

Field evaporation tailoring of nanotubes and nanowires

P Poncharal, P Vincent, J-M Benoit, S Perisanu, A Ayari, M Choueib and S T Purcell

Laboratoire de Physique de la Matière Condensée et Nanostructures (UMR CNRS 5586),
Université Claude Bernard, 69622 Villeurbanne, France

Received 19 January 2010, in final form 29 March 2010

Published 30 April 2010

Online at stacks.iop.org/Nano/21/215303

Abstract

We explore here the use of field evaporation in a transmission electron microscope for controlled apex modification, opening, and shortening of various types of individual nanotubes and nanowires. The technique works well for conducting carbon nanotubes but also for large bandgap silicon carbide nanowires and insulating boron nitride nanotubes. Since the length reduction does not affect the diameter of the object, we can thus compare mechanical properties at a given diameter for different lengths or, conversely, precisely tune the mechanical resonance frequencies. Opening the nanotubes also creates perspectives for their use as nano-capillaries.

Controlling the length and diameter of nanotubes and nanowires (NNs) is a key issue for their use in nano-electro-mechanical systems (NEMS) [1]. Since the direct control of nanotube dimensions during growth is still elusive [2], post growth modification methods are required to obtain predefined mechanical resonance frequencies.

One way to tune the resonance frequencies of NNs is by electrostatic tuning [3]. The electrostatic force stretches the NNs and thus tunes the frequency, similar to the tuning of a guitar string. Despite its simplicity and fairly large tuning range (up to 20×), electrostatic tuning cannot be used in all integrated systems to accord the resonator frequency as rather high DC bias may be required.

Several methods have been proposed to shorten nanotubes to the required lengths, of which STM [4] or AFM [5] cutting are the more accurate, but these have only been done with nanotubes deposited on surfaces. E-beam assisted cutting [6], and current-induced failures during field electron emission [7–9] have been used to shorten free-standing nanotubes that can be used as cantilevers for NEMS. However, except in special cases the accuracy of these methods is often too poor to ensure adequate fine tuning (accuracy ~ 100 nm) and the high induced temperatures can change the nanotube properties. The field emission method suffers two main drawbacks. Firstly, the object has to be conductive to reach large current densities. Secondly, these failures are abrupt and highly unstable, leading to uncontrolled shortening. Moreover the remaining tip is usually torn apart, which might affect its final properties (see [7] for field emission). In a recent paper, however, Chin *et al* [9] have shown a better control of the

final shape by running current through a nanotube contacted between two metallic tips. Their length control remains, however, around 10 nm and the nanowire must be electrically conductive.

We describe here a method based on field evaporation [10] that allows much finer length control (sub nanometer range), ensures a clean open tip termination and does not modify the properties along the length of the nanotubes. Field evaporation removes atoms from the tip through the action of high electric fields and is the basis of the atom probe [11]. It occurs for positive fields (F) roughly 10 times higher than the negative fields required for electron extraction (i.e. ~ several volt per angstrom) and, in contrast to shortening by current-induced-heating, this method can be applied to low conductivity or insulating materials such as SiC or BN as there is typically negligible electrical current flow. In principle, evaporation can be controlled to the single atom level. Field evaporation has been used previously to open multiwalled carbon nanotubes (MWNTs) in a field emission microscope [12] and to analyze Si nanowires in an atom probe [13], but without detailed transmission electron microscopy (TEM) sideviews, imaging of the length changes, or exploration of the variable resonance frequencies of the nanowires.

MWNTs were prepared using the arc-discharge method [14]. Details of their structural quality and diameter distribution can be found in [15]. SiC nanowires and BN nanotubes were produced by a patented vapor–solid process [16, 17].

