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Plasma chemistry modeling for an inductively coupled plasma used for the growth of carbon nanotubes

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Abstract

A hybrid model, called the hybrid plasma equipment model (HPEM), is used to describe the plasma chemistry in an inductively coupled plasma, operating in a gas mixture of C_2H_2 with either H_2 or NH_3, as typically used for carbon nanotube (CNT) growth. Two-dimensional profiles of power density, electron temperature and density, gas temperature, and densities of some plasma species are plotted and analyzed. Besides, the fluxes of the various plasma species towards the substrate (where the CNTs can be grown), as well as the decomposition rates of the feedstock gases (C_2H_2, NH_3 and H_2), are calculated as a function of the C_2H_2 fraction in both gas mixtures.

1. Introduction

Carbon nanotubes (CNTs) are gaining increasing interest, due to their unique physical, chemical and electronic properties, giving rise to a variety of (potential) applications, including nanoelectronics, hydrogen storage and field emission devices [1-3]. CNTs can be produced by arc discharges [4], laser ablation [5], chemical vapor deposition (CVD) [6], as well as by plasma enhanced CVD (PE-CVD) [7-25], which appears to be a very promising technology for the synthesis of vertically aligned CNTs, of interest for field emission devices [7]. Several plasma sources have been applied already for the growth of CNTs, including direct current (dc) glow discharges [8-12], capacitively coupled (cc) radiofrequency (rf) discharges [13-15], inductively coupled plasmas (ICPs) [16-22] and microwave (MW) discharges [23-25]. The feedstock gases most often used are CH_4 or C_2H_2, mixed with either H_2 or NH_3 as so-called etchant gases, i.e., to produce "clean" CNTs, with a limited fraction of amorphous phases.

In this paper, we present results of plasma chemistry modeling performed for an ICP, operating in a mixture of C_2H_2 with either H_2 or NH_3, in order to investigate the role of the various plasma species created in these gas mixtures, for the CNT growth. The effect of the C_2H_2 fraction in both gas mixtures will be analyzed, and the influence of the two different etchant gases (H_2 or NH_3) will be compared.

2. Model description

The model used in this work is the so-called hybrid plasma equipment model, developed by Kushner and coworkers [26]. It consists of three main modules, i.e., (i) an electromagnetics module, which calculates the electric and magnetic fields in the reactor, (ii) an electron energy transport module, which simulates the behavior of the (fast) electrons by a Monte Carlo procedure or the Boltzmann equation, and (iii) a fluid kinetics simulation, which treats the other plasma species by conservation equations. A full explanation about this hybrid model can be found in [26].

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The focus of the present calculations is on the plasma chemistry. Therefore, a large number of different plasma species have to be taken into account, including electrons, various ions, molecules and radicals, which can react with each other in various collision processes. The plasma species and their reactions considered in the model depend on the gas mixture under study. In [27] we have investigated the detailed plasma chemistry in CH_4/H_2, CH_4/NH_3, C_2H_2/H_2 and C_2H_2/NH_3 gas mixtures. The different species taken into account in the model, as well as their reactions, were tabulated in detail [27].

Table 1: Overview of the species taken into account in the C_2H_2/H_2 model

Molecules	Radicals	Ions	Electrons
H_2	H	H^+, H_2^+	e^-
C_2H_2	C_2H, C_2H_3, C_2, CH_2, CH, C	$C_2H_2^+$, C_2H^+, $C_2H_3^+$, C_2^+, CH_2^+, CH^+, C^+	
C_4H_2	C_4H, C_4H_3	$C_4H_2^+$, C_4H^+, $C_4H_3^+$	
C_6H_2, C_6H_4	C_6H, C_6H_3	$C_6H_2^+$, C_6H^+, $C_6H_4^+$	
C_8H_2, C_8H_4, C_8H_6	C_8H	$C_8H_2^+$, C_8H^+, $C_8H_4^+$, $C_8H_6^+$	
$C_{10}H_2$, $C_{10}H_6$	$C_{10}H$	$C_{10}H_6^+$	
$C_{12}H_2$, $C_{12}H_6$	$C_{12}H$	$C_{12}H_6^+$	

In the present paper, we focus only on the gas mixture of C_2H_2 with either H_2 or NH_3. Table 1 summarizes the plasma species included for the C_2H_2/H_2 chemistry, whereas Table 2 presents the extra species added when NH_3 is used as the dilution gas. In the C_2H_2/H_2 plasma, 31 electron impact reactions, 45 ion-neutral and 29 neutral-neutral reactions are taken into account, whereas an extra number of 43 electron impact reactions, 48 ion-neutral and 67 neutral-neutral reactions were added to the model when NH_3 is used as the dilution gas. All details about this plasma chemistry can be found in [27].

