

Multi-walled carbon nanotubes on amorphous carbon films

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Abstract

Nanotubular structures composed of layered graphite sheets or other layered materials have been studied intensely by both scanning and transmission electron microscopy. In this paper, we will show how graphite structures, that are inherent to the production process of the amorphous carbon support films, used for both SEM and TEM studies can be easily mistaken for the actual sample structures. We will further report that these artifacts appear in both commercial as well as homemade holey carbon support films on copper grids, and suggest that to successfully study the “real” nanotubular structures only support films made from materials other than carbon should be used.

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1. Introduction

The discovery of one dimensional carbon nanostructures [1] has stimulated great research interest, due to their unique physical properties and potential practical applications in areas such as materials science, physics, and engineering [2]. These carbon structures are coaxial cylinders of rolled graphite sheets with a diameter of nanometer size while their length can be a few microns [1]. Thanks to the development of new synthesis methods, a broad range of new nanotubular materials such as carbon nanotubes filled with metals [3], encapsulated with oxides [3], doped with B or N atoms [4], or even layered materials other than carbon [5,11] were synthesized over the past years.

Due to the wide variety of synthesis methods used to create such nanotubular structures, the exact structure of the tubes is in many cases unknown, i.e. whether they are single or multi-walled, their length and diameter. The majority of studies on these nanotubular materials is performed by either SEM or TEM, where the specimen are prepared by dispersing the sample onto a holey

carbon film supported by a copper grid. The production techniques of these amorphous, holey carbon support films are in many cases very similar to the synthesis technique of the nanotubular structures. It is therefore conceivable that during the production process of the carbon support films, graphite structures are also created that closely resemble those of nanotubes. Once the SEM, TEM sample is prepared, it becomes impossible to distinguish such unwanted graphite structures from the “real” specimen [7]. Previously, Harris studied a variety of carbonaceous contaminants present on commercial carbon support films by TEM imaging only [6,7].

In this paper we will show that on both commercial as well as homemade carbon support films, a relatively high density of graphitic structures is found that are produced during the coating process. Further, we will show that on continuous carbon support films created by electron beam evaporation such graphite structures were not detected, which can be either attributed to the films production process, or to the fact that on the continuous film the nanotubular structures are harder to detect. In conclusion, we suggest that only support films, other than amorphous carbon should be used in the future to avoid studying the by-products of the carbon evaporation process.

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2. Experiments

We used three different kind of samples in this experiment. Initially, we started with a commercial holey carbon film on a 200 mesh Cu grid (SPI supplies). These commercial carbon films, pierced with a large number of circular holes with sharp edges and diameters in the range 0.1–1.0 μm , are typically used for TEM studies. A variety of methods are used to prepare holey films; here are two basic protocols for producing the holes:

- (1) Minute droplets of water are condensed onto the surface of a drying Formvar film. As the film dries, the water droplets pierce the film leaving circular holes.
- (2) Formvar is dissolved in a solvent containing water. This mixture, containing a non-polar solvent for the Formvar (e.g. ethylene dichloride) plus a partially polar solvent miscible with both water and Formvar (e.g. glycerol) will dry such that the more volatile solvents evaporate first, leaving minute water droplets to pierce the film. The holey film is detached from the support onto a water surface, the TEM grids are applied, picked up, dried, and a layer of evaporated carbon is added.

The carbon film is applied by d.c. arc-discharge evaporation. The apparatus used to evaporate thin layers of carbon consists of a bell jar that is evacuated to about 10^{-5} Torr which is low enough so the mean free path of vaporized atoms is long in comparison with the distance they are to travel. Carbon is evaporated by passing a current of 50 A through two rods, one sharpened down to ~ 1 mm diameter and the other ~ 3 mm. The two rods are held in contact by a spring while the current flows through the rods. Heat produced at the junction is sufficient to cause rapid evaporation. The amount evaporated can be estimated by the decrease in length of the narrow portion of the carbon rod or by noting the blackening of a piece of filter paper in the region surrounding the shadow cast by a small object (e.g. thumb tack) placed on the paper. Finally the Formvar film is removed and only the holey carbon film remains on the copper grids. The thickness of these films is usually estimated between 20 and 30 nm.

The second set of holey carbon films is produced in our laboratory by a similar technique on 200 mesh copper grids. Three millimeter copper grids are coated with a thick holey carbon film. The open areas are 5–10 μm in diameter which will support the thin (2–3 nm thick) carbon film substrate. The thin carbon film is prepared by ultrahigh vacuum evaporation onto a freshly cleaved crystal of rock salt. The thin carbon film is then floated on a dish of clean water. Grids covered with holey film, assembled in rings and caps for han-

dling in the microscope, are placed face down on the floating thin carbon film. The grids are picked up from above one at a time such that the thin carbon film retains a droplet of water.

