Ultramicroscopy ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Framed carbon nanostructures: Synthesis and applications in functional SPM tips

I.S. Mukhin [a,b], I.V. Fadeev [b], M.V. Zhukov [b], V.G. Dubrovskii [a,b,d], A.O. Golubok [b,c]

[a] St. Petersburg Academic University, Khlopina 8/3, 194021 St. Petersburg, Russia
[b] ITMO University, Kronverksky pr. 49, 197101 St. Petersburg, Russia
[c] Institute for Analytical Instrumentation of the Russian Academy of Sciences, Rizhsky 26, 190103 St. Petersburg, Russia
[d] Ioffe Physical Technical Institute of the Russian Academy of Sciences, Politekhnicheskaya 26, 194021 St. Petersburg, Russia

ARTICLE INFO

Article history:
Received 29 November 2013
Received in revised form
3 October 2014
Accepted 7 October 2014

Keywords:
Framed carbon nanostructures
Nanoscalpel
SPM probes
Growth model
Nanomanipulation
Nanosurgery

ABSTRACT

We present a synthesis method to fabricate framed carbon-based nanostructures having highly anisotropic shapes, in particular, the nanofork and nanoscalpel structures which are obtained systematically under optimized growth conditions. A theoretical model is developed to explain the formation of such nanostructures on Si and W cantilevers exposed to a focused electron beam. We then demonstrate the potentials of these nanostructures as functional tips for scanning probe microscopy. Owing to their anisotropic shapes, such tips can be very useful for nanolithography, nanosurgery of biological objects, and precise manipulation with surface particles. Overall, our method provides a simple and robust way to produce functional scanning probe microscopy tips with variable shapes and enhanced capabilities for different applications compared to standard cantilevers.

1. Introduction

Carbon nanomaterials of different types, such as nanodiamonds [1], fullerenes [2,3], graphenes [4,5], nanotubes [6–8], and nanowires [9], have recently gained a rapidly increasing interest for their unique fundamental properties and promising applications. By pursuing advanced nanofabrication methods, rather sophisticated functional nanomaterials can be synthesized which combine carbon nanostructures of different types. In particular, using carbon-based nanotubes or nanowires as building blocks, one can produce functionalized framed carbon nanostructures (FCNSs) with tunable geometry [10]. These FCNSs can be grown from a gaseous carbon environment. Formation process is induced by a focused electron beam, either via the directional catalyzed elongation or by the self-induced mechanism, as in the case of semiconductor nanowires [11,12].

FCNSs present an interesting example of nanographs with tunable orientation and dimensionality. From fundamental viewpoint, such nanographs can become quantum graphs [13] under certain conditions. FCNSs can be used as functional elements of nano-antennas or specialized tips for scanning probe microscopy (SPM). Such tips can be advantageous for visualization of deep channels or vertical walls, nanomodification of solid surfaces, manipulation of micro- and nano-objects, and in nanosurgery.

Consequently, this paper is devoted to synthesis, characterization and SPM applications of FCNSs constructed from highly anisotropic carbon nanowires or nanosheets with different arrangements. A high aspect ratio of "nanoscalpel" geometries considered hereinafter can bring about some new capabilities compared to the standard silicon cantilevers whose aspect ratio is of the order of one. Indeed, a symmetric cantilever has limitations in visualization of deep asymmetric channels, in particular, for the precise determination of the position and length of sharp elongated structures such as submicron surface steps or horizontal nanowires. In lithography, the channel profiles always reflect the geometry of the cantilever tip used and thus it is hard to achieve deep and narrow microchannels as well as produce straight incisions with predefined depth (which is often required in nanosurgery). A small radius of the tip (1–50 nm) does not enable the necessary mechanical stability of the cantilever in contact with a submicron particle. This does not favor a robust micromanipulation with surface particles which need to be relocated over large distances from the origin.