Table 2: Overview of the extra species taken into account when NH_3 is used as the dilution gas

Molecules	Radicals	Ions
NH_3	NH, NH_2	NH^+, NH_2^+, NH_3^+, NH_4^+
N_2, N_2H_2, N_2H_4	N, N*, N_2*, N_2H, N_2H_3	N_2^+, N^+
HCN	CN, H_2CN	HCN^+

3. Results and discussion

First some general calculation results will be presented for the C_2H_2/H_2 gas mixture, at a ratio of 20/80, a total gas pressure of 50 mTorr, and 100 sccm total gas flow rate. The other operating conditions are 300 W source power, 30 W bias power at the substrate electrode, both applied at an operating frequency of 13.56 MHz. The substrate is heated to 823 K. Next, the effect of the C_2H_2/H_2 gas ratio will be investigated and a comparison will be made with the C_2H_2/NH_3 gas mixture.

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3.1. General calculation results for the C_2H_2/H_2 gas mixture

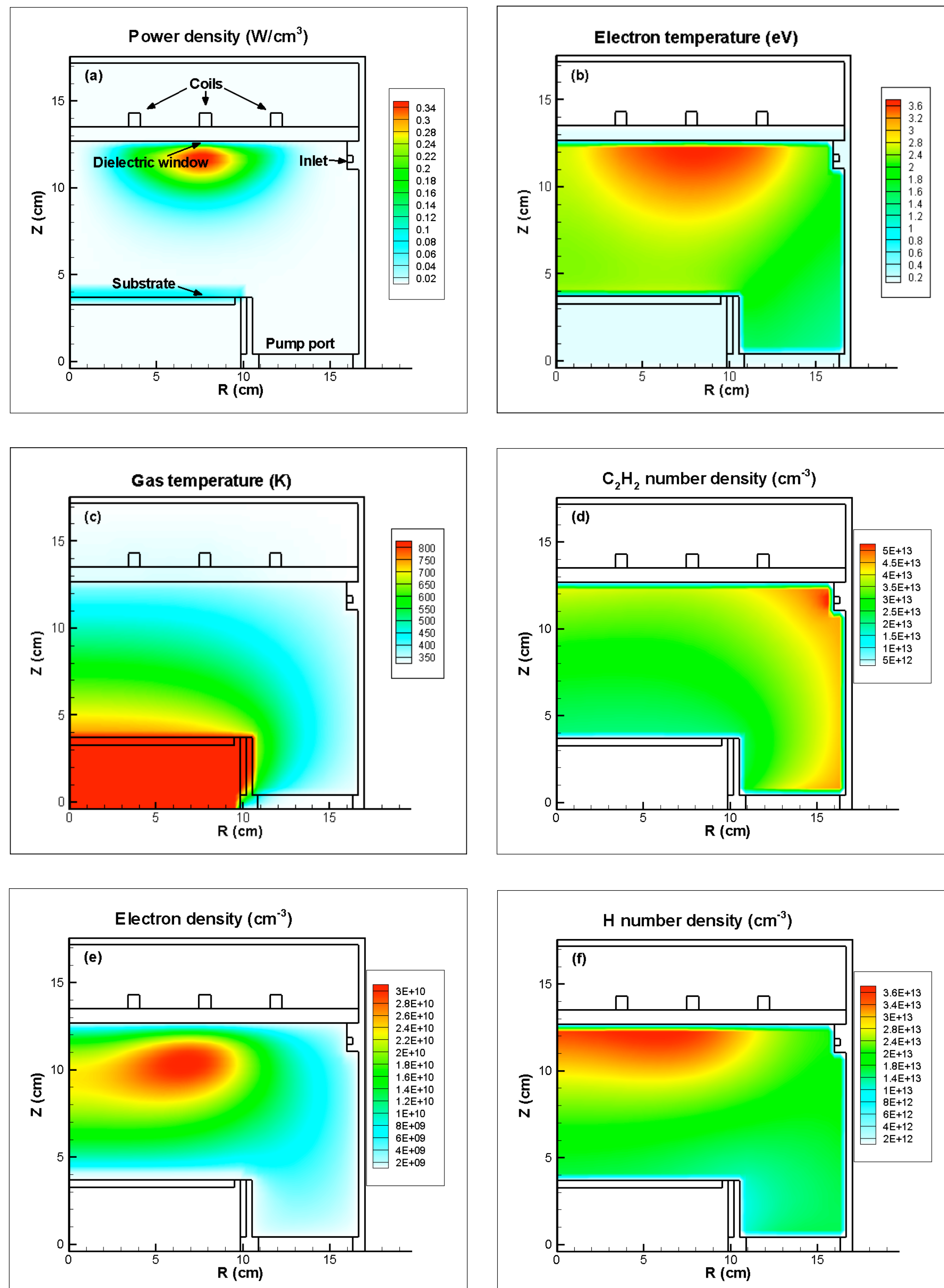

Figure 1: Calculated 2D profiles of (a) the power density, (b) the electron temperature, (c) the gas temperature, (d) the C_2H_2 gas density, (e) the electron density, and (f) the H atom density, in the C_2H_2 gas mixture at a ratio of 20/80, a total gas pressure of 50 mTorr, and a total gas flow rate of 100 sccm. The power applied at the coil and at the substrate is 300 W and 30 W, respectively, both with a frequency of 13.56 MHz. The substrate is heated to 823 K. Only one half plane of the cylindrically symmetrical reactor is shown. The coils, dielectric window, gas inlet, substrate and pump port are indicated in figure (a).

Figure 1 presents calculated 2D profiles of the power density (a), electron temperature (b), gas temperature (c), C_2H_2 gas density (d), electron density (e) and H density (f), in the ICP reactor under study. It is a transformer coupled plasma (TCP) reactor, with a flat coil at the top, which has been applied also experimentally for the growth of CNTs [16,18]. The reactor is cylindrically symmetric, so only one half plane of the reactor is shown. The coil, dielectric window, gas inlet, substrate and pump port are indicated in figure 1(a).

