Poster

THE ROLE OF PLASMA IN PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION OF NANOSTRUCTURE GROWTH

David B. Hash, M. Meyyappan
NASA Ames Research Center, Mail Stop 230-3, Moffett Field, CA 94035-1000, USA
E-mail: David.B.Hash@nasa.gov
http://www.ipt.arc.nasa.gov

Kenneth B. K. Teo, Rodrigo G. Lacerda, Nalin L. Rupesinghe
Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, UK
E-mail: kbkt2@eng.cam.ac.uk
http://www-g.eng.cam.ac.uk/cnt/

Chemical vapour deposition (CVD) has become the preferred process for high yield growth of carbon nanotubes and nanofibres because of its ability to pattern growth through lithographic positioning of transition metal catalysts on substrates. Many potential applications of nanotubes such as field emitters [1] require not only patterned growth but also vertical alignment. Some degree of alignment in thermal CVD processes can be obtained when carbon nanotubes are grown closely together as a result of van der Waals interactions. The alignment however is marginal, and the van der Waals prerequisite makes growth of freestanding nanofibres with thermal CVD unrealizable. The application of electric fields as a means of alignment has been shown to overcome this limitation [2-5], and highly aligned nanostructures can be grown if electric fields on the order of 0.5 V/μm are employed. Plasma enhanced CVD in various configurations including dc, rf, microwave, inductive and electron cyclotron resonance has been pursued as a means of enabling alignment in the CVD process. However, the sheath fields for the non-dc sources are in general not sufficient for a high degree of alignment and an additional dc bias is usually applied to the growth substrate. This begs the question as to the actual role of the plasma. It is clear that the plasma itself is not required for aligned growth as references [3] and [4] employed fields through small applied voltages (3-20 V) across very small electrode spacings (10-100 μm) and thus avoided striking a discharge.

One additional role of the plasma that has been in some cases ignored in the nanotube community is that of substrate heating. Power is deposited into ions and electrons as they move through the sheath fields through Joule heating. Some of this power is then transferred to the gas through collisions with neutrals. The substrate is subsequently heated by conduction from the heated gas or directly through ion bombardment. Some form of substrate heating is required to sustain a growth temperature on the order of 700 °C which is necessary for superior crystallinity. A variety of heating systems have been employed for this purpose including substrate platform resistive heaters and hot filaments. In this work, the magnitude of the plasma heating is characterized, and it is demonstrated the plasma alone is sufficient to heat the substrate to the desired growth temperature.

The reactor employed for this study is a simple dc configuration of equal area (10 cm^2) cathode and anode with a 5 cm separation. The feedstock of 54:200 sccm of C_2H_2/NH_3 is injected through a showerhead, which also acts as the anode. The graphite cathode has a rigid tungsten wire heater embedded that is coupled with an electrically isolated thermocouple to allow independent temperature control of the substrate when desired. Growth is performed at a pressure of 12 mbar, and varying the applied voltage from 600 to 700 V varies the plasma power from 20 to 200 W.

The role of the plasma is investigated with a 1-D radially averaged computational model. Equations for the conservation of species mass, momentum, and ion, electron, and neutral gas thermal energy are solved axially between the two electrodes. The model includes 18 neutral

species, 4 charged species, and 120 reactions. As a boundary condition for the gas energy equation, a cathode energy balance is incorporated to model ion bombardment, thermal radiation, and solid and gas conduction to be able to predict the cathode temperature.

Figure 1 shows the variation of cathode temperature with plasma power as seen in experiment and simulation without additional heating from the embedded tungsten heater. Even at a low power of 20 W, the cathode reaches a temperature between 200 and 250 °C which shows the significance of plasma heating. Figure 2 displays SEM images of nanofibres grown at the same conditions (12 mbar, 54:200 sccm C_2H_2/NH_3, and 700 °C). The only difference is the way in which the 700 °C growth temperature is attained. In Fig. 2a, the plasma is the only source of heating with 200 W of power. In Fig. 2b, a lower plasma power of 66 W is employed with the embedded tungsten heater used to raise the temperature up to the same 700 °C. The obvious difference is that the nanofibres in 2b are twice as long as in 2a. From this, it would appear that the plasma is actually hindering growth. This is partially a result of a conversion of the feedstock acetylene to methane and hydrogen cyanide by the plasma, which then decompose less readily on the Ni catalyst decreasing the growth rate.

The plasma does provide the required electric fields for alignment and contributes to the substrate heating to attain growth temperatures necessary for superior crystallinity. At the same time, however, it converts the gas to less effective carbon-bearing precursors. Therefore, the optimal condition in this work employs the lowest power necessary to provide sheath fields on the order of 0.5 V/μm with additional substrate heating provided by an external source.

References:

[1] M. A. Guillorn, A. V. Melechko, V. I. Merkulov, D. K. Hensley, M. L. Simpson, and D. H. Lowndes, Appl. Phys. Lett., **81** (2002) 3660.
[2] Y. Avigal and R. Kalish, Appl. Phys. Lett., **78** (2001) 2291.
[3] Y. Zhang, A. Chang, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, and H. Dai, Appl. Phys. Lett., **79** (2001) 3155.
[4] A. Ural, Y. Li, and H. Dai, Appl. Phys. Lett., **81** (2002) 3464.
[5] L. Delzeit, R. Stevens, C. Nguyen, and M. Meyyappan, Int. J. Nanoscience, 1 (2002) 197.

Figures:

Figure 1. Measured and simulated cathode temperatures as a function of plasma power.

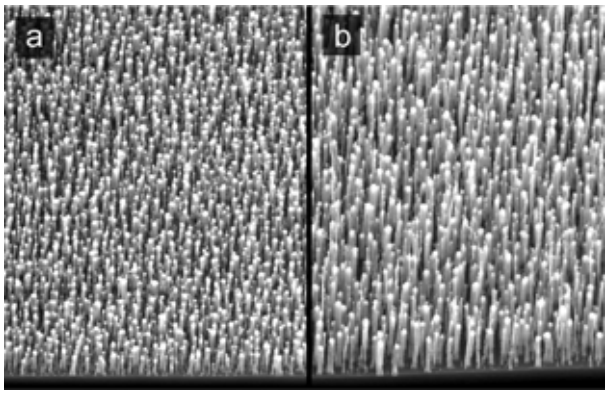

Figure 2. Nanofibres grown at 700 °C after 15 minutes. **a)** 200 W plasma power with embedded cathode heater turned off, **b)** 66 W plasma power with heater turned on.