to 1000W, the change in DC bias voltage is only 56V (i.e., until -286V at 1000W). These calculated results are consistent with the observations reported by Lin *et al.*[20]. Indeed, they found that the RF peak voltage changed from around 300 Vrms to 450 Vrms (corresponding to a bias voltage changing from -212V to -318V) when the bias power increased from 300W to 500W.

The increase of DC bias voltage as a function of bias power indicates that more energetic ions will bombard the substrate with high bias power. The bombardment of more energetic ions will probably result in a higher surface temperature and hence lead to a higher CNT/CNF growth rate. In addition, the high-energy ions will promote the ion-enhanced etching of amorphous carbon by atomic hydrogen to improve the surface diffusion of carbon on the catalytic nanoparticles. Indeed, Lin *et al.*[20] reported that the growth rate of CNFs increased significantly with the bias power.

The sheath electric field in front of the substrate changes from 0.034V/ μm without any bias power to 0.133 V/ μm at a bias power of 1000W in our simulation. In [21] it was reported that the sheath electric field is in the range of $\sim 0.01\text{-}0.06$ V/ μm in an ICP-PECVD system at low pressure of 17~50 mTorr. Somewhat higher values of $\sim 0.1\text{-}0.15$ V/ μm are reported by Chhowalla[7] and Bower and Zhu[49] for pressures in the order of Torr. These values are consistent with our results, which suggest that the conditions in our study are indeed suitable for CNT/CNF growth. Moreover, the higher electric field in the plasma sheath at higher bias power will probably result in better aligned CNTs/CNFs.

3.6. Effect of substrate temperature

It is well known that CNTs/CNFs are typically grown at some elevated temperature of the substrate containing the metal catalysts, in the order of 550°C-800°C [5, 11, 17]. Therefore, we want to investigate the effects of the elevated substrate temperature on the plasma chemistry and plasma behavior.

In order to calculate the gas temperature distribution, the full momentum equation plus energy equation for all heavy species (neutrals and ions) have been taken into account. The free convection term has been included in the momentum equation, and the inhomogeneous gas density distribution is also taken into account. More details can be found in the review paper of Kushner [38].

As shown in our previous paper[38], the substrate temperature plays a key role in the gas temperature distribution at lower pressures (50 mTorr). The calculated 2D profiles of the gas temperature at a substrate temperature of (a) 0 °C and (b) 550 °C are illustrated in figure 16. Note that the reactor walls are kept fixed at a temperature of 324 K (i.e., 51 °C). This value is defined based on typical values used in the semiconductor industry. It is clear that the plasma for the conditions under study is not efficiently heated without substrate heating, because the gas temperature is only about 34 K higher in the bulk plasma compared to the walls (see figure 16(a)). However, when the substrate is heated to 823 K (i.e. 550 °C), the heat transfer towards the bulk plasma is clearly displayed in figure 16(b). The gas temperature gradually changes from 823 K at the substrate to about 600 K in the bulk plasma, and reaches 324 K at the walls.

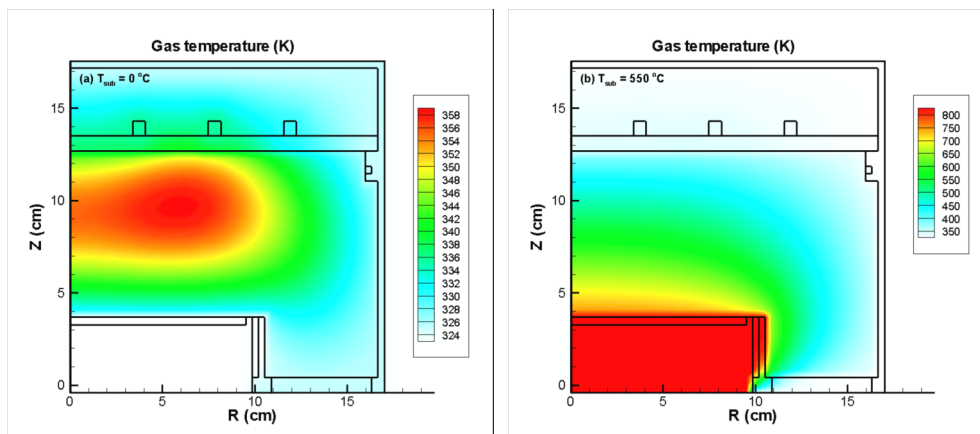


Figure 16 Calculated 2D gas temperature profiles for a CH_4/H_2 gas mixture at a pressure of 50 mTorr with a gas ratio of 20:80. The other operating conditions are the same as in figure 2. The substrate is heated to (a) 0 °C and (b) 550 °C.

