

Single-Wall Carbon Nanotube Devices Prepared By Chemical Vapor Deposition

P.R. Poulsen, J. Borggreen, J. Nygård, D.H. Cobden, M.M. Andreasen,
and P.E. Lindelof

Ørsted Laboratory, Niels Bohr Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Abstract. We have fabricated single-wall carbon nanotubes by chemical vapor deposition from methane using a catalyst consisting of iron oxide with molybdenum supported by alumina particles. The nanotubes are grown both on loose catalyst powders, which allows for transmission electron microscopy studies, and on catalyst islands deposited on a substrate to enable direct growth on the substrate surface and subsequent evaporation of metal electrodes over the nanotubes for transport measurements. In the latter case, the nanotubes are characterized by scanning electron microscopy and atomic force microscopy. They are found to be single-walled and occur both individually and in small bundles.

1. INTRODUCTION

The standard methods for single-wall carbon nanotube (SWCNT) production rely on co-vaporization of graphite and transition metal catalysts in an inert gas atmosphere, either by an electrical arc [1,2] or by laser vaporization [3]. During the last three years, however, chemical vapor deposition (CVD) using hydrocarbons as feedstock has emerged as a promising alternative for SWCNT synthesis [4,5]. The advantages of CVD include lower preparation temperatures, simpler equipment, better perspectives for large-scale production, and the possibility to grow long and impurity-free carbon nanotubes in specified locations on a substrate for incorporation into electronic devices. In the present work we describe our success in CVD-growth following the technique introduced by Kong *et al.* [6,7]. The nanotubes are grown from methane using catalysts consisting of iron oxide with molybdenum supported by alumina particles. We confirm that this is indeed a practical and straightforward method for making SWCNT devices.

2. EXPERIMENTAL

Two types of catalysts were produced: a powder catalyst and a suspended catalyst. The powder catalyst was prepared in a similar way to that reported in ref. [5]. 1 g of alumina nanoparticles (Degussa, 'Aluminiumoxid C'), 228 mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 12 mg $\text{MoO}_2(\text{acac})_2$ were added to 30 ml methanol. The suspension was stirred overnight before the solvent was evaporated in a rotary evaporator. The resulting powder was ground in a mortar and baked overnight at 180°C.

A suspended catalyst was made either by sonicating 1 mg of the powder catalyst in 1 ml methanol, or by a procedure similar to that described in ref. [6]. In the latter case, 15 mg alumina nanoparticles, 20 mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 5 mg $\text{MoO}_2(\text{acac})_2$ were added to 15 ml methanol, sonicated for 1 h, stirred overnight, and sonicated for 1 h again. One drop of the suspension was placed on a substrate surface, which was then spun at 2000 r.p.m. for 60 seconds. The substrates were either bare Si wafers or thermally grown SiO_2 covered with a layer of polymethylmethacrylate (PMMA) in which windows had been patterned by electron beam lithography. In the latter case, the PMMA was removed in acetone after the catalyst deposition, leaving isolated islands of catalyst particles on the surface.

The CVD growth was performed with the powder catalyst or the substrates with spun-on catalyst particles in a tube furnace held at 900°C . A methane flow rate of $5000 \text{ bar}\cdot\text{cm}^3/\text{min}$ was maintained for typically 10 minutes at a pressure of $\sim 1.1 \text{ bar}$.

After CVD, grains of the powder catalyst were placed on holey carbon films for high resolution transmission electron microscopy (HRTEM) characterization. The results with the catalysts spun on substrates were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). SWCNTs grown on SiO_2 substrates were contacted electrically by a further lithography step and metal evaporation.

3. RESULTS

HRTEM images of the powder-grown material are presented in Fig. 1. Only SWCNTs were observed. When the nanotubes are very short, they are mostly individual and their closed ends can occasionally be resolved as for the 3 nm thick SWCNT in Fig. 1(a). Most nanotubes, however, grow to lengths of several micrometers. In that case, they often occur either as individual tubes or as thin bundles of a few tubes, which assemble to thicker bundles as illustrated in Fig. 1(b). Fig. 1(c) shows a part of a twisted bundle consisting of a few SWCNTs. Generally, the nanotubes appear defect-free with only occasional traces of amorphous carbon deposits on their surface.

