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The Formation of a Connection between Carbon Nanotubes in an Electron Beam

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ABSTRACT

Crossing multiwalled carbon nanotubes are connected by irradiating the junction in a scanning electron microscope. The aggregation of hydrocarbons and successive transformation into amorphous carbon under the electron beam is used to solder nanotubes and to make a mechanical junction. Transmission electron microscopy is carried out to study the graphitization of the junction under further irradiation or annealing.

In the past years, the electrical characterization of carbon nanotubes (CNT) has been a subject of intense research. These one-dimensional objects show most interesting electrical properties. For example, the conductivity of CNTs depends on their diameter and chirality; in particular, it has been found theoretically[1] and later eperimentally[2,3] that two-thirds of all possible single-walled nanotubes are one-dimensional semiconductors, whereas the remaining one-third are one-dimensional metals. Due to the small diameter of CNTs, quantized conductance and ballistic electron transport are observable;[4] hence, CNTs can act as quantum wires.[5] Devices such as transistors based on CNTs have already been demonstrated.[6] Even possible superconductivity of CNTs has been reported recently.[7] (For an overview of the electronic properties of CNTs, the reader is referred to the review by Dekker.[8]) On a CNT basis, semiconducting devices can be made as well as conductive wires to connect devices electrically. Thus, CNTs are most promising candidates for applications in future nanoelectronics.

The realization of circuits on a CNT basis requires a technique that is able to connect the tubes electrically with each other and with their periphery. However, as previous studies show, making an electrically conductive connection between nanotubes is not straightforward. Instead of the desired ohmic contacts, tunnel junctions are often generated. Studies of unmodified crossed single-walled metallic nanotube junctions show a resistance of approximately 200 kΩ.[9] Such a high resistance has to be interpreted in view of the small contact area on the order of 1 nm^2 (crossing tubes touch at one point only). Improvements may be expected when a connection by a technique such as welding, soldering, or pasting can be established that joins the tubes with an electrically conductive material over a larger surface area. Conventional techniques such as pasting with conductive epoxys or soldering with liquid metals (like tin) are hardly applicable due to the small dimensions of the arrangements. A promising approach toward mechanical manipulation of nanotubes has been demonstrated recently by Ruoff et al.,[10,11] who showed that the focused electron beam in a scanning electron microscope (SEM) can be used to deposit a small amount of hydrocarbon contamination so as to attach the tubes on an AFM tip.[10] Such a "nanowelding" technique has been used to manipulate CNTs under a scanning electron microscope and to carry out mechanical testing experiments.[11]

The present work explores the possibility to join CNTs mechanically by forming an aggregate of amorphous carbon in the beam of an electron microscope. Hydrocarbon molecules from the air and other environments are attracted by CNTs as they are by most other specimens. At room temperature, these molecules are highly mobile on almost all surfaces. Once such molecule migrates into the area that is irradiated with an electron beam of sufficient energy, dissociation under the beam leads to the transformation into amorphous carbon, which is immobile and remains in the irradiated area.[12,13] Thus, sustained irradiation of a slightly contaminated surface leads to the accumulation of amorphous carbon. Such a contamination-induced modification of specimen surfaces is normally unwelcome in scanning or transmission electron microscopy but can be made use of in lithography[14] or other applications where nanometer-sized patterns have to be deposited in a controlled way. The electrical conductivity of such a deposit has not been studied in detail; however, amorphous and graphitic carbon are known to be conductive, whereas hydrocarbons are insulators. The conductivity of the deposit depends therefore on the completeness of the transformation of hydrocarbons to amorphous or graphitic carbon.

Modern SEMs with field emitters focus the electron beam onto a spot of less than 1 nm in diameter. These instruments

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