The distribution of gas temperature influences the plasma chemistry in two aspects: First, the reaction rate constants for neutral reactions are often temperature-dependent (see tables in [40]). When the substrate is heated to 823 K or more, a large temperature difference (several hundred K) can be found in the plasma bulk, which will lead to 1-2 orders of magnitude difference in the rate constants. Second, the gradient of gas temperature will push the species to the low-temperature region in order to keep a constant pressure (cf. ideal gas law). Although the first effect will enhance the rate constants for neutral reactions, the lower density of neutrals in the higher temperature region due to the second effect will result in only a slight change in the plasma chemistry.

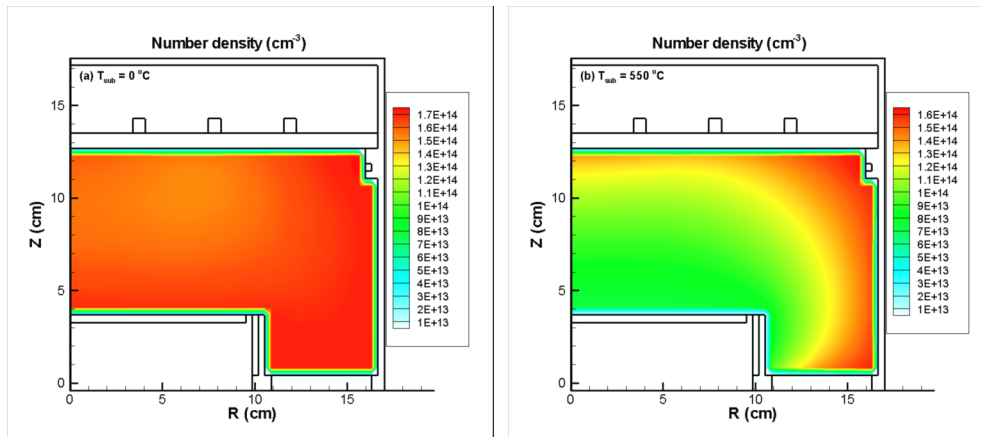


Figure 17 Calculated 2D number density profiles of CH_4 at the same conditions as in figure 16.

The calculated 2D number density profiles of CH_4 for the substrate temperatures of 0 °C (a) and 550 °C (b) are shown in figure 17. As expected from above, a relatively uniform distribution of the CH_4 density is observed when the substrate is not heated. On the other hand, when the substrate is heated to 823K, the CH_4 density shows a distribution opposite to the corresponding gas temperature, i.e., the CH_4 density exhibits relatively low values in the high temperature region. This indicates that the gradient of gas temperature indeed plays a key role in the species distribution when the substrate is heated, at least for low gas pressure.

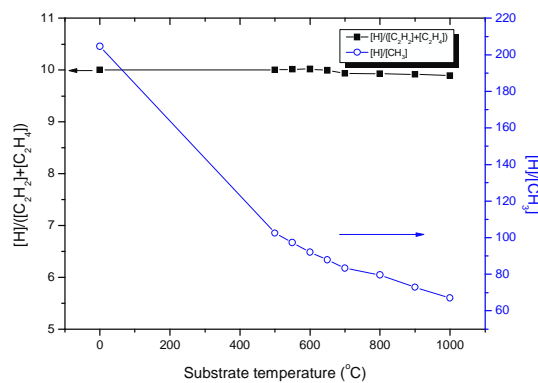


Figure 18 Ratio of etching species (H) to the carbon source for CNTs ($\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$) and to the carbon source for an amorphous film (CH_3) as a function of substrate temperature at the same operating conditions as in figure 2.