The NNs were glued onto electrochemically etched tungsten tips. Such tips were then fixed on a custom built

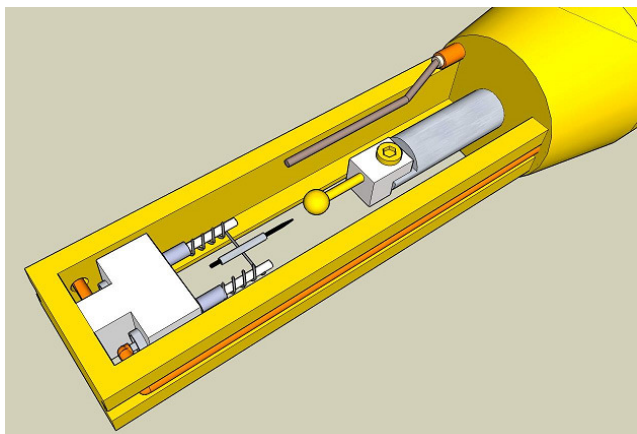


Figure 1. Sketch of the specially designed TEM sample holder. The tips were mounted on a resistive heating loop (left) that could be floated up to 2 kV. The electrode (ball on the right) is mounted on a one-axis micrometer that permits *in situ* control of the electrode–tip distance. The RF lead appearing on the top radiates into the TEM cavity for electro-mechanical resonance studies.

(This figure is in colour only in the electronic version)

TEM sample holder (figure 1) equipped with a radiofrequency (RF) lead and with a heating stage that can be floated up to 2 kV. A grounded spherical electrode (on the right on figure 1) can be approached *in situ* from the tip (on the left) using an external micrometer. Typical distances used in our experiments are in the range of 10 μm . Shorter distances are technically possible, but were not required. Images were recorded with a 200 kV TEM (TOPCON) using a wide gap pole-pieces that can accommodate the sample holder. The resolution is thus limited compared to the standard high resolution setup but was sufficient for our purposes.

The RF lead allowed us to excite the NNs, thus determining their mechanical resonance frequencies. The Young's modulus could then be extracted once the length and diameter were determined and the Q factor could be measured directly from the images [18]. Applying a negative bias to the tip allows field emission experiments which we do not explore in this paper.

Figure 2(a) shows a sequence of the field evaporation shortening of a carbon MWNT (arrow) for about 50 nm in total (a much finer control is possible—see below). We have accompanied the observation of the length changes with measurements of the mechanical resonance frequency, ν_M of the cantilever. Length and resonance measurement were done at zero applied field. From classical mechanics, $\nu_M \propto L^{-2}$ for a fixed diameter. Figure 2(b) reports ν for four shortening steps. The predicted $\nu_M \propto L^{-2}$ dependence is well respected which demonstrates that field evaporation does not modify the nanotube mechanical properties. Note that the two other carbon nanotubes at the top of the picture do not evaporate as the local electrostatic field is different and thus below the evaporation threshold. They are nevertheless pulled by electrostatic forces (see also [18] for an example of static deflection) and are finally detached from the tip when the electrostatic pulling force exceeds the nanotube–tip attachment strength (in the last image).

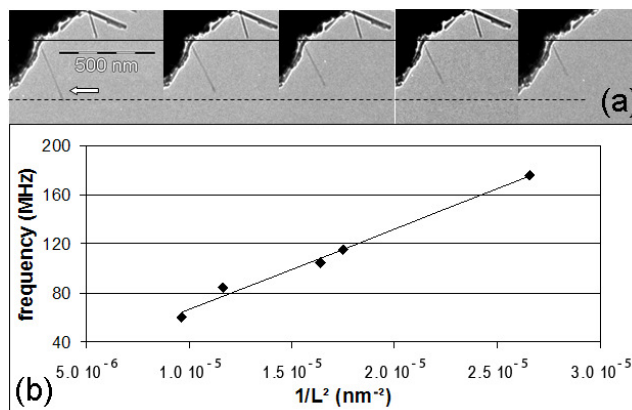


Figure 2. (a) From left to right, four steps of a length reduction sequence observed on a carbon MWNT (arrow). (b) Measured mechanical resonance frequency plotted as a function of $1/L^2$ showing the expected linear behavior.