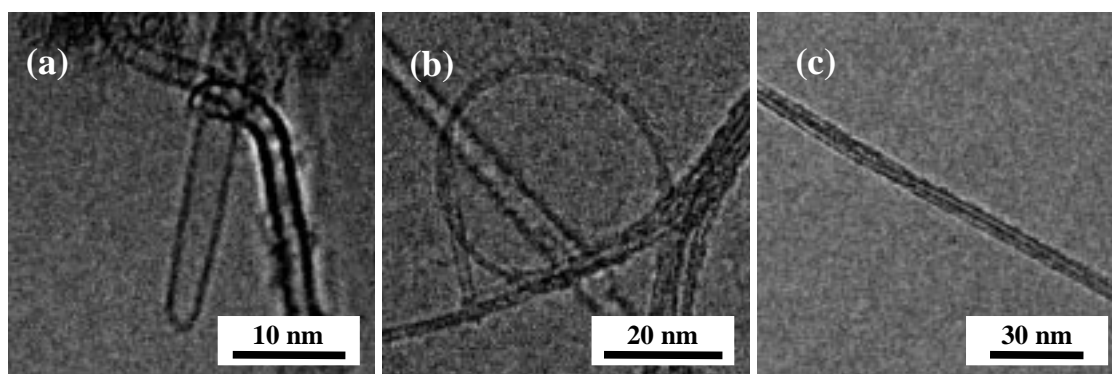


FIGURE 1. HRTEM images showing SWCNTs grown on the powder catalyst.

Fig. 2(a) and 2(b) are SEM micrographs of a large and a small powder catalyst grain, respectively, after CVD synthesis. A web-like network of nanotubes is covering

the catalyst surface. As seen in Fig. 2(b), nanotubes are extending to, and lying on, the surface that supports the catalyst grains.

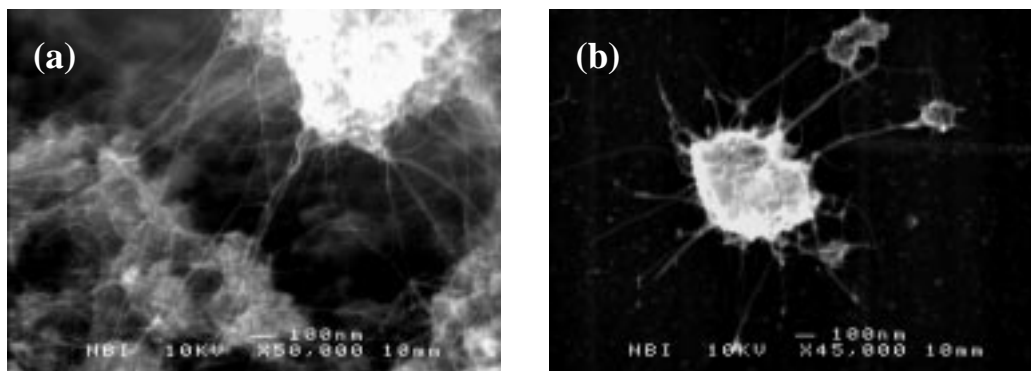


FIGURE 2. SEM images showing nanotubes grown on powder catalyst grains lying on a Si support.