The power density (figure 1(a)) is at maximum just beneath the coil (i.e., the inductive region), and a second maximum is seen in front of the substrate electrode (i.e., the capacitive region). This is logical because the coil power is 300 W, whereas the power applied at the substrate electrode is only 30 W. As a result of this power input, the electrons in the plasma are heated to temperatures of a few eV, as is seen in figure 1(b). Again, the maximum is found beneath the coil. The gas temperature, on the other hand, is at maximum near the substrate, see figure 1(c). Indeed, the substrate is heated to 823 K to enable growth of CNTs [19-22], and the heat is spread out into the plasma. Without substrate heating, the gas would also heat to some extent, but only to about 350 K, as was demonstrated in [28]. Hence, the electron temperature is much higher than the gas temperature, as is typical for a non-LTE plasma.

As a result of this gas temperature profile, the C_2H_2 gas density reaches a minimum in front of the substrate, following the ideal gas law, as is shown in figure 1(d). Further, it is at maximum at the gas inlet, and drops to some extent in the reactor, as it disappears due to ionization and dissociation reactions. The electron density (figure 1(e)) reaches a maximum under the coil, similar to the electron temperature. This means that most of the electron impact reactions (ionization, excitation, dissociation,…) will take place in this region, and that most of the reactive species (i.e., ions, excited species, radicals) will also reach a maximum in this region. This is illustrated in figure 1(f) for the H atom density, but most of the other reactive plasma species indeed exhibit the same profile. The importance of the various reactive species will be discussed in the next section.

3.2. *Effect of the C_2H_2/H_2 gas ratio*

The carbon source for CNT growth is defined by the species impinging on the substrate and the decomposition activity on the catalyst surface. Therefore, the fluxes of the various plasma species arriving at the substrate surface are plotted in figure 2, as a function of the C_2H_2 fraction in the gas mixture. It is clear from figure 2(a) that H_2 is the dominant species at low C_2H_2 fraction, whereas C_2H_2 becomes more important at high C_2H_2 fraction. However, the turnover point is not seen at 50% C_2H_2, but at 80% C_2H_2, which indicates that H_2 is also formed to a large extent out of C_2H_2. Besides these two background gases, H atoms are also formed in large amounts, due to various reactions, such as dissociation and ionization of C_2H_2 and H_2, as is obvious from figure 2(b).