Finally, we used continuous carbon films prepared by electron beam deposition. The carbon films were grown either in high vacuum (HV) system with base pressure of about 1×10^{-7} Torr or in an ultrahigh vacuum deposition machine (UHV) with base pressure $< 5 \times 10^{-10}$ Torr. An ultrahigh purity graphite rod 1–2 cm in diameter was used as source in both instruments. The deposition rate was monitored using in situ quartz thickness monitor. The deposition rate was between 1 and 5 $\text{\AA}/\text{s}$. The total thickness of the electron deposited films was between 70 and 200 \AA (thickness varies from film to film depending what the film is intended for—thicker for patterning, thinner for biological samples). In electron beam evaporation a beam of 4 kV or (10 kV in the HV machine) is used to heat the graphite source to a temperature sufficiently high to evaporate carbon atoms from graphite. Typically the pressure during deposition does not exceed 5×10^{-9} Torr (UHV machine) or 1×10^{-6} Torr in HV system. Furthermore it is possible that if electron beam evaporation is used the carbon arrives at the substrate atom by atom. This can be different from discharge deposited amorphous carbon films where there may be a possibility of removal and consequent arrival of multi-atom pieces of material onto the substrate. The high pressure backfill inert atmosphere sometimes used to reduce the deposition rates for discharge deposited carbon films can lead to gas-phase condensation.

3. Results

Fig. 1(a) shows a typical needle-like structure that can be found on the nominally empty commercial holey carbon films. The density of such structures varies for each copper grid hole, but on average three clusters of such structures as shown in Fig. 1(a) can be found per grid hole (i.e. grid hole size $\sim 97 \mu\text{m}$). In Fig. 1(b) a large number of bent graphite sheets can be recognized. These kinds of structures are usually found adjacent to the tubular structures. Fig. 1(c) shows a high-resolution TEM-image that can be clearly identified as a multi-walled nanotube (MWNT). The micrograph shows the central needle axis and several sheets, separated by a distance of 3.4 \AA , which matches that in bulk graphite. The wall thickness of these tubes are of the order of ~ 20 sheets and the tube diameter range from 13.9 to 16.5 nm. Electron energy-loss spectroscopy (EELS) (not shown here) independently confirmed that these tubes consist of C only, and the EELS C near-edge fine structure resembles closely that of graphite [8,9]. Due to the thickness of the amorphous C-films (~ 20 – 30 nm) these structures can be seen only when they extend into the

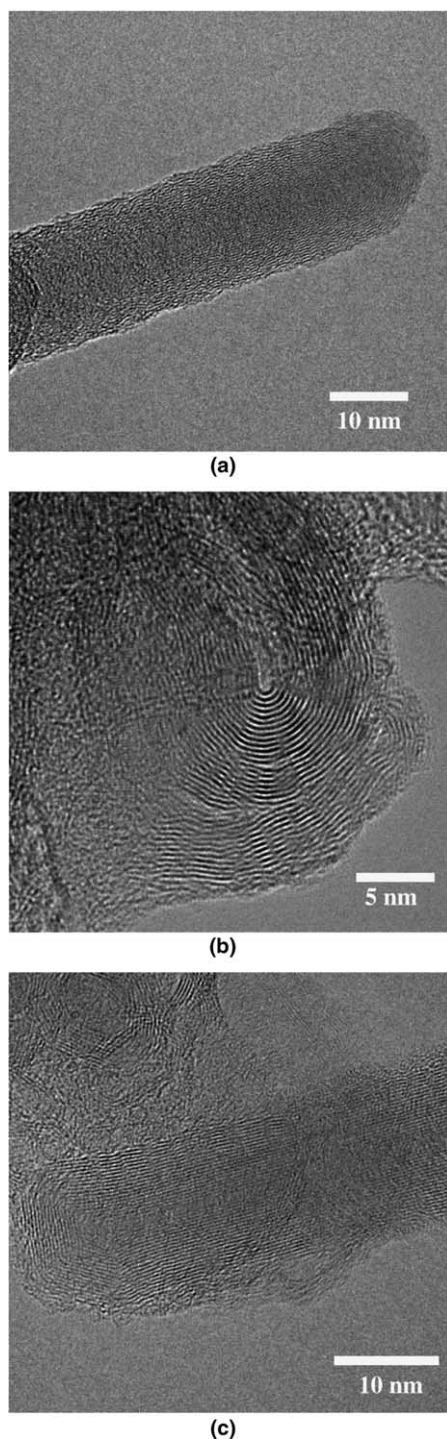


Fig. 1. (a) Low-magnification phase contrast image showing a carbon tube as frequently found on commercially available support films; (b) high-magnification image of curved C graphite sheets; (c) higher magnification micrograph of one of the multi-walled nanotubes, with the channel clearly visible in the center.

holes of the amorphous films. In total, we studied five different commercial holey carbon film grids, which presumably originated from two different production batches and the structures shown in Fig. 1 could be found on every grid.

