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Batch processing of nanometer-scale electrical circuitry based on in-situ grown single-walled carbon nanotubes

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Abstract

We present a fabrication method for a nanometer-scale conducting network made of self-assembled single-walled carbon nanotubes. The electrical connection of the suspended nanotubes to the metallic contacts is obtained during the nanotube synthesis itself, which involves the hot-filament CVD technique. We directly characterize, without any further processing, the electronic transport properties of samples with different pad geometries. At room temperature, all tested samples show ohmic behavior in the kΩ range, for both two-probe and four-probe geometries. At low temperature, non-linear transport is observed and a large discrepancy of resistance arises between two-probe and four-probe geometries, suggesting the dominant influence of the contact resistance. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Single-walled carbon nanotubes (SWNT) can be described as cylindrically shaped carbon molecules composed of a rolled up single sheet of graphite [1]. Since their discovery 10 years ago, they have proven to be an exceptional material in many fields covering mechanics and nanoelectronics. One of their main characteristics is their exceptional geometrical ratio. Typical diameters are of the order of 1 nm and the length can reach a few μm. On the other hand, SWNTs possess outstanding electronic transport properties. They can act as nearly ideal 1D quantum wires with two conduction channels. Moreover, depending on the wrapping angle of the carbon sheet, they behave either as a metal or as a semiconductor.

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For all these reasons, SWNTs appear to be very promising nanostructures to bridge the technology gap between nanoelectronics and the emerging field of molecular electronics [2]. In the past few years, the possibility of using SWNTs as 1D wires in passive electronics has been demonstrated [3]. Moreover, the ability to selectively dope carbon nanotubes [4] and to perform intramolecular functionalization [5] has recently opened up the possibility of using nanotubes as active electronic devices.

However, in most cases, building a reliable electrical contact between nanotubes and metallic contacts involves difficult and time-consuming manipulation and alignment steps [6–8]. These are non-compatible with the connection of a large assembly of nanotubes on the same circuit. In order to become a technology suitable for VLSI, one should be able to grow SWNTs on specific locations in a single batch process. Our idea is to perform the connection of the SWNT during the synthesis itself, thus suppressing the critical manipulation/alignment steps. For that purpose, we prepared and characterized nanometer-scale electrical circuitry based on a self-assembled single-walled carbon nanotube network. Further study of the electronic transport properties can then be performed without any post-growth treatment.

2. Device fabrication

The carbon nanotube network was synthesized using the hot filament chemical vapor deposition (HFCVD) technique [9]. The self-assembled nanostructure was grown from pre-patterned sub-micron metallic contacts which act as ''catalytic anchors'' [8].

A mixture of methane and hydrogen comprises our CVD precursor. A tungsten filament, placed 1 cm above the substrate holder, was heated in the 1900–2100 °C temperature range. We controlled the deposition temperature with an additional heater placed in the substrate holder. Typical deposition temperatures were in the 700–900 °C range.

Starting substrates were thermally oxidized silicon wafers. Sub-micron contacts were defined by evaporation of a 50 nm thick layer of titanium followed by a thin Co catalyst film through a lift-off mask obtained using conventional e-beam lithography.

Fig. 1 shows typical SEM images of SWNT growth morphology on pre-patterned samples with

