

Controlled synthesis and directed assembly of vertically aligned carbon nanofibers for functional nanoscale devices

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ABSTRACT

We describe the controlled synthesis and directed assembly of vertically aligned carbon nanofibers. Using the plasma enhanced chemical vapor deposition process described here, we demonstrate exquisite control of nanofiber diameter, height, placement, shape, orientation, and chemical composition. We demonstrate the utility of this process by showing several types of devices constructed using nanofibers.

Keywords: carbon nanofibers, carbon nanostructures, nanoscale materials, nanoscale devices

1 INTRODUCTION

The controlled synthesis and directed assembly of materials at the nanoscale remain two of the most difficult challenges for the realization of functional nanoscale devices. For example, while there has been a great deal of significant nanoscale science accomplished with carbon nanotubes (CNT), difficulties in the control of CNT placement, orientation, and chirality have limited the development of technology based on this science. In contrast, the synthesis and assembly of vertically aligned carbon nanofibers (VACNFs) is highly controllable, allowing the definition of VACNF location, length, tip diameter, shape, orientation and chemical composition. This control capability enables numerous potential applications in scanning microscopy, field emission devices, nanoelectronics, and nanobiotechnology.

2. Vertically Aligned Carbon Nanofiber Growth

Forests of vertically aligned carbon nanofibers (VACNFs), produced by plasma-enhanced chemical vapor deposition (PECVD) first were synthesized by Ren *et al.* (1). However, deterministic growth of isolated VACNFs is required to make them attractive for various applications.

Deterministic growth of VACNFs implies the ability to control their location, height, tip diameter, shape, orientation, and chemical composition during a *large-scale* synthesis process and thereby enable fabrication of practical devices. VACNFs similar to those described here often are referred to in the literature as carbon nanotubes. However, we prefer the term “nanofibers” because, despite the superficial external morphological similarity between VACNFs and multi-walled carbon nanotubes (MWNTs), their crystalline structures are quite different. While MWNTs consist of concentric graphene cylinders, VACNFs are composed of graphitic “funnels” and cones, also called “herring-bone” structure, and often have internal walls, which is referred to as a “bamboo-like” structure. Thus, the difference between VACNFs and MWCNTs is not simply the higher degree of crystallinity of MWCNTs, but essentially different long-range crystalline structures. As a result, the physical and chemical properties of VACNFs are expected to be quite different from those of MWNTs, so that clear differentiation is highly desirable.

Synthesis of VACNFs involves many deposition parameters, such as plasma power, gas mixture, temperature, pressure, etc., and each of them can have a profound effect on the growth and properties of resultant VACNFs (2-8). On the other hand, the ability to control properties is essential for device fabrication and operation (9-11). The following is a description of typical VACNF growth (Fig. 1). We grow VACNFs using direct current (dc) plasma-enhanced chemical vapor deposition (PECVD). Nickel (Ni) catalyst dots (~100 nm in diameter and ~40 nm thick) are prepared on Si substrates using conventional electron-beam lithography. A 10 nm thick Ti layer is deposited between the Ni catalyst and Si substrate to prevent catalyst silicide formation at the moderately high growth temperature of ~700° C. The sample is mounted directly on a heater plate, which served as a cathode. After reaching the base pressure, ammonia (NH₃) is introduced into the chamber and the sample is pretreated with the NH₃ plasma and temperature. As a result of this treatment, catalyst nanoparticles are formed from the deposited

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catalyst dots. With the diameter and thickness used here, only a single nanoparticle is formed from each catalyst dot. These nanoparticles act as the necessary seeds for the catalytic growth of isolated VACNFs. After the pre-etching step, with the NH_3 plasma still on, acetylene (C_2H_2) is introduced into the chamber and the VACNF growth began. The VACNF tip diameter is approximately equal to that of the nanoparticle. Fig. 2 shows SEM images of an individual VACNFs and an array of VACNFs.

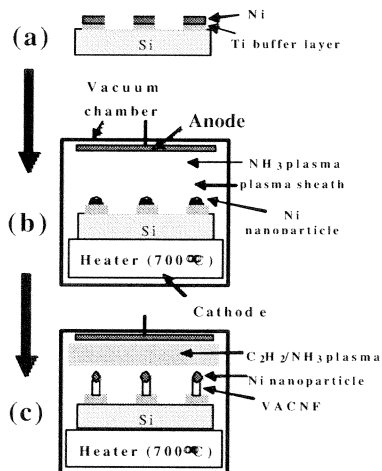


Fig. 1. Typical VACNF growth process.

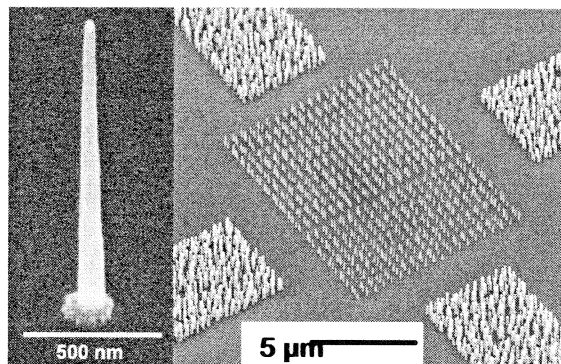


Fig. 2. (a) SEM image of an individual VACNF. (b) SEM image of a VACNF Array

We have demonstrated that this process provides a great deal of control over VACNF synthesis. In addition to placement and diameter that can be selected through

manipulation of the catalyst particle, VACNF orientation (12, 13), shape (4, 8), and chemical composition (2, 3, 7) can be controlled by manipulation of the growth process. Fig. 3 demonstrates both the control of orientation using the plasma E-field (13), and the control of VACNF shape using plasma gas mixture (8).