2. Synthesis of carbon structures

Growth of FCNSs was performed on the tips of Si or W cantilevers fixed on a scanning electron microscope (SEM) stage, as shown in Fig. 1. The electron beam (1) exposes the cantilever tip (2) as well as the underlying target with a carbon coating (3) which produces a flux of carbon ions (4). The beam is focused either directly on the tip or up to 20 nm away from its edge, after which the beam is scanned on a small surface area (typically 15×15 nm^2). FCNSs (5) nucleate on

http://dx.doi.org/10.1016/j.ultramic.2014.10.008
0304-3991/

the tip surface exposed to the electron beam, and are monitored by SEM, which allows for a precise in-situ characterization of geometry.

In this method, the distance between the SEM tip and target and the type of the carbon film used do not critically influence the growth process. The distance between the tip and the target can be varied within a wide range from 5 to 20 mm, while the carbon coating of the target is accessed via standard thermal sputtering of carbon electrodes or by simply sticking a carbon scotch. It is noteworthy that carbon nanostructures can even be grown without any carbon coating if the residual atmosphere within the SEM vacuum chamber contains the C–H groups which play the role of a carbon precursor. Also, there is no direct correlation between the scan area and the size or geometry of the nano-objects produced. The geometry of the structure is defined by the trajectory of the focused electron beam, where the minimum size (~50 nm) is set by the area from which the secondary electrons are emitted rather than by the area exposed to the beam.

By varying the direction and the moving speed of the electron beam, the accelerating voltage and the current, we are able to tune the growth process of individual carbon nanostructures and to fabricate FCNSs of different types. In particular, varying the moving direction of the beam yields rather complex geometries that will be considered elsewhere.

Here, the simplest process is considered where the beam is moved along a fixed direction with a constant speed. In this case, we systematically observe a submicrometer-sized base, followed by several nanowires having 50–100 nm diameters and a parallel alignment, as in Fig. 2(a). We will call this shape "nanofork". The nanoforks are formed within the 25–30 keV window of the electron beam energy. A lower energy (15–25 keV) usually yields two-dimensional corrugated structures with a corrugation period of 50–100 nm, as in Fig. 2(b) and (c) (nanoscalpel [23]). Below 10 keV, the shape of FCNSs systematically transforms to a rod-like (Fig. 2(d)). X-ray chemical analysis of these FCNSs reveals that they are purely carbon structures.

In order to identify the crystal structure of the FCNSs, we performed the transmission electron microscopy (TEM) of the representative samples. The typical TEM images of a carbon nanoscalpel on top of a W cantilever are shown in Fig. 3, along with the corresponding electron diffraction patterns. The diffraction pattern in the insert of Fig. 3(a) reveals the presence of well-resolved bright spots and the two diffuse and low intensity rings. Fig. 3(b) displays the enlarged image of a nanoscalpel part close to its surface with the Fourier transform of the corresponding diffraction pattern shown in the insert. The bright spots on the diffraction pattern represent the (311) crystallographic direction of the W crystal, which is perpendicular to the tip axis. The diffuse rings in the insert of Fig. 3(a) and the broadened reflexes in the insert of Fig. 3(b) should correspond to a short-range order of C atoms in the nanoscalpel. Therefore, our FCNSs are deemed to have emerged in nearly amorphous form with a short-range crystallinity.

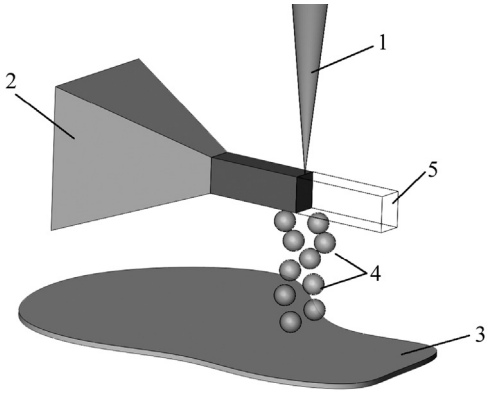

Fig. 1. Experimental setup for FCNS growth: (1) the electron beam, (2) the cantilever tip, (3) the underlying target with a carbon coating, (4) the influx of carbon ions, and (5) the growing carbon nanostructure.

