AFM and STM investigation of carbon nanotubes produced by high energy ion irradiation of graphite

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Abstract

Carbon nanotubes (CNT) were produced by high energy, heavy ion irradiation (215 MeV Ne, 246 MeV Kr, 156 MeV Xe) of graphite. On samples irradiated with Kr and Xe ions large craters were found by atomic force microscopy, these are attributed to sputtering. Frequently one or several CNTs emerge from the craters. Some of the observed CNTs showed a regular vibration pattern. No other carbon based materials, like amorphous carbon or fullerenes were evidenced. Focused ion beam cuts were used to compare CNTs with surface folds on graphite. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The investigation of carbon nanotubes emerged from the field of fullerene research originated by the work of Smalley, Kroto, and Curl in 1985 [1]. In 1991, Iijima observed the first carbon nanotubes using high resolution transmission electron microscopy [2]. The experimental and theoretical work showing the remarkable electronic, mechanical and quantum properties of these nanoobjects has been summarized recently [3,4]. Most recently, the room temperature operation of an electronic device, based on a single wall carbon nanotube – called “TUBEFET” – was demonstrated [5].

A single wall carbon nanotube is a single sheet of carbon atoms arranged like in graphite and faultlessly rolled into a cylinder. The typical
diameters of single wall nanotubes are in the range of 1 nm, while the multi-wall ones – built by “encapsulating” one into to other several single-wall tubes of increasing diameter, in a way that the distance between the concentric walls is 3.3 Å (i.e., the same like between the c planes of graphite) – may have exterior diameters up to 100 nm.

There are three well established methods to produce large quantities of carbon nanotubes: the electric arc method [6], the laser ablation method [7], and the catalytic procedure [8]. The first two are based on the generation of carbon vapors at typically 2000–3000°C, while in the catalytic procedure the building material for the growth of nanotubes is produced by dehydrogenation of hydrocarbons at 700°C. These methods yield together with the entangled, single-, or multi-wall carbon nanotubes other forms of carbon: fullerenes, bucky-onions, amorphous carbon, graphitic material, etc. The separation of carbon nanotubes is achieved by tedious chemical procedures.

In the present paper we describe a new method for the production of carbon nanotubes, which is based on the irradiation of highly oriented pyrolytic graphite (HOPG) targets with high energy (\(E>100\) MeV) heavy ions. This method yields individual carbon nanotubes of several microns length without producing amorphous carbon or other unwanted carbon based materials.

2. Experimental results and discussions

HOPG was irradiated with low dose, high energy, heavy ions: \(10^{12}\) \(\text{cm}^{-2}\), 215 MeV Ne or 246 MeV Kr, or with \(10^{11}\) \(\text{cm}^{-2}\) 156 MeV Xe. During the same run, HOPG, muscovite mica, and Si samples were irradiated. HOPG was freshly cleaved before irradiation, a special care was taken to avoid any post-irradiation contamination of the samples.

Sample evaluation was done by scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Although, for several years we investigated by STM and AFM in great detail the surface structures produced on all of these materials [9–11], we never found carbon nanotubes on Si, or muscovite mica, but we regularly found carbon nanotubes on the HOPG samples. STM examination was carried out in ambient atmosphere, in constant current mode, using mechanically prepared Pt tips. Typical tunneling currents were in the range of 1 nA, with biases of 100 mV, a wide range of scan speeds were used, but slow scans were preferred to obtain better resolution. Contact mode (CM) and tapping mode (TM) AFM were used in ambient atmosphere to image the irradiated samples. Tips with large radii of curvature, \(R>100\) nm were preferred, which due to convolution effects between the tip shape and the tube shape facilitated the finding of carbon nanotubes in scan windows of 100 \(\mu\)m².

On the HOPG samples irradiated with Kr and Xe ions, craters with diameters in the \(\mu\)m range and depths of 20–80 nm were found. A typical example is shown in Fig. 1. The volume of the missing material is estimated to be \(2\times10^{-14}\) \(\text{cm}^3\), this corresponds to \(2.28\times10^9\) carbon atoms. In the vicinity of the crater the height – i.e., the diameter – of the tubular object which emerges towards the upper side of Fig. 1(a), is 7 nm, its total length is 25.4 \(\mu\)m. Assuming that this object has at least two walls – a single wall nanotube would collapse at this diameter [12] – and taking in account that the diameter decreases continuously towards the end of the tube, one can estimate that the missing C atoms are sufficient for building 20 nanotubes of similar size. A smaller nanotube is seen in Fig. 1(a) emerging towards the lower, left corner.