Other important neutral species bombarding the substrate, are $C_{2n}H_2$ (n=2, 3), C_6H_4 and $C_{2n}H_6$ (n=4, 5, 6) (see figure 2(a)), as well as the radicals $C_{2n}H_3$ (n=1, 2, 3) (see figure 2(b)).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 less dependent on the C_2H_2 gas fraction. Indeed, the $C_{2n}H_2$ are mainly formed by C_2H insertion into $C_{2n-2}H_2$, which results in similar trends of the $C_{2n}H_2$ fluxes, whereas the

C_6H_4 and $C_{2n}H_6$ species are formed by neutralization of the corresponding ions on the wall. The H atom flux drops significantly with rising C_2H_2 fraction (and hence decreasing H_2 fraction), whereas the $C_{2n}H_3$ fluxes reach a maximum at about 40% C_2H_2. Indeed, these radicals are mainly produced by H insertion into $C_{2n}H_2$, and the decreasing trend of the H flux upon increasing C_2H_2 fraction, in combination with the increasing trend for the $C_{2n}H_2$ flux, results in a maximum at an intermediate C_2H_2 fraction of 40%.

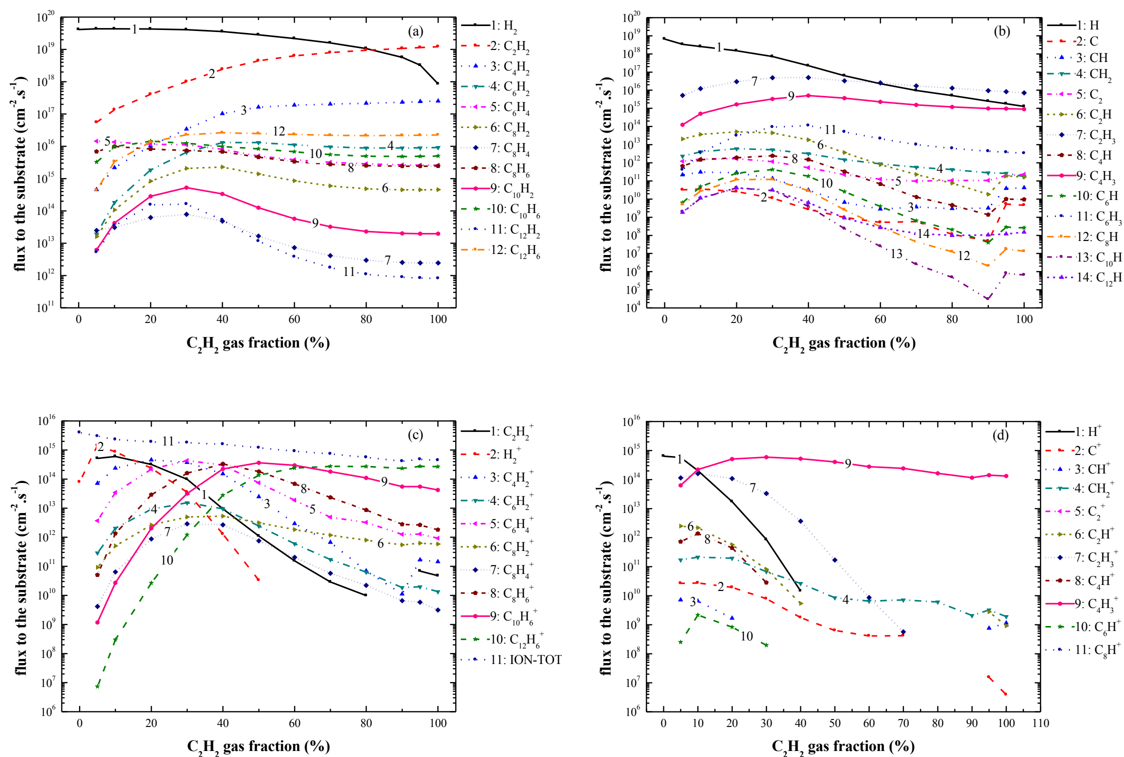

Figure 2: Calculated radially-averaged fluxes of the various molecules (a), radicals (b) and ions (c,d) bombarding the substrate, as a function of the C_2H_2 gas fraction, for the C_2H_2/H_2 gas mixture. The other operating conditions are the same as in figure 1.

With respect to the ions, it is clear from figure 2(c,d) that the lighter ions, such as H^+, H_2^+, $C_2H_2^+$ and $C_2H_3^+$, are predominant under H_2-rich conditions, whereas the heavier ions, such as $C_{10}H_6^+$ and $C_{12}H_6^+$, turn to be important under C_2H_2–rich conditions. $C_4H_3^+$ is characterized by a high flux for all gas fractions (see figure 2(d)), suggesting that this ion might be important in the CNT growth for the conditions under study. It is stated that hydrocarbon ions play a key role in the formation of amorphous carbon films [29]. Therefore, the fact that the larger hydrocarbon ions are predominant under C_2H_2-rich conditions might explain why these conditions are not so often used for CNT growth, and that most experiments are performed for a C_2H_2 fraction below 20% (e.g., [8,9,20]).