3. Growth mechanism

Generally, two kinetic mechanisms for the formation of nanoforks or nanoscalpels could be considered: (i) coalescence of several nanowires into a plane FCNS or (ii) a self-induced decay of a plane FCNS into several parallel nanowires. In Ref. [14], we have proposed a simple model that is capable of describing the formation of flat FCNSs (nanoscalpels) under a focused electron beam. Within the model, ~30 keV electrons bombard a carbon target and induce a flux of carbon ions. The emitted ions are confined near the beam axis by the own electric field of the beam. As a result, growth of each FCNS is directed along the beam axis, while the linear displacement of the beam gives rise to a plane nanoscalpel shape. Numerical simulations have confirmed that such plane shapes eventually emerge, while the initial growth step leads to the formation of tapered submicrometer bases similar to that shown in Fig. 2(a). A more detailed modeling should account for different kinetic pathways of growth including the surface diffusion, the radial extension of nanowires and the coalescence mechanisms, as in Refs. [11,15–19]. This will allow for a better control over the entire growth process by technological parameters.

Here, we present only the elementary energetic considerations to explain the formation of the fork-like structures. From the SEM image shown in Fig. 2(a), we assume that the tapered base forms at the initial growth step and then transforms into the nanowires. We consider the model geometry shown in Fig. 4(a), with the cantilever tip of the width d_*, the tapered FCNS base of the length l_0 that extends toward the top with the taper angle α, and n identical rectangular nanowires having the width $d = const$ and height h_1 atop the base of width$d_0 = d_* + 2l_0 \tan\alpha$. The thickness of the whole structure equals $\Delta = const$. The total volume $V_1$and the surface energy F_1 of the nanofork structure in Fig. 4(a) are given by

$$V_1 = dnh_1\Delta; F_1 = \gamma_p\, d_0\Delta + 2\gamma_v nh_1(d+\Delta). \quad (1)$$

Here, γ_p is the surface energy of the planar interfaces that are parallel to the top surface of the tip and γ_v is the surface energy of all the vertical surfaces (see Fig. 4). While a uniform surface energy of all solid-vapor interfaces would be a good approximation for a completely amorphous and isolated FCNS, the asymmetry in surface energies could arise from the fact that the planes are oriented differently with respect to the electron beam (see Fig. 1). In any case, the nanowire fork is energetically preferred to the plane nanoscalpel structure which just continues to extend after the length l_0 [Fig. 4(b)] if the surface energy F_2 of the upper (dark) part of the structure shown in Fig. 4(b) is larger than F_1 for the same volume. Free energy of forming the nanofork is than lower due to a smaller surface energy term for the same volume energy [12]. The volume V_2 and the surface energy F_2 of the tapered nanoscalpel structure of the height h_2 are given by

$$V_2 = (d_0h_2 + h_2^2 \tan\alpha)\Delta; F_2 = \gamma_p(d_0 + 2h_2 \tan\alpha)\Delta + 2\gamma_v(d_0h_2 + h_2^2 \tan\alpha) + 2\gamma_i h_2\Delta/\cos\alpha. \quad (2)$$

where γ_i is the surface energy of the inclined surface as shown in Fig. 4(b). Taking the difference $F_1 - F_2$ under the condition $V_1 = V_2$, the nanofork is preferred to the nanoscalpel when the function

$$f(h) = h - \frac{d_0}{2}\left(\frac{\gamma_p}{\gamma_v} + \frac{\gamma_i}{\gamma_v \sin\alpha}\right)\left(\sqrt{1 + \frac{4dh\tan\alpha}{d_0^2}} - 1\right) \quad (3)$$

is negative, in which $h = nh_1$ is the effective height of the structure.

Please cite this article as: I.S. Mukhin, et al., Framed carbon nanostructures: Synthesis and applications in functional SPM tips, Ultramicroscopy (2014), http://dx.doi.org/10.1016/j.ultramic.2014.10.008