The ratio of etching species (H) to carbon sources for CNTs ($\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$) and for an amorphous carbon film (CH_3) are plotted in figure 18, as a function of substrate temperature. It is clear that the ratio of H flux to CH_3 flux decreases from 200 for a substrate temperature of 0°C, to 100 at 550°C, and further to 60 at 1000°C, while the ratio of H flux to C_2H_2 and C_2H_4 flux remains almost unchanged. This indicates that an amorphous carbon film could be removed more efficiently at a lower substrate temperature. On the other hand, a higher substrate temperature will result in a higher temperature on the catalytic surface,

which will enhance the carbon diffusion into the particles and increase the surface reaction rate constants, thereby increasing the growth rate of CNTs/CNFs[50]. Moreover, the DR of the feedstock molecules, CH₄ and H₂, increase with substrate temperature, as is shown in figure 19. Without substrate heating, the H₂ is not decomposed (i.e. a negative value of -0.18 is calculated for the DR, which indicates that there are more H₂ molecules formed than decomposed), but the DR increases to 0.2 (i.e. 20%) for a substrate temperature of 1000 °C. The DR of CH₄ increases almost 2 times (from 0.3 to 0.56) when the substrate is heated to 1000 °C, thereby forming other hydrocarbon species, which can react more easily at the catalyst surface, and contribute to CNT/CNF growth. Hence, due to these opposite effects, most probably there will be an intermediate temperature range, which is most suitable for CNT/CNF growth. It is indeed reported in literature [7, 11, 12, 16, 19] that a temperature range of 550~900°C, is most suitable.

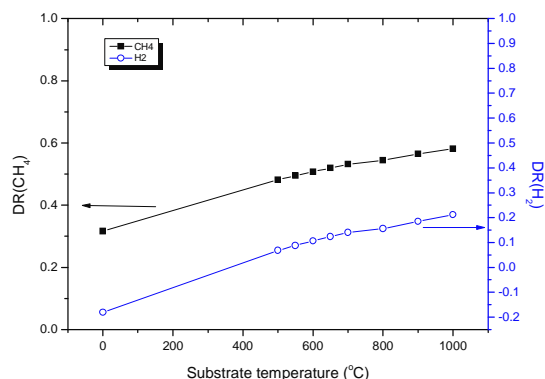


Figure 19 Decomposition rates (DR) of the background gas molecules as a function of substrate temperature for the same conditions as in figure 2.

4. Conclusions

An ICP reactor operating under conditions typically used for CNT/CNF growth was investigated by means of hybrid plasma simulations. The influence of processing parameters including gas mixture ratios for four different gas mixtures (i.e., CH₄/H₂, CH₄/NH₃, C₂H₂/H₂ and C₂H₂/NH₃), ICP power, gas pressure, bias power, and substrate temperature on the plasma chemistry is investigated. The fluxes of the various plasma species bombarding the substrate, as well as the decomposition rates (DR) of the feedstock gas molecules, are calculated and analyzed for a large range of process parameters. Furthermore, the ratio of etching species (H) to the carbon source both for CNT/CNF growth (C₂H₂ + C₂H₄) and for amorphous carbon film deposition (CH₃) is investigated in the same parameter range, because this can give more insight in the conditions for “clean” CNT growth.

In general, it was observed that the fluxes of C and C₂ to the substrate were the lowest of all radicals, which confirms that the carbon source for CNT/CNF growth mainly arises from the decomposition of hydrocarbon molecules on the surface of the catalyst[41].

With respect to the gas mixture ratios, in the CH₄/H₂ mixture, a low CH₄ fraction (below 20%) resulted in a high ratio of etching species (H) to growth precursors for CNTs/CNFs (C₂H₂ + C₂H₄) as well as for an amorphous phase (CH₃). This is expected to result in “clean” conditions for CNT/CNF growth, as the amorphous phase, which might be present in the growing tube, will be etched away by the H-flux and moreover, the carbon supply for CNT/CNF growth is also well controlled. Moreover, the DR of CH₄ in the plasma was found to be the highest for a low CH₄ fraction, both in the CH₄/H₂ and CH₄/NH₃ gas mixture, which also points out towards favorable conditions for CNT/CNF growth, as it is generally accepted that CH₄ cannot easily decompose at the catalyst surface, in contrast to higher hydrocarbons[41].