Finally, it is worth to mention that atomic carbon is hardly formed in the plasma (see figure 2(b)). Therefore, we can conclude that the carbon sources for CNT growth arise mainly from the decomposition of hydrocarbon molecules and radicals on the catalyst surface, as is also stated in [30].

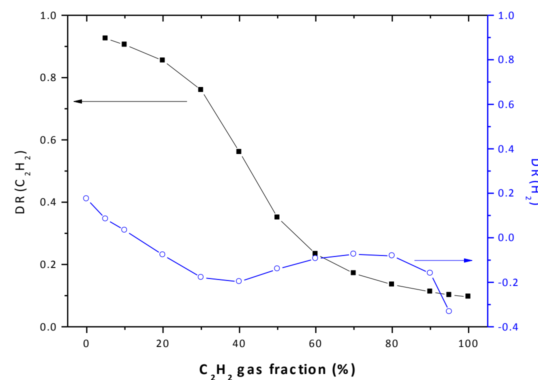

Figure 3: Calculated decomposition rates (DR) of the feedstock gas molecules (C_2H_2 and H_2), as a function of the C_2H_2 gas fraction, for the C_2H_2/H_2 gas mixture. The other operating conditions are the same as in figure 1.

Figure 3 illustrates the calculated decomposition rate (DR) of both background gases (C_2H_2 and H_2) in the plasma, as a function of C_2H_2 fraction. The DR is defined as follows:

$$DR=1-\frac{\text{volume-averaged density of background gas}}{\text{density of background gas at inlet}}$$

Hence, a DR of 1 indicates 100% decomposition, or conversion into other species. C_2H_2 has a high DR at low C_2H_2 gas fraction (see left axis), and the DR drops significantly upon increasing C_2H_2 fraction, especially in the range between 30 and 70%. The C_2H_2 species are believed to be the main precursors for CNT growth in a PE-CVD system [10,12]. Hence, a high DR of C_2H_2, in combination with a low C_2H_2 fraction in the gas mixture, gives rise to a low C_2H_2 flux to the substrate, which might suggest a relatively low (and hence: controlled) growth rate for the CNTs. This is indeed observed experimentally [9,20]. The DR of H_2 is found to be very low at low C_2H_2 fraction, and it is even negative at C_2H_2-rich conditions, as is obvious from figure 3 (right axis). These negative values for the DR indicate that more H_2 molecules are formed, e.g., out of C_2H_2, rather than decomposed.

3.3. Comparison of H_2 and NH_3 as dilution gases

When NH_3 is used as the dilution gas instead of H_2, some new species appear in the plasma, as is clear from Table 2 above. Figure 4 illustrates the fluxes of these extra species towards the substrate, as a function of the C_2H_2 gas fraction. N_2, N_2H_2 and NH_4^+ appear to be important neutrals and ions, respectively, besides the background gases C_2H_2 and NH_3. It was reported [25] that the presence of N_2 can enhance carbon diffusion into the catalyst, promoting CNT growth. Hence, this might explain why in many papers (e.g., [8-10,12,24]) NH_3 is used as the dilution gas, rather than H_2.

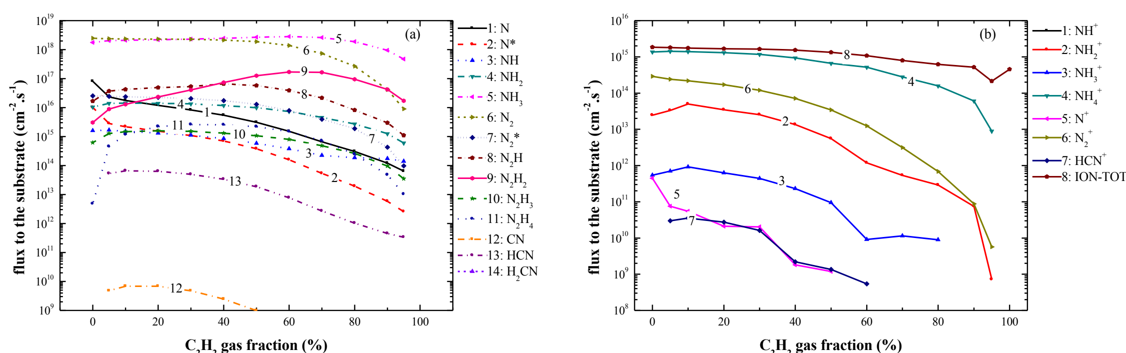

Figure 4: Calculated radially-averaged fluxes of the extra neutral species (a) and ions (b) bombarding the substrate, as a function of the C_2H_2 gas fraction, for the C_2H_2/NH_3 gas mixture. The other operating conditions are the same as in figure 1.