For a studied carbon MWNT, we estimate the length reduction rate to be $\simeq 5 \text{ nm s}^{-1}$ for the specific experimental conditions of applied bias, $V_A = 1 \text{ kV}$ and temperature, $T \simeq 800 \text{ K}$. Despite the low resolution that prevents us from exactly counting the number of layers, we estimate for a specific MWNT an evaporation rate of $\sim 2 \times 10^4$ carbon atoms s^{-1} (15 nm in length were removed in 3 s for a 8 nm outer diameter and 4 nm inner diameter nanotube). The Arrhenius–Frenkel formula for the frequency of atom evaporation can be written as equation (1) where $E_d(F)$ is the field-dependent evaporation energy. The local electrostatic field F is expressed in (V m^{-1}). In this simple model, ν_0 is the attempt frequency with which an atom tries to accumulate the escape energy E_d .

$$\nu = \nu_0 \exp(E_d(F)/k_B T). \quad (1)$$

The evaporation energy can be expressed as [19]

$$E_d(F) = \Lambda + \Sigma I_n - n\Phi_0 - (ne)^{3/2} F^{1/2} / (4\pi\epsilon_0)^{1/2} \quad (2)$$

Λ the sublimation energy, ΣI_n the total ionization energy for an n charged atom and Φ_0 the work function. The value of ν_0 depends on the adsorption type and is $\sim 10^{13} \text{ s}^{-1}$ for physisorption [20].

The field F at the NNs apexes is of course higher than the applied voltage divided by the distance between tip and counter electrode because of the tip effect. This effect is encapsulated in what is called β , the geometrical field enhancement factor. The exact value of F is thus rather hard to calculate because it is very sensitive to local geometrical details.

As the β factor is length dependent, field evaporation turns out to be self-limited i.e. for a given voltage, the NNs length will reduce following equation (1) until the local field reaches a threshold value and stays stable.

In principle, one can extract F from our experimental data from the measured evaporation rates. However, the main problem here is to know if carbon will evaporate as a monomer, dimer, or larger sized clusters that could be singly or doubly charged. According to Miller and Smith [21], the most common species experimentally observed in field

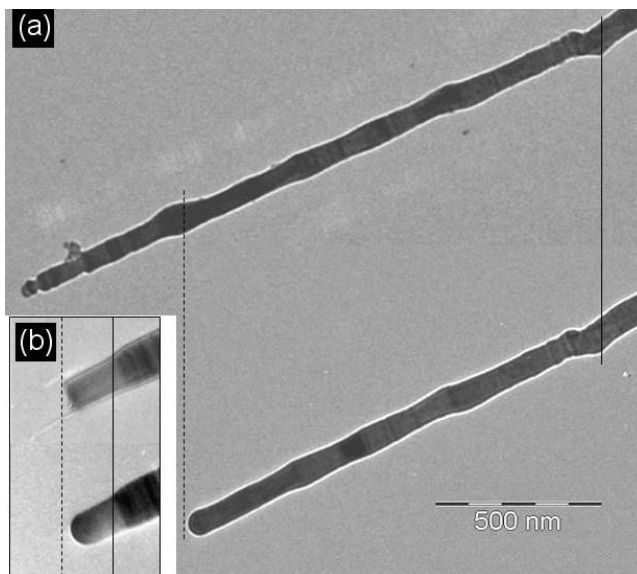


Figure 3. Example of field evaporation on SiC nanowire. (a) Initial nanowire (top) and final state (bottom) after a length reduction of about 500 nm despite the highly insulating characteristics of the material. Vertical lines are guides for the eye. (b) Top: fractured tip of a SiC nanowire (100 nm diameter) used to demonstrate a much finer desorption work, the result (bottom) is a smooth field-controlled shape.

evaporation of carbon ranges from C to C₃, singly or doubly charged. We have then only considered these commonly occurring charged states and used tabulated values collected from different sources for carbon cluster ionization potentials, sublimation, and formation energy [22–24], as well as carbon nanotube workfunction [25].

Using equation (2) for these different species (C⁺, C²⁺, C₂⁺, C₂²⁺, C₃⁺ and C₃²⁺) with our measured evaporation rate and temperature, we found a value of F between 7 and 9 V Å⁻¹. Although this value is rather high compared to the usual value of 4–5 V Å⁻¹ for metallic tips, it compares well with recent results obtained in the pulsed field evaporation of graphite (8 V Å⁻¹ [26]) and with the calculated value of 10.3 V Å⁻¹ for doubly charged carbon ion field evaporation [21].