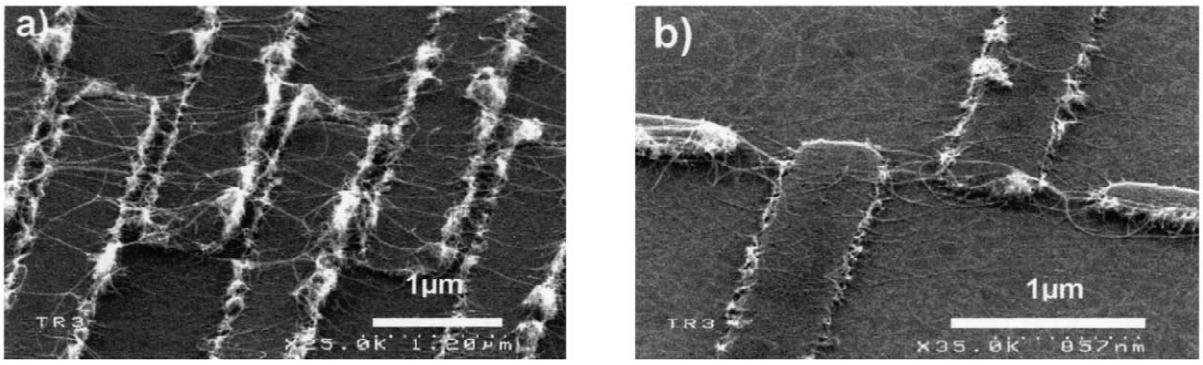

Fig. 1. Scanning electron micrographs of SWNTs linking pre-patterned titanium contacts in a brush-like geometry (a), and in a cross geometry (b).

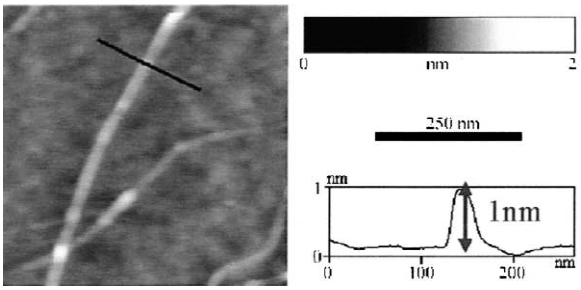

Fig. 2. Atomic force micrograph acquired in non-contact mode of a nanotube deposit prepared by HFCVD on an oxidized silicon substrate. The 1 nm high cross section (right) ensures that the imaged nanotube is single-walled.

contacts following either a brush-like geometry (Fig. 1a) or a cross geometry (Fig. 1b). Bridging of the metallic contacts by carbon nanotube bundles of 10–20 nm diameter is clearly evidenced. Improving the synthesis conditions allowed us to reduce the diameter of the SWNT bundles. As shown in Fig. 2, the ability of the process to grow isolated single-walled carbon nanotubes is confirmed by atomic force microscopy.

3. Sample characterization by Raman spectroscopy

Samples were characterized by micro-Raman spectroscopy at 633 nm, probing an area of the order of 1 μm^2.

Raman spectroscopy is a very useful probe for obtaining structural data from nanotube deposits [10]. The resonant frequency characterizing a specific vibration, the so-called ''radial breathing mode $\overline{\omega}_{RBM}$ '', can be directly related to the SWNT diameter according to the relation $d = a_0/\overline{\omega}_{RBM}$, with $a_0 = 248$ nm cm^{-1} [11].

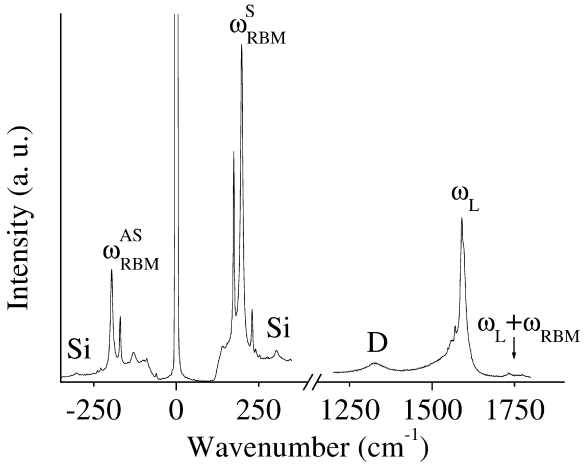

Fig. 3. Raman spectrum of suspended SWNT bundles. $\overline{\omega}^{S,AS}_{RBM}$ and $\overline{\omega}_L$ correspond, respectively, to SWNT radial breathing modes, Stokes (S) or anti-Stokes (AS), and to longitudinal modes. Si indicates Raman lines of the substrate at ± 303 cm^{-1}.

Fig. 3 shows a typical Raman spectrum of the suspended SWNT bundles illustrated in Fig. 1a. The Raman signal confirms the growth of SWNT bundles. It is composed of Stokes and anti-Stokes RBM lines in the $\pm$128–460 cm^{-1} wavenumber range, as well as longitudinal Raman lines around 1200–1600 cm^{-1} and second-order Raman modes in the 1730–1780 cm^{-1} range.