The DRs of C_2H_2 and NH_3 are plotted against C_2H_2 fraction in figure 5. The DR of C_2H_2 shows the same trend as in the C_2H_2/H_2 gas mixture (cf. figure 3 above). Moreover, the DR of NH_3 drops also from nearly 1 at low C_2H_2 gas fraction to values around 0.4 at high C_2H_2 fraction. This leads to a pronounced drop in the atomic H production. It is generally known that H can etch away amorphous carbon phases formed in the growing CNTs [20]. Therefore, the large flux of H atoms at low C_2H_2 gas fraction, in combination with the low fluxes of hydrocarbon ions towards the substrate, suggests that "clean" CNT growth conditions can be achieved at a low C_2H_2 gas fraction. This is also reported in literature. Indeed, Chhowalla et al. [8] found that CNTs could be grown at a C_2H_2 fraction between 5 and 30%. Also in [24] 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.

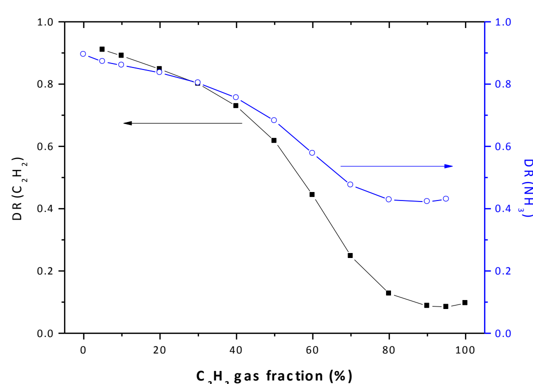

Figure 5: Calculated decomposition rates (DR) of the feedstock gas molecules (C_2H_2 and NH_3), as a function of the C_2H_2 gas fraction, for the C_2H_2/NH_3 gas mixture. The other operating conditions are the same as in figure 1.

5. Conclusions

We have applied a hybrid model to investigate the plasma chemistry in an ICP reactor in C_2H_2/H_2 and C_2H_2/NH_3 gas mixtures. First, some general calculation results were illustrated, such as the power density, electron and gas temperature, electron density

and densities of some other plasma species. Subsequently, the fluxes of the various plasma species bombarding the substrate, as well as the decomposition rates (DRs) of the feedstock gases were analyzed for different C_2H_2/H_2 and C_2H_2/NH_3 gas ratios.

It is found that both gas mixtures give rise to a very rich plasma chemistry, with several large hydrocarbon molecules, radicals and ions, especially at a high C_2H_2 gas fraction. When NH_3 is applied as the dilution gas, N_2, N_2H and N_2H_2, as well as NH_4^+, are also important plasma species. The C flux, on the other hand, was found to be the lowest of all radicals, which confirms that the carbon source for CNT growth mainly arises from the decomposition of hydrocarbon molecules on the catalyst surface [30].

The calculated DRs of the feedstock gas molecules illustrate that C_2H_2 is almost fully decomposed at low C_2H_2 fraction in both gas mixtures, but the DR drops significantly upon higher C_2H_2 gas fraction. The DR of H_2 was found to be very low, or even negative at a C_2H_2 fraction above 10%, indicating that more H_2 molecules are formed (out of e.g., C_2H_2), rather than decomposed. The DR of NH_3 follows a similar trend as the C_2H_2 DR, being high at low C_2H_2 fraction, and decreasing for higher C_2H_2 fractions. This results in a drop of the atomic H flux towards the substrate (or the growing CNT) at high C_2H_2 fraction. Moreover, the higher hydrocarbon fluxes also exhibit a maximum at these conditions. Therefore, we expect that an amorphous carbon film will be formed under these conditions, which cannot easily be etched away, because of the low amount of etching H atoms, and this will suppress the growth of CNTs. Hence, we expect that a low fraction of C_2H_2 and hence a higher fraction of H_2 or NH_3 in the gas mixture will result in more “clean” conditions for CNT growth. Indeed, experiments reported in literature appear to be performed typically at a C_2H_2 fraction below 20% (e.g., [8,9,20]).

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