

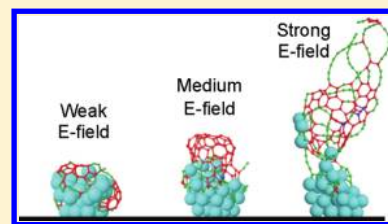
# Insights in the Plasma-Assisted Growth of Carbon Nanotubes through Atomic Scale Simulations: Effect of Electric Field

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**ABSTRACT:** Carbon nanotubes (CNTs) are nowadays routinely grown in a thermal CVD setup. State-of-the-art plasma-enhanced CVD (PECVD) growth, however, offers advantages over thermal CVD. A lower growth temperature and the growth of aligned freestanding single-walled CNTs (SWNTs) makes the technique very attractive. The atomic scale growth mechanisms of PECVD CNT growth, however, remain currently entirely unexplored. In this contribution, we employed molecular dynamics simulations to focus on the effect of applying an electric field on the SWNT growth process, as one of the effects coming into play in PECVD. Using sufficiently strong fields results in (a) alignment of the growing SWNTs, (b) a better ordering of the carbon network, and (c) a higher growth rate relative to thermal growth rate. We suggest that these effects are due to the small charge transfer occurring in the Ni/C system. These simulations constitute the first study of PECVD growth of SWNTs on the atomic level.



## 1. INTRODUCTION

Single walled carbon nanotubes (SWNTs) continue to attract much attention because of their outstanding properties. Especially attractive is the fact that their electronic and optical properties critically depend on their structure, and can therefore be tuned. Indeed, SWNTs can be either semiconducting or metallic, depending on their chirality. This property therefore offers perspective to use SWNTs in novel electronic applications, such as their use as ballistically conductive interconnects, sensors, field effect transistors, etc.<sup>1,2</sup> Each of these applications, however, essentially requires a pure material, i.e., a sample containing only semiconducting or only metallic tubes. This can be achieved by two methods. Either the material is grown nonspecifically, in which a mixture of both is obtained. Subsequently, a postsynthesis step separates the wanted material from any unwanted material. Various techniques have been developed for this separation process, including ultracentrifugation, electrophoresis, chromatography, selective solubilization, and selective reaction.<sup>3</sup>

Alternatively, one could also try to directly grow only the desired material. In the first instance, this would mean the growth of only semiconducting or only metallic tubes. In a next step, perhaps tubes of a specific chirality could be grown. Recently, many studies have been appearing in the literature demonstrating both highly selective SWNT synthesis as well as narrow chirality distributions, both with thermal CVD and plasma-enhanced CVD.<sup>4–7</sup> Of crucial importance is having control over the exact growth conditions and hence the growth process. In this sense, plasma-enhanced chemical vapor deposition (PECVD) offers additional control parameters not available in thermal CVD experiments, which allow steering the growth process. Most notably, these control parameters include the applied discharge voltage and power, and the type of plasma

reactor. Indeed, the very use of PECVD implies the presence of electromagnetic fields, ions (possibly with high energy), electrons, photons, radicals, excited species, as well as neutral atoms and molecules. By adjusting the operating conditions, such as the plasma voltage, gas pressure, or temperature, the extent of these plasma properties, and hence the resulting growth process itself, can be adjusted.<sup>8</sup>

As a result, PECVD has been shown to allow the growth of CNTs e.g. at lower temperatures, which is useful for growth on, e.g., temperature-sensitive substrates. Low temperature growth has also been demonstrated to allow for selective growth.<sup>9</sup>