Fig. 2(a) shows the typical topology of material that can be found on the “empty” holey carbon films produced by d.c. arc-discharge in our laboratory. For this kind of sample, we looked at three different holey carbon films to assure that the described features are not unique to one film only. All holey carbon films were taken from the same d.c. arc-discharge production batch. From the low-magnification image we can identify a wide variety of graphite structures, including graphite onions, fullerenes, and MWNT. Fig. 2(b) shows a higher magnification image from one of the tubular structures, that exhibits the typical features of carbon MWNT. The tubes diameter ranges from 9.4 to 14.2 nm, with wall thicknesses of the order of ~ 15 sheets of graphite. The distance between the individual sheets is with 3.4 \AA the same as in Fig. 1. Although the overall structure is similar to that in Fig. 2(a), the cluster density is generally lower in these films, but the size and

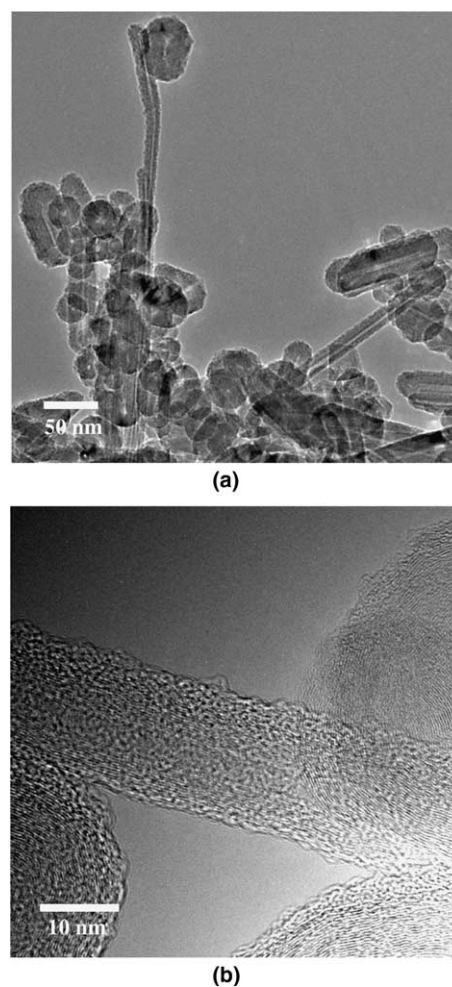


Fig. 2. (a) Low-magnification phase contrast image showing the cluster of carbon tubes and onions as found on a self-made C-support film; (b) higher magnification micrograph of one of the multi-walled nanotubes, with the channel clearly visible in the center.

diversity of these structures is larger than in the commercial holey carbon films.

The film, prepared by electron beam evaporation (not shown here) did not exhibit any of the features seen in the carbon films prepared by d.c. arc deposition. Note, that the films prepared by electron beam evaporation were continuous, but with a film thickness that is significantly lower than in the films prepared by d.c. arc deposition. On this film, we were not able to find any graphite-like structures, and only a small number of other contaminants was found.

4. Discussion and conclusions

As shown in the previous section, amorphous carbon films made by d.c. arc-discharge contain a relatively high density of graphitic structures that can be easily mistaken for genuine sample structures. Previously, such structures were always disregarded as contamination on the sample film. Since the discovery of carbon nanotubes [1], and the search for nanotubes of materials other than carbon [5,10], the sample material will look very similar to the structures that already exist on the nominally empty carbon films. Hence, there will always be the risk of studying the structure produced during the carbon film coating, rather than the actual sample of interest. It has to be noted here, that for samples with a large fraction of nanotubes the chance of looking at one of the carbonaceous contaminants is low. Furthermore, single-walled nanotube studies should largely be unaffected by the presence of the multi-walled nanotubes by-products of the carbon film production. Nevertheless, for samples with low sample purity or low sample density on the grid, the risk of studying the structures described in this paper, rather than the desired sample material is very high.

There are three possible solutions to this problem for samples with low sample density or purity. The usage of uncoated copper mesh grids will lead to contamination-free results, but the overall density of the sample material will be significantly reduced. Since the sample material will only stick to the copper grid, if at all, only the material that will hang over the copper support and into the grid hole can be studied. We do not recommend this method, although certainly the cheapest solution, since the sample is additionally not very well supported and might become unstable under beam exposure. The second solution involves the amorphous carbon films made by electron beam evaporation. Although we have only examined continuous carbon films, the density of observed carbonaceous contaminants was significantly lower than in the other films. After careful study of the electron beam evaporated carbon films, we can exclude that the lower density of contaminants is simply due to a lack of holes in the film, and hence due to the decreased

contrast of the contaminants on the film. Based on the growth conditions of the carbon films, we do not expect to see any graphite structures on the amorphous carbon film. Nevertheless, the fact that the film is continuous might make the study of carbon or even lighter materials, such as boron nanotubes rather difficult. But for thicker or more heavy sample structures, these films certainly provide a translucent and adequate support.

Hence, for the study of multi-walled nanotubular structures, we recommend the use of holey or lacey films made from other amorphous materials, such as SiO_x . These films are commercially available and although we have not tested such films yet, we do not expect to detect structures that can be easily mistaken for nanotubes of any kind.

In conclusion, we have shown that even on nominally empty holey carbon support films, a large quantity of graphitic structures can be found that look very similar to those of carbon nanotubes. As a precautionary measure, we suggest to use support films made from materials other than carbon or completely dispense with amorphous support films.

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