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Investigating the plasma chemistry for the synthesis of carbon nanotubes/nanofibers in an inductively coupled plasma enhanced CVD system: Parametric study

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Carbon nanotubes and nanofibers (CNTs/CNFs) have attracted more and more attention in the past decades due to their unique physical, chemical and electronic properties, as well as their wide potential applications including nanoelectronics [1], hydrogen storage [2], and field emission devices [3].

Plasma enhanced chemical vapour deposition (PECVD) has become a very promising technology for the direct synthesis of vertically aligned CNTs/CNFs. The high-energy electrons decompose the feedstock gases into reactive radicals, which provide the carbon sources for CNT/CNF growth. In addition, an independent power can be applied on the substrate, which results in the formation of a self-biased electric field. The latter plays a key role in growing vertically aligned CNTs/CNFs.

To better control the plasma-based CNT/CNF growth, a 2D hybrid plasma model, the so-called HPEM [4], is used to investigate the plasma chemistry under CNT/CNF growth conditions. Figure 1 illustrates the calculated volume-averaged densities of all plasma species present in a gas mixture of 20%CH_4 and 80%H_2, at 300W ICP power, 30W bias power, 50 mTorr gas pressure and the substrate is heated to 600 ℃. It is observed that H_2, C_2H_2, C_2H_4 and C_2H_6 are the dominant molecules. The primary radicals are H and CH_3. The most important ions are $C_2H_2^+$, $C_2H_3^+$, and $C_2H_5^+$, but CH_5^+, CH_3^+, CH_4^+, and H_3^+ are also quite important. In general, the ion densities are, however, five orders of magnitude lower than the important neutrals densities.

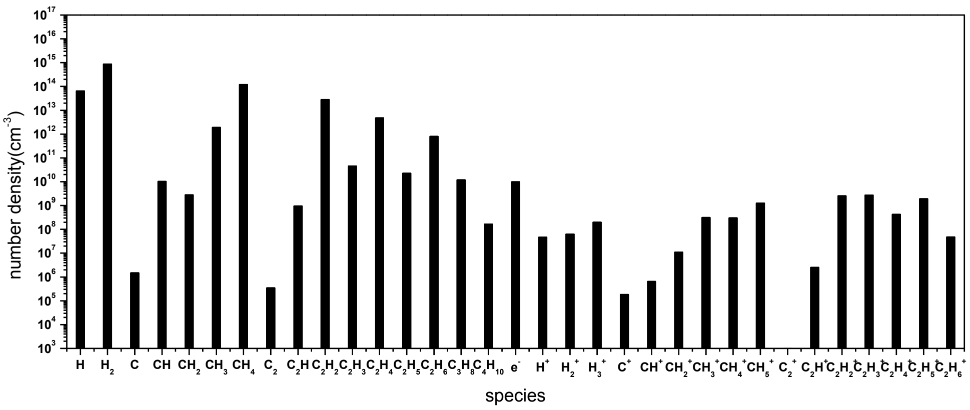

Figure 1. Calculated volume-averaged densities of the various plasma species in the CH_4/H_2 plasma at pressures of 50 mTorr with gas ratio of 20:80. The operating conditions are: 100 sccm gas flow rate, 300W source power, 30W bias power at the substrate and 13.56 MHz operating frequency at the coil and at the substrate electrode. The substrate is heated to 600 ℃.

The influence of ICP power (50~1000W), bias power (0~500W), operating pressure (10mTorr~1Torr), gas ratio for four different gas mixtures typically used for CNT/CNF growth (i.e., CH_4/H_2, CH_4/NH_3, C_2H_2/H_2 and C_2H_2/NH_3) and temperature of the substrate (0~1000 ℃) on the plasma chemistry is also investigated and the optimized conditions for CNT/CNF growth are analyzed.

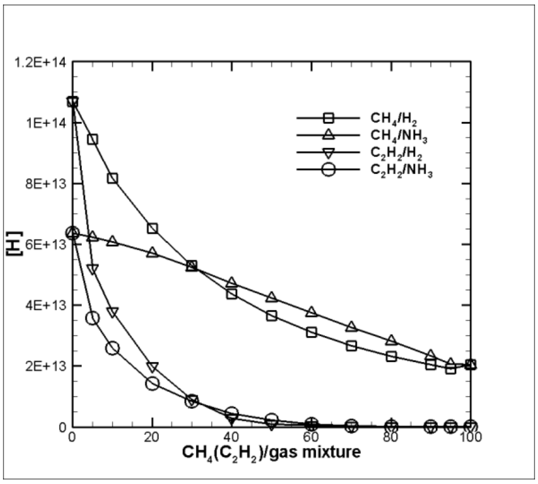

Fig. 2: Calculated volume-averaged atomic hydrogen density as a function of the % CH_4 or C_2H_2 for the four different gas mixtures under study. The operating conditions are: 50 mTorr gas pressure, 100 sccm gas flow rate, 300W source power, 30 W bias power at the substrate and 13.56 MHz operating frequency at the coil and at the substrate electrode. The substrate is heated to 600 ℃.

Figure 2 shows the influence of gas composition, more specifically the percentage of CH_4 or C_2H_2 in the gas mixture, on the H atom density. It is clear that the H atom density drops significantly upon decrease of the percentage of H_2 or NH_3 in the gas mixture. This is because, when the hydrocarbon feedstock gas is fed into the reactor, the atomic hydrogen is quickly consumed by hydrogen insertion/abstraction reactions to generate hydrocarbon radicals. This result can be important for the process of synthesizing CNTs/CNFs. Indeed, atomic hydrogen plays a key role in removing the amorphous carbon film from the surface of the catalyst to keep it clean. However, an excess of atomic hydrogen will also etch the CNTs/CNFs. Hence, there should be an optimum in the H atom density in the reactor. Numerical simulations can be useful, as they can predict at which gas composition this optimum density can be reached.

Reference

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