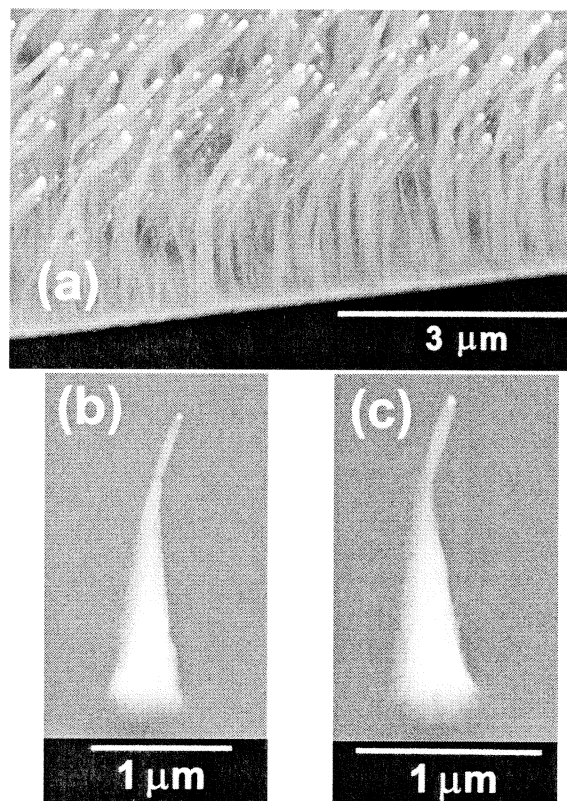


Fig. 3. Examples of the controlled synthesis of VACNFs.

3. VACNF Devices

The controlled synthesis of VACNFs allows the realization of a variety of functional nanoscale devices. We have described field emission or vacuum microelectronic (10, 11, 14-17) biomimetic (18), electrochemical (9), and other (19) devices that make use of VACNF controlled synthesis and directed assembly properties. Examples of these devices are shown in Figs. (4) – (6)

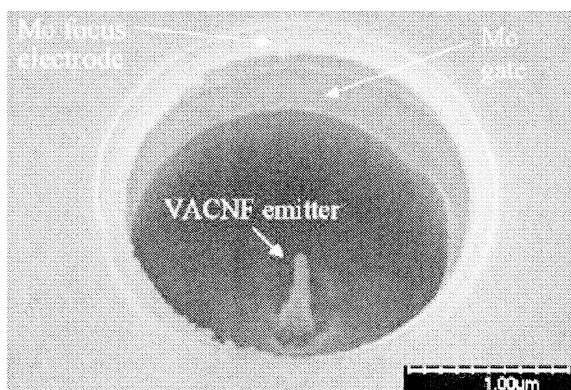


Fig. 4. A triode device constructed with a VACNF field emission element.

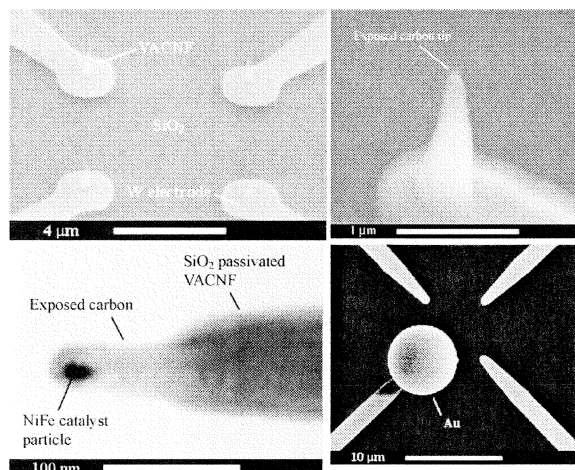


Fig. 5. Nanoscale electrochemical realized using VACNF active elements. (a) Array of four individually addressable elements. (b) and (c) Close-up images showing the exposed VACNF tip and the insulated shaft. (d) A Au sphere electroplated onto one of the VACNF elements.

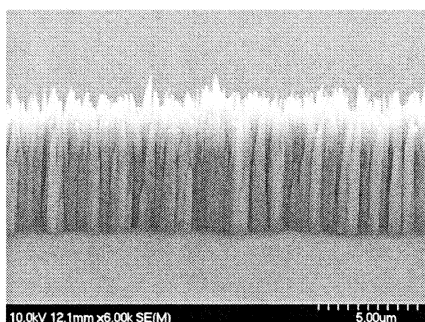


Fig. 6. An array of VACNF used as a membrane mimic.

4. Conclusions

We have briefly described the controlled synthesis and directed assembly of vertically aligned carbon nanofibers. We have demonstrated the utility of this nanoscale synthesis process by showing several types of devices that have been constructed using VACNFs as the functional element.

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