Similar results were also obtained for the C₂H₂-containing gas mixtures. The DR of C₂H₂ turns out to drop significantly upon increasing C₂H₂ fraction, suggesting a lower CNT/CNF growth rate, because C₂H₂ is considered as the main growth precursor. Moreover, the DR of NH₃ also drops significantly with increasing C₂H₂ fraction, thereby reducing the supply of etching H species to the growing CNTs. Finally, at higher C₂H₂ fraction, there is an excess of heavy hydrocarbon ions, which typically give rise to an amorphous carbon film. Hence, these calculation results lead us to conclude that an amorphous carbon film

will be formed at higher C_2H_2 fraction, which cannot easily be etched away because of the low amount of etching H atoms, and this will suppress the growth of CNTs/CNFs.

Therefore, in general it can be concluded that a lower fraction of carbon-supplying gases (CH_4 and C_2H_2) compared to etching gases (H_2 and NH_3) will lead to more “clean” CNT/CNF growth conditions, which is in agreement with literature observations[7, 8, 11, 16, 18, 47].

A higher ICP power will increase the dissociation and ionization of molecules, which results in lower fluxes of the molecules (CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , and C_4H_{10}), and an increase of the lighter radicals (H, CH, C, and C_2) and ions. The reduction of CH_3 and increase of H radicals at higher ICP power indicates that a relatively “clean” condition for the formation of CNTs/CNFs could be achieved with higher ICP power.

With respect to the gas pressure, the low ratio of H flux to fluxes of $C_2H_2 + C_2H_4$ and the high ratio of H flux to CH_3 flux at pressures above 100 mTorr, in combination with the reduced DR of CH_4 indicates that SWCNTs could be synthesized at moderate pressure of around 1 Torr, where the carbon supply for CNTs/CNFs could be well controlled in the CH_4/H_2 plasma. This is indeed reported in literature[20].

The DC bias voltage and sheath electric field are calculated for different values of the bias power, and our results are consistent with experimental observations, which indicate that aligned CNTs/CNFs could be grown at the conditions under study. The increase of DC bias voltage with rising bias power indicates that more energetic ions will bombard the substrate, which might result in a higher surface temperature, and consequently in a higher CNT/CNF growth rate. In addition, the high-energy ions will promote the ion-enhanced etching of amorphous carbon film by atomic hydrogen to improve the surface diffusion of carbon on the catalytic nanoparticles. Indeed, Lin et al.[20] reported that the growth rate of CNFs increased significantly with the bias power.

Finally, we investigate the effect of the substrate temperature on the plasma behavior, as CNTs/CNFs are typically grown at elevated substrate temperature [5, 11, 17]. It is found that the substrate temperature influences the distribution of gas temperature, and further affects the profiles of neutral species in the plasma bulk. Indeed, the large gradient of gas temperature drives the species to the low temperature region, which leads to a lower density of species in the region above the substrate where a high gas temperature exists. At higher substrate temperature, the ratio of etching species (H) to the carbon source for an amorphous carbon film (CH_3) drops, leading to less favorable conditions for clean CNT growth. On the other hand, the surface reaction rates, as well as the DR of CH_4 , increase with substrate temperature, giving rise to species which can more easily react at the catalyst surface. These two opposite effects will result in an optimum temperature window for CNT/CNF growth, which is indeed reported in literature [7, 11, 12, 16, 19] (i.e., in the range of 550~900°C).

In summary, we conclude that a lower fraction of hydrocarbon gases (CH_4 or C_2H_2 , i.e., below 20%) and hence a higher fraction of etchant gases (H_2 or NH_3) in the gas mixture result in more “clean” conditions for controlled CNT/CNF growth. The same applies to a higher ICP power, a moderate gas pressure above 100 mTorr (at least for SWCNTs), a high bias power (for aligned CNTs), and an intermediate substrate temperature.

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