The crater itself is attributed to sputtering produced by simultaneous, dense nuclear cascades – Brinkman type cascades [13] – propagating from the bulk of the sample towards the irradiated surface. This kind of a cascade may originate as a higher order event, i.e., after several collisions suffered by one of the knocked-on target atoms. To get more insight in this kind of process, the TRIM code [14] was used for modeling the crater production. 1 MeV C atoms slowing down in carbon will have a projected range \(R_p=1.2\) \(\mu\)m, and a radial spread of 1.16 \(\mu\)m at \(R_p\). The energies deposited during the slowing down of a 1 MeV C atom in carbon at a location at 1.2 \(\mu\)m from the point where the C atom started moving, are as follows: energy transferred to recoils, \(E_r=12\) eV/ ion/Å; energy of lattice vibrations, \(E_v=1.5\times10^{-2}\) eV/ ion/Å; and energy deposited by ionization,
$E_i = 7.9 \times 10^{-2}$ eV/ion/Å. These values show that when the region where the 1 MeV C atoms stop is close to the sample surface, crater production may take place, mainly, due to kinematic effects. In the case of simultaneous, dense, nuclear cascades, due to cooperative effects between neighboring sub-cascades, material corresponding to several atomic layers may be ejected from the sample surface. The fastest particles immediately leave the region while the slower ones generate an “expanding cloud” in which they may aggregate into carbon nanotubes. After the growth is terminated the nanotubes will collapse onto the surface of the target and they may vibrate if excited by the tip of the TM-AFM. The lighter region in Fig. 1 indicates that the cascade intersected the surface under a direction different from the normal.

In the case of heavier ions like Kr and Xe the surface densities of the nanotubes observed by AFM were in the range of 2–3$\times$10$^{-3}$ nanotube/μm$^2$ for the ion doses used. In the case of Ne ion irradiation with the same dose as Kr, the nanotubes were only rarely observed, but they were found on every sample investigated in detail. The sputtering rates given by TRIM simulation, expressed as the ratio of sputtered C atoms to the number of incident ions: 6$\times$10$^{-5}$ for Ne, 8.5$\times$10$^{-3}$ for Kr, and 2.3$\times$10$^{-2}$ for Xe show a similar trend.

In Fig. 2 a TM-AFM image of a carbon nanotube is presented, which originates from a
crater and shows a regular vibration pattern along the tube axis as seen in the line cut. The amplitude of the oscillation is 0.7 nm, while the associated spatial period is 194 nm. It has to be emphasized that the line cut running on the flat HOPG does not show any vibration, nor any profile taken across the crater, these observations exclude that the vibration pattern observed on the nanotube may be a consequence of improper imaging conditions.

To get a better insight in the way how does the TM-AFM generates the image of a vibrating object, computer modeling was used. As a first approximation a simple model consisting of a cylindrical rod of 36 nm diameter which vibrates with a period of 51.2 s was used. The rod was scanned in a window of 50×50 μm² at a scan frequency of 1 Hz by a tip with a radius of 300 nm. The window was sampled in 256×256 pixels, with an averaging of 64 kHz, the value used in the TM-AFM. Similar vibration patterns like those measured experimentally were obtained.

By high resolution STM imaging carbon nanotubes with an apparent height of 4 Å were found. Taking in account the reduction in the apparent height of a carbon nanotube laying on HOPG due to the differences in the electronic structure of HOPG and of the nanotube, and due to the existence of the second tunneling gap between the nanotube and its support, these objects may be identified with single wall carbon nanotubes.

When cleaving HOPG, surface folds may be produced. Although such folds are not expected to vibrate when scanned with the AFM, to clearly distinguish the nanotubes from these folds we used focused ion beam (FIB) milling for cutting both carbon nanotubes and surface folds. In Fig. 3 two thick, inter-crossing carbon nanotubes are presented. In the left upper inset three locations are shown where cutting attempts were done. One may note the bright rims around the rectangular holes milled in the surface. These rims are produced by the re-condensation of the sputtered material. In the lower right inset the rectangular hole milled right at the inter-crossing is shown. A small hole in the section of the nanotube is marked by A, a more detailed image is presented in the upper right inset. Unfortunately, the hollows expected inside the carbon nanotubes are regularly filled with the sputtered material. However, the comparison with a partial FIB cut through a surface fold, Fig. 4, very clearly shows the difference between the structure of the nanotubes and that of a surface fold.

3. Conclusions

Carbon nanotubes were evidenced on HOPG irradiated with high energy, low dose, heavy ions. In the case of heavier ions like Kr and Xe large area, shallow surface craters were found from which frequently emerge one or several nanotubes. Some of the observed nanotubes vibrate during scanning with an AFM probe. The formation of carbon nanotubes from the C atoms sputtered...
Fig. 3. Scanning electron microscope images of carbon nanotubes cut by FIB. Main image: two inter-crossing carbon nanotubes; left upper inset: locations where FIB cuts were done; right lower inset: inclined view of the cut at the inter-crossing, note the dark region labeled by A; right upper inset: detail around A.

Fig. 4. Scanning electron microscope image of a fold on the graphite surface partially cut by FIB.
from the shallow craters is proposed. Cross-sectional examination of carbon nanotubes and surface folds of HOPG clearly showed different structures for these two kinds of features.

No amorphous deposits were observed, this indicates that the method used may prove useful to produce carbon nanotubes without producing other, unwanted materials like, amorphous carbon.

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