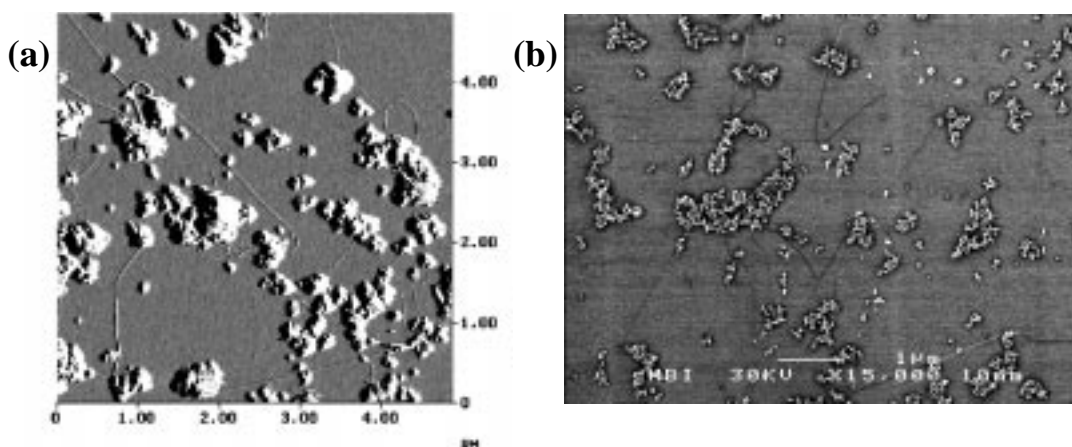


FIGURE 3. (a) AFM and (b) SEM images showing carbon nanotubes grown from suspended catalyst particles that have been deposited uniformly on a Si surface.

When suspended catalyst particles were deposited on a substrate, the CVD growth lead to nanotubes that lie on the substrate surface as illustrated in Fig. 3. Similar results were obtained with both types of catalyst suspensions.

The height of the nanotubes measured by AFM is in the range from 0.5 nm to ~4 nm, consistent with their being either individual SWCNTs or very thin bundles. Often nanotubes or thin bundles are seen to merge into a thicker bundle, or to change thickness abruptly. Also kinks are occasionally observed.

In the SEM micrograph in Fig. 3(b), the nanotubes appear dark in regions where they touch the surface, and white in those parts that are supported on catalyst particles rather than on the silicon surface.

Fig. 4(a) is an example of nanotubes that have been grown on a substrate with lithographically defined catalyst islands. Selected nanotubes grown on SiO₂ surfaces were successfully contacted by evaporating metal contacts over the nanotube ends. An example is shown in the SEM micrograph in Fig. 4(b) where the two contacts consist of 6 nm chromium under 43 nm of gold. The resistance of this particular nanotube at

room temperature was 51 k Ω . With a metallic-doped silicon substrate used as gate, such devices can operate as field effect transistors [8].

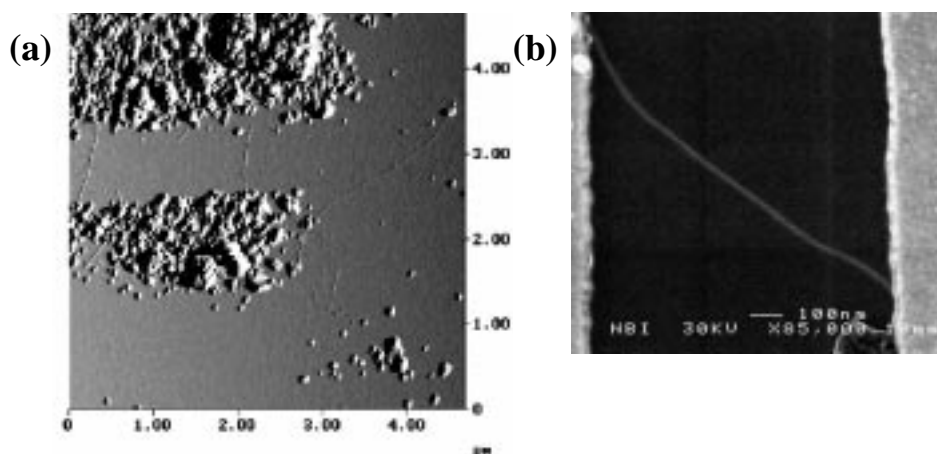


FIGURE 4. (a) AFM image of carbon nanotubes bridging catalyst islands on a Si surface. (b) SEM image showing two Cr/Au contacts evaporated on top of a nanotube which runs across a SiO₂ surface.

4. CONCLUSIONS

We have confirmed that CVD is a practical method for growth of SWCNTs directly on a substrate surface, allowing for integration of the nanotube growth into the fabrication of electronic devices based on carbon nanotubes.

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