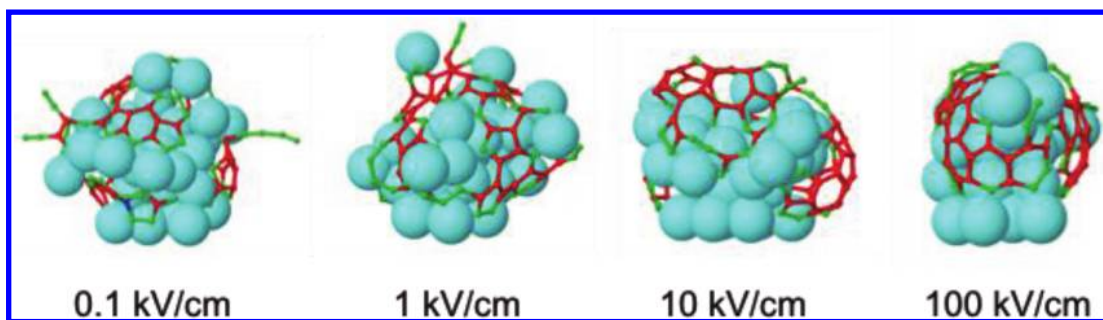
Typically, PECVD used to result in the growth of (aligned) multiwalled CNTs and fibers.<sup>8</sup> Since a number of years, various groups have succeeded in the PECVD growth of SWNTs as well. Furthermore, also the growth of aligned, freestanding SWNTs has been demonstrated in a PECVD setup.<sup>10,11</sup> In addition to the low temperature growth and selective growth, this is perhaps one of the most appealing advantages of using PECVD, as growing aligned freestanding SWNTs is not possible in a thermal CVD setup.

However, a fundamental understanding on the atomic scale of the impact and influence of the plasma on the growth process is currently still lacking. As molecular dynamics (MD) simulations provide an atomistic view of the growth process, such simulations may contribute to our understanding of the process.

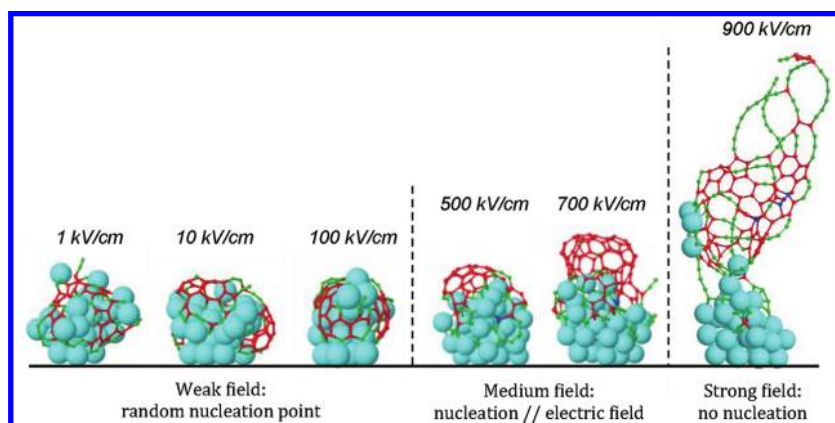
Many groups have previously simulated the growth of SWNTs, both using Monte Carlo (MC) techniques<sup>12–14</sup> as well as MD<sup>15–28</sup> either from first principles or in a classical approach. Two recent reviews can be found in refs 29 and 30.

Received: October 13, 2011

Published: November 30, 2011



**Figure 1.** Effect of increasing the electric field value in the range 0.1–100 kV/cm on the structure and ordering of the nucleating carbon network. The small red atoms are 3-coordinated carbon atoms, the small green atoms are 2- or 1-coordinated carbon atoms. The large atoms represent nickel atoms.



**Figure 2.** Effect of applying an electric field on the nucleation of a SWNT cap. The color coding is the same as in Figure 1.

Previously, we have demonstrated for the first time the importance of taking into account long time-scale events, by combining MD with force-biased MC (fbMC). It was demonstrated that the growth of both semiconducting tubes<sup>31</sup> as well as metallic tubes<sup>32</sup> could in fact be accomplished. While a multiscale model on PECVD growth of SWNTs was recently presented,<sup>33</sup> until now there are no reported atomistic simulations exploring the PECVD growth of SWNTs. As a first step toward an atomistic insight in the PECVD growth process of SWNTs, this report focuses on the simulation of SWNT growth assisted by electric fields.

## METHODOLOGY

The simulation model is identical to the model previously used to simulate thermal CVD of SWNTs,<sup>31,32</sup> but with the important difference being the application of an electric field. In short, hybrid MD/MC simulations are carried out using the ReaxFF potential, which essentially models all types of bonding, ranging from covalent to ionic bonding and everything in between.<sup>34</sup> Additionally, longer-range forces are also taken into account, namely van der Waals forces and Coulombic forces. Charges on the atoms are calculated using the electron equalization method (EEM) approach. More information on the simulation techniques can be found in refs 31, 32, 35, 36 and references therein.