To demonstrate that this method can be applied to poorly conducting materials, we tested it on SiC (bulk resistivity about 10⁵ Ω cm) nanowires and BN (bulk resistivity > 10¹⁴ Ω cm) nanotubes. In the reported experiments, and for the sake of comparison, we have decided to use the same temperature as for carbon nanotubes (i.e. 800 K) for these two materials. We found that SiC nanowires are more difficult to evaporate than carbon nanotubes, but surprisingly BN nanotubes evaporate quite easily. Note that the NNs defect concentration and conductivity might differ significantly from bulk values. Temperature effects are currently under study.

In figure 3, a poly-crystalline SiC nanowire is shortened progressively by about 500 nm. In principle, the evaporation rate can be arbitrarily slowed down, either by decreasing the voltage or the temperature. Figure 3(b) shows a better controlled process on another SiC tip. The 20 nm reduction during which the fractured SiC nanowire tip is rounded was

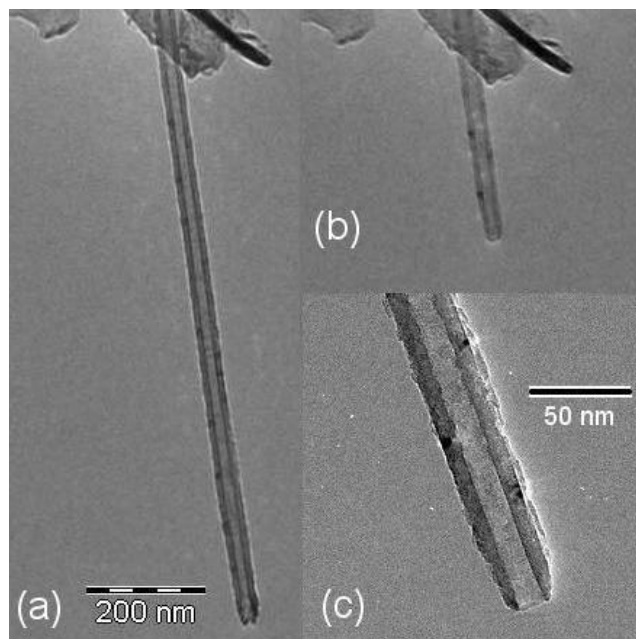


Figure 4. Example of field evaporation of a boron nitride nanotube. About 600 nm of length have been evaporated between images (a) and (b). (c) Magnified image of the final end that shows that evaporation leaves the nanotube tip open.

obtained after 6 min, i.e. roughly 0.5 Å s⁻¹ evaporation rate. The tip structure is extremely smooth as evaporation will follow the equipotential contours with atomic accuracy. Figure 4 shows results obtained for a BN nanotube. A total length reduction of about 600 nm was easily obtained. Note also that on hollow structures, the field evaporation process leaves an open end unlike Joule heating where excess energy will be available to reorganize and close the structure. This is thus a very controlled way to prepare nano-capillary tubes.

In this paper we have used field evaporation to shorten individual NNs to chosen lengths with nanometric accuracy. Unlike the shortening of nanotubes by Joule heating, this method can also be applied to insulating materials. Small and large length reductions, sub-nanometer to several hundreds of nanometers, are routinely achieved over controllable timescales without degradation of the overall cylindrical shape of the object.

Acknowledgments

This work was supported by French National Research Agency (ANR) through its *Nanoscience and Nanotechnology* Program (NEXTNEMS, ANR-07-NANO-008-01), *Jeunes Chercheuses et Jeunes Chercheurs* Program (AUTONOM, ANR-07-JCJC-0145-01), the Région Rhône-Alpes *CIBLE* Program and the 'Plateforme nanofils et nanotube lyonnaise de l'Université Lyon1'. The authors acknowledge M Bechelany and D Cornu for their fruitful collaboration. Special thanks to D Guillot for his technical support.

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