

Controlled growth of vertically aligned carbon nanofibers for applications in nanoscale devices

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While the study of the catalytic growth of filamentous carbon has a decade-long history, interest in the growth of carbon nanofibers (CNFs) has resurged recently due to the variety of applications. In particular, vertically aligned CNFs (VACNFs) produced by plasma-enhanced chemical vapor deposition (PECVD)¹ have numerous potential applications in scanning microscopy, field emission devices, nanoelectronics, and nanobiotechnology. This is largely due to the ability to grow VACNFs deterministically, since the exact location, length, tip diameter, shape, orientation and chemical composition all can be controlled in a large-scale synthesis process². Some aspects of the growth process have been already reported in the literature³. However, our experience in nanofabrication indicates that numerous effects often have to be taken into account in order to be able to achieve a high degree of control over the properties of resultant VACNFs. While controlling the VACNF growth is fairly easy at certain conditions, the necessity for integration of this process into micro/nanofabrication of complete devices requires a much wider knowledge base.

In this work we present a systematic study of the crucial aspects of the growth of carbon nanofibers that was performed in the course of process engineering for nanoscale devices^{4,5} (Fig. 1). The DC PECVD process, in which a substrate with patterned catalyst is immersed into

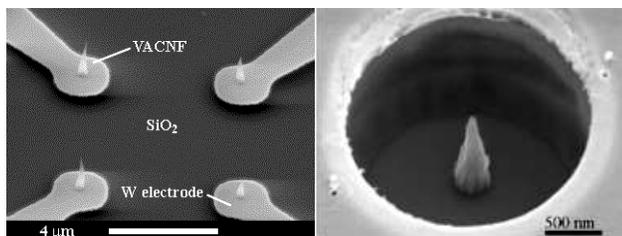


Figure 1. Nanodevices employing VACNFs. (a) Individually addressable vertically aligned carbon nanofiber-based electrochemical probes. SEM micrograph of four VACNF probes on individual W pads taken at 45° from normal incidence. (b) SEM micrograph of a diode-type gated cathode structure.

a dc glow discharge with a mixture of acetylene and ammonia, even though fairly simple in principle, is a very complex process due to the large number of control parameters. Gas flow rates, gas pressure, plasma current, plasma voltage, and substrate temperature constitute its basic multidimensional parameter space. To control the

properties of the CNFs it is necessary to know multidimensional phase diagram of the CNF growth. For example, a section of such a phase diagram in the temperature-gas composition plane is shown in Fig. 2.

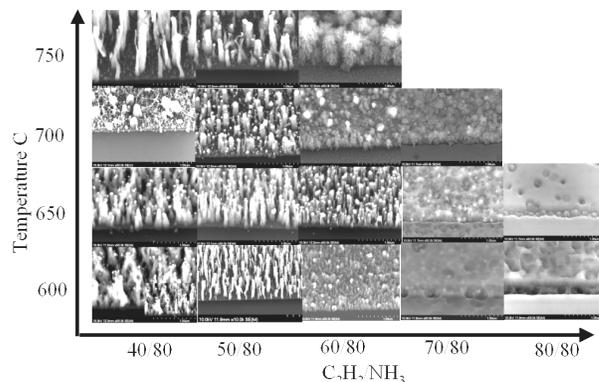


Figure 2. Phase diagram of VACNF growth in temperature - C₂H₂/NH₃ section of the parameter space. SEM micrographs of VACNF forests on a patterned catalyst stripe grown at different conditions.

Additionally, several other factors affect the production of the desired structures. First is the choice of substrate and catalyst materials, which affects the growth rate, the size of the nanoparticles, the atomic structure of CNFs and the growth mode. For example, by choosing an appropriate substrate and growth parameters it is possible to produce CNFs with the catalyst particle at the base or at the tip⁶ (Fig. 3). Another factor is the geometry of the catalyst

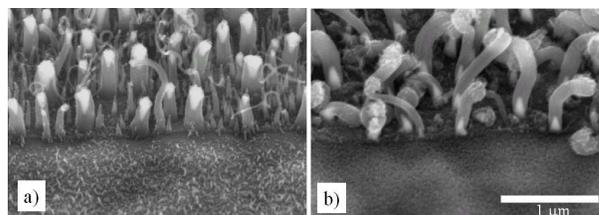


Figure 3. Tip-type (a) and base-type (b) growth modes. SEM images of CNF forests on a Ti (100nm)/Si substrate.

pattern. Conditions for the growth of dense CNF forests differ considerably from the conditions for sparse arrays of single CNFs. There are several issues that are of high significance for the growth of stand-alone nanofibers but that are much less important for dense VACNF forests. One of them is the reduction of the catalyst particle size with the growth time. This effect allows, by choosing initial catalyst size and growth time, the sharpening of the CNF tips⁷ that may be beneficial for several applications. Other important details, such as catalyst pretreatment, substrate holder conditioning and many others, must be understood in order to integrate CNFs into practical devices.

⁶ Melechko et al. (submitted to publication)

⁷ Merkulov et al., Chem.Phys. Lett., **350**, 381 (2001)

¹ Ren et al. Science **282**, 1105 (1998)

² Merkulov et al., Appl. Phys. Lett. **79**, 1178 (2001).

³ Chhowalla et al. J. Appl. Phys. **90**, 5308 (2001)

⁴ Guillorn et al. (in press) J. Appl. Phys. (2002)

⁵ Guillorn et al. Appl.Phys. Lett. **79**, 3506 (2001)