The initial structure forming the starting point of the simulation is a prethermalized Ni<sub>32</sub> nanocluster complemented with an eight-atom fixed layer of Ni underneath, in order to model surface-bound growth.<sup>32</sup> The growth temperature was set to 1000 K. An electric field is added, with a strength varying in the range 0.1–1000 kV/cm, directed toward the substrate. For electric field values of 0.1, 1, 10, and 900 kV/cm, five simulations were carried out, while for the simulations corresponding to electric field values of 100, 300, 500, 600, 700, and 800 kV/cm, 10 simulations were carried out in order to gather

statistics. In the case of 1000 kV/cm, three simulations were carried out. In total, 83 simulations were carried out. In the following, representative structures for these collections of simulations are shown in the figures. Growth was accomplished by introducing C atoms in the simulation box, such that at any moment there is only one C atom in the gas phase. The carbon atom moves through the box until it impinges on the metal cluster and becomes incorporated in the growing structure. Every 4 ps, the structure is allowed to relax by application of the force-biased Monte Carlo scheme. During the relaxation stage, no new carbon atoms are allowed to impinge.

## RESULTS AND DISCUSSION

The question we wish to answer is simple: how does the presence of an electric field affect the SWNT growth process? In Figure 1, the effect of applying an electric field on the initial network formation is shown. Corresponding to the thermal CVD simulations,<sup>31,32</sup> applying a weak electric field leads to the formation of polyene chains and a somewhat disordered network in the initial state. In fact, in this initial stage, there is not one continuous network formed, but rather multiple small graphitic islands that are scattered over the surface of the nanocatalyst. It can also be seen in the figure, that for an electric field value of 0.1 kV/cm, some short chains protrude from the surface. Increasing the field strength to 1 kV/cm slightly affects the overall C-network structure: some carbon chains now interlink the small graphitic networks. Furthermore, it is also observed that fewer carbon chains now protrude from the surface. Further increasing the electric field strength to 10 kV/cm affects the structure of the carbon network further: now, the carbon atoms more easily form a closed network, rather than multiple smaller networks scattered over the surface. When ramping up the electric field value to 100 kV/cm, however, a

major change is observed. Now, the network is fully interconnected, not by single carbon strands, but by carbon rings: only a single network is now formed, which (partially) covers the surface of the nanocatalyst. Note in this respect that a complete coverage of the surface is undesirable. Indeed, provided that carbon atoms cannot be incorporated in the structure from the substrate, this would poison the catalyst and therefore terminate the growth. Applying an electric field therefore seems to increase the ordering in the carbon network. Specifically, the carbon atoms seem to find each other more easily in the case of a stronger electric field than in the case of a weaker electric field. This is important, as the initial impact point of the carbon on the metal catalyst surface is intrinsically random. This seems to indicate that the electric field changes the mechanism by which the carbon atoms move over the catalyst surface and through the catalyst bulk. Note, however, that although the application of an electric field seems to increase the ordering in the carbon network in the initial nucleation stage, it is not a requirement in order to finally obtain a well-structured SWNT.<sup>31</sup>

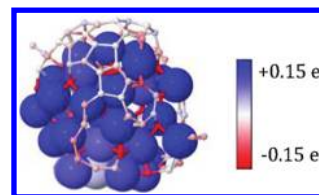
Further insight can be obtained by continuing the simulation to the next growth stage, in which a cap can effectively be nucleated. The formation of a SWNT cap occurs when the nanocluster becomes supersaturated in carbon. Then, when more carbon is added to the cluster, the dissolved carbon starts to segregate at the surface, forming the graphitic islands mentioned above. These islands continue to grow, until they lift off from the surface. Alternatively, in the case when the work of adhesion is too large, the graphitic islands do not lift off from the surface, and the nanoparticle becomes encapsulated,<sup>24</sup> effectively terminating the growth.

The effect of applying an electric field on this nucleation process is shown in Figure 2. As depicted in the figure, three regimes can be distinguished. In the first regime, in which only a weak electric field is applied (in the range 1–100 kV/cm), it is observed that a SWNT cap may nucleate on any point of the catalyst surface. Therefore, the location of the nucleating cap is random, and the resulting SWNT that grows out of this randomly positioned nucleated cap has a random orientation with respect to the surface. This corresponds to the typical thermal CVD spaghetti growth.<sup>8</sup>

By increasing the electric field value, in the range 100–800 kV/cm, an interesting effect can be seen. Indeed, with increasing electric field strength, we observe that the graphitic network nucleates close to the tip of the catalyst (i.e., most distant from the surface). Above applied electric field values of ~300 kV/cm, the cap is always observed to nucleate at or near the tip of the catalyst. Therefore, the cap nucleation process occurs antiparallel to the electric field, i.e., perpendicular to the surface. This is of particular interest for applications such as gas sensors, in which single freestanding SWNTs with a controlled diameter are of use. If the electric field value is increased further, above ~800 kV/cm, no cap nucleation is observed anymore, i.e., only long carbon chains protruding into vacuum are observed.

We propose the following hypothesis to explain these observations. The Pauling electronegativity of nickel is 1.91, while the electronegativity of carbon is 2.5, a difference of 0.6. Hence, when a nickel–carbon bond is formed, there will be a small charge transfer from the nickel atom to the carbon atom. The Ni–C bond is therefore polarized. As a result, the nickel atoms attain a slightly positive charge, while the carbon atoms which are connected to the nickel cluster attain a slightly

negative charge. This can be seen in Figure 3. Note that this small charge separation was also observed by Ohta et al. in their



**Figure 3.** Calculated charge on the carbon atoms (small balls) and the nickel atoms (large balls) in the cap nucleation stage.

DFTB simulations and by Wang et al. in their DFT simulations of Ni/C.<sup>37,38</sup>

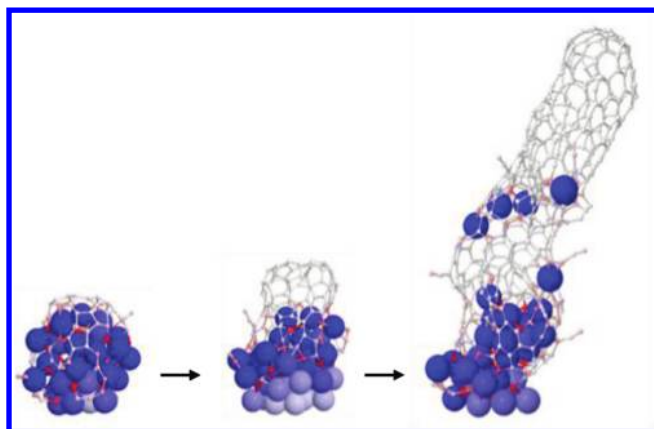
Specifically, it can be seen in the figure that the carbon atoms that are in direct contact with the nickel, i.e., those carbon atoms that form a chemical bond with the nickel, have a non-negligible charge. On the other hand, the carbon atoms that are in the hexagonal carbon network, at and near the tip of the catalyst particle, do not form a chemical bond with the nickel, and are almost neutral. Because of this small charge separation, the electric field can act on the carbon atoms. This induces a competition between the thermally induced motion of the carbon atoms (i.e., thermal diffusion), and their motion induced by the electric field (i.e., migration). In the case of a weak field, the thermal diffusion will dominate the migration, and the carbon atoms will randomly wander over the substrate and through the bulk of the particle until they finally connect randomly to other carbon atoms. The nucleation of a graphitic patch, and the subsequent nucleation of the SWNT cap, will therefore occur at a random location. However, in the case of a strong electric field, the migration will dominate the diffusion, and the atoms will preferentially move in the direction opposite to the field, i.e., toward the tip of the cluster. Therefore, under these circumstances, the carbon atoms have a higher probability of connecting to each other near the tip of the catalyst, and the cap will preferentially nucleate parallel to the applied field.

This process remains operative when new carbon atoms are added. Carbon atoms already assimilated by the network hardly feel the electric field (as they are almost neutral), but the newly incoming carbon atoms must first interact with the metal cluster (“catalyzed”) before being incorporated in the network. Therefore, these newly added carbon atoms are invariably gaining some charge, migrate upward by the action of the electric field, and thereby push the growing SWNT upward. The effect of this can be seen in Figure 4, for a continued growth simulation.