Probing different areas of the sample leads to a shifting of the RBM peak due to the diameter dispersion from location to location on the sample. Statistical measurements of the diameter histogram averaged over different sample areas indicate a mean diameter of 1.17 nm with a standard deviation of 0.27 nm.

The absence of any Raman carbon signals other than those attributed to the SWNT, combined with the strong intensity of the RBM modes as compared to the longitudinal mode, and the low intensity of the ''D'' band near 1330 cm^{-1}, provides strong evidence of the purity of our samples.

To our knowledge, similar results have only been obtained using a CVD deposition method for which nanometer-sized iron particles acted as catalysts [12].

4. Electrical transport measurements

For electronic transport measurements, two types of electrical connections were tested. The first geometry (the so-called ''brush geometry'') involves two interdigitized electrodes (see Fig. 1a). It has the advantage that we can maximize the developed length of the metallic edges of each electrode facing each other; the probability of bridging each contact with SWNTs is then optimized. The second geometry tested (the so-called four-probe geometry) is much closer to situations that could be encountered in large-scale integration. The nanotube deposits link four fingered metallic electrodes that can be independently contacted. Such a structure allows a four-wire measurement in a region of length 2–3 μm (Fig. 1b).

Electrical transport measurements were performed using either the constant current or the constant voltage method. Four-probe measurements were conducted using a lock-in technique, while cryogenic measurements were performed in a liquid-helium dewar.

All samples tested exhibited purely ohmic behavior at room temperature, varying between 1 and 100 kΩ (see Fig. 4a). We checked that the conductance for samples synthesized with the same CVD parameters scaled linearly with the number of nanotubes involved in the contacts. As expected, the samples based on the ''brush'' geometry showed the lowest resistance, suggesting that many nanotubes are connected in parallel.

Gate polarization can be obtained by biasing the bulk silicon substrate. No gate effect was observed either at room temperature or at low temperature. This suggests that conduction is predominantly dominated by metallic SWNTs, while semiconducting ones are either marginally synthesized or completely shunted by the metallic ones.

At low temperature (Fig. 4a), all samples showed increased resistance of at least 40% with respect to room temperature. Furthermore, reproducible non-linear transport is observed for voltages below 20 mV. Finally, a discrepancy of three orders of magnitude occurs between the resistance obtained using two-wire and four-wire probing (see Fig. 4b). This indicates that a contact resistance with an energy barrier exists between the nanotube and the contact. Further post-treatment [6] could diminish the influence of the contact resistance.

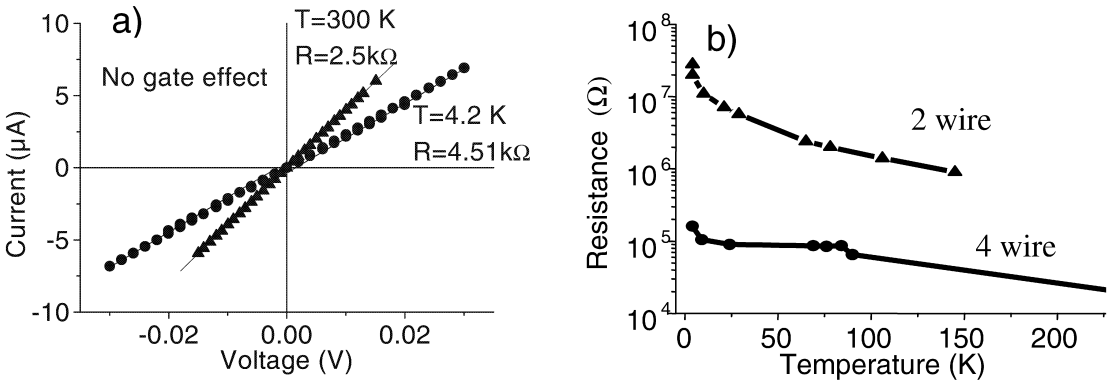

Fig. 4. (a) *I–V* characteristic of the typical ''brush geometry'' device shown in Fig. 1a at 300 and at 4.2 K. (b) Temperature dependence of the resistance of the ''cross'' device shown in Fig. 1b following two-wire and four-wire probe geometry.

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