Understanding plasma growth of SWNTs: Effect of electric field and ion bombardment

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We performed hybrid Molecular Dynamics / Monte Carlo simulations to investigate the effect of applying an electric field on the Ni-catalyzed growth of single walled carbon nanotubes (SWNT) to mimic the growth under plasma conditions. We found that at sufficiently strong field values, the nucleating cap is aligned wth the electric field. We hypothesise that this is due to the electric field acting on the partially negatively charged carbon atoms in polarized Ni-C bonds. Additionally, we investigated the effect of ion bombardment on the cap formation. We found that at impact energies above about 35 eV, the network is destroyed. At lower impact energies, however, network formation is enhanced.

Introduction

Carbon nanotubes keep on attracting a lot of interest due to their extraordinary properties, including extreme stength, electric current carrying capacity, thermal conductivity and light absorbance in the 200 nm – 200 μm range. Furthermore, depending on their structure, they can be metallic or semiconducting. As a result, they are envisaged for various applications, such as components in superstrong polymer composites, heat sinks in computers nanotube opto-electronic devices, electron field emitters, and many more.

One of the major obstacles in making SWNTs applicable in everyday (electronic) applications on the large scale, is our current inability to control the exact properties, and specifically the chirality of the tube. On a fundamental level, the mechanism of chirality determination is indeed not yet known. Typically, SWNTs are produced in a chemical vapor deposition (CVD) setup, using metallic nanoparticles as catalyst.

Low temperature plasmas are a very promising tool to achieve this goal of chirality control. However, little is currently known about the exact fundamental mechanisms that are operative on the atomic scale in PECVD growth of carbon nanotubes. Besides the lower growth temperature, PECVD has additional advantages over thermal CVD such as control over length and diameter, or the formation of freestanding, aligned SWNTs. Indeed, in thermal CVD growth, either spaghetti growth is observed, or aligned growth by a crowding effect [1].

Methodology

We employ atomic scale simulations to unravel the mechanistic details of the growth process, based on the ReaxFF potential. This potential is based on the bond order / bond length relationship. The total energy is expressed as a sum over contributions from lone pairs, over- and undercoordination, valence and torsion interactions, as well as Coulomb and van der Waals interactions. Recently, we obtained for the first time SWNTs with a specific chirality in computer simulations under CVD conditions [2, 3] employing this potential. Growth is accomplished by allowing C-atoms to impinge on a pre-thermalized Ni-nanocluster at 1000 K.

Results

In this contribution, we aim at taking plasma effects into account in simulating the growth process. This includes the effect of applying electric fields as well as ion bombardment on the growth of SWNTs.. Using small, surface bound nickel nanoparticles as catalysts, we demonstrate how the electric field can enhance the phase separation between the carbon and the nickel. Indeed, the C-Ni bond is polar due to the difference in electronegativity. Therefore, the C-atoms are slightly negatively charged. The electric field can act on these partial charges, pushing the C-atoms towards the tip of the nanocluster. Using the right electric field strength, phase separation is enhanced and the nucleation of the SWNT cap is found to occur in alignment with the field, resulting in aligned SWNT growth [3]. This is illustrated in Figure 1.

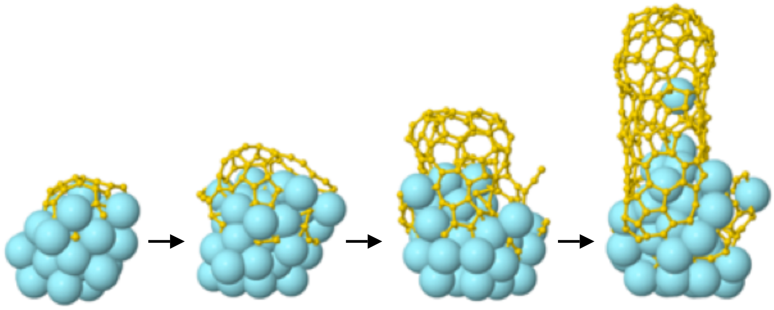

Fig. 1: Evolution of a vertically growing SWNT on a Ni-nanocluster, in alignment with an applied E-field.

Furthermore, we have also investigated how low energy Ar ion bombardment in the energy range of 5 eV – 100 eV influences the cap formation process. It is found that at the lowest ion impact energies (up to 10 eV), the ion bombardment has practically no effect. When using high energy impacts, in the order of ~40 eV or higher, the nucleating cap is destroyed. However, by bombarding the nucleating cap with ions having intermediate energies, in the order of 15 eV – 35 eV, the cap formation is effectively enhanced. This is illustrated in Figure 2. These simulations are the first to demonstrate how ion bombardment can contribute to the growth of SWNTs.

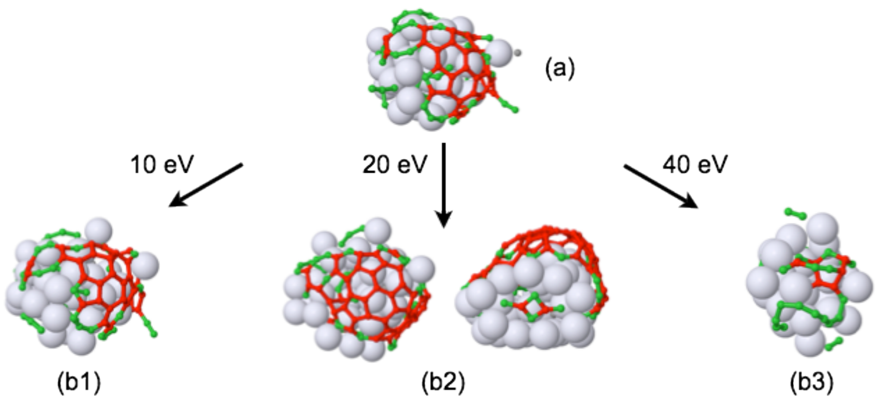

Fig. 2: Effect of Ar ion bombardment energy on the carbon network. (b1) At low energy, no effect is observed. (b2) At intermediate energy, the network is enhanced. (b3) At high energy, the network is destroyed.

References

[1] M. Meyyappan, *J. Phys. D: Appl. Phys.* **42** (2009) 213001
[2] E. C. Neyts, Y. Shibuta, A. C. T. van Duin. A. Bogaerts, *ACS Nano* **4** (2010) 6665-6672
[3] E. C. Neyts, A. C. T. van Duin, A. Bogaerts, *J. Am. Chem. Soc.* **133** (2011) 17225-17231
[4] E. C. Neyts, A. C. T. van Duin, A. Bogaerts, *J. Am. Chem. Soc.* **134** (2012) 1256-1260