As can be seen in Figure 4, a relatively straight and well-aligned SWNT is formed. Similar to our observations in thermal CVD growth,<sup>31</sup> some nickel atoms are found to desorb from the metal nanocluster, due to some thermal fluctuations.

As mentioned above and as shown in Figure 2, no nucleation takes place when the electric field becomes too strong (i.e., above about 800 kV/cm). We suggest that this is a result of the competition between the binding strength between the carbon and the nickel atoms on the one hand (preferring nucleation of a carbon network on the catalyst surface), and the migration of the carbon atoms due to the electric field on the other hand (pulling the carbon atoms away from the surface).

One more effect is observed when applying an electric field. In the case of thermal CVD, relatively many C-atoms are needed before a graphitic patch and from there a cap nucleates.



**Figure 4.** Evolution of a growing SWNT under the influence of an electric field of 700 kV/cm.

Also, these atoms need time before they find each other, as their motion is purely random. However, in the case of a sufficiently strong electric field, the carbon atoms all migrate toward the point of nucleation, i.e., the tip of the catalyst, such that this nucleation process occurs much faster. Because of this, an enhanced growth rate is observed in these simulations relative to the thermal CVD simulations,<sup>31,32</sup> i.e., fewer carbon atoms are needed to nucleate a SWNT. However, because the Monte Carlo scheme inherently does not have an associated time scale, it is difficult to quantify this enhancement.

Finally, it should be noted that the values for the electric field that are needed in the current simulations to observe alignment of the SWNTs are very high. In fact, we estimate that these values are at least 1 order of magnitude too high. Indeed, actual field values were estimated by Kato et al. for their experimental diffusion plasma SWNT growth setup.<sup>6</sup> These authors obtained a value of  $1.7 \times 10^4$  V/m for a power input of  $P = 200$  W. According to the authors, this value should be multiplied by the field magnification factor due to the curvature of the nanoparticle in order to obtain the local electric field. Estimating this magnification factor to be around 100 for a freestanding SWNT,<sup>10</sup> one would arrive at a field value of 17 kV/cm, which is indeed a factor of about 30 lower than the optimal values predicted in our simulations.

However, while the field values are most probably too high, the essential conclusion remains valid: in the case when no field or a “weak” field is applied, no alignment is observed. In the case where a “stronger” field is applied, alignment of the cap with the electric field is predicted, ultimately resulting in a freestanding SWNT.

Of course, in a PECVD setup, many more ingredients are present besides the electric field, including reactive species (radicals), electrons, ions, and photons, all of which may contribute to the growth process.<sup>8,39,40</sup> In a next step, these other ingredients also need to be taken into account in order to fully simulate the PECVD process.

## CONCLUSIONS

Reactive hybrid MD/MC simulations were carried out to investigate the effect of applying an electric field on the nucleation process of single-walled carbon nanotubes (SWNTs). It is found that with increasing electric field strength, the structuring of the network is facilitated. Second, we observe that when sufficiently strong electric fields are applied, the SWNT is aligned with the field. Finally, it is

observed that the growth rate is enhanced relative to thermal CVD growth. These observations are in agreement with the literature, and can be explained by considering the small charge separation that occurs in the Ni/C system, due to their different electronegativities. In the case of a weak field, the thermal diffusion motion of the carbon atoms will result in a random nucleation point of the SWNT cap. In the case of sufficiently strong fields, however, the migration of the slightly negatively charged carbon atoms toward the tip of the catalyst dominates their thermal diffusion motion, and the SWNT cap will preferentially nucleate near the tip of the catalyst. These simulations constitute the first atomistic simulations on the plasma-enhanced chemical vapor deposition (PECVD) growth of SWNTs.

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## ACKNOWLEDGMENTS

E.N. acknowledges the FWO-Flanders (Fund for Scientific Research-Flanders) for financial support. We also gratefully acknowledge financial support from the Prime Minister's Office through IAP VI. We also thank R. Hatakeyama and T. Kato for insightful discussions. This work was carried out in part using the Turing HPC infrastructure at the CalcUA core facility of the Universiteit Antwerpen, a division of the Flemish Supercomputer Center VSC, funded by the Hercules Foundation, the Flemish Government (department EWI) and the Universiteit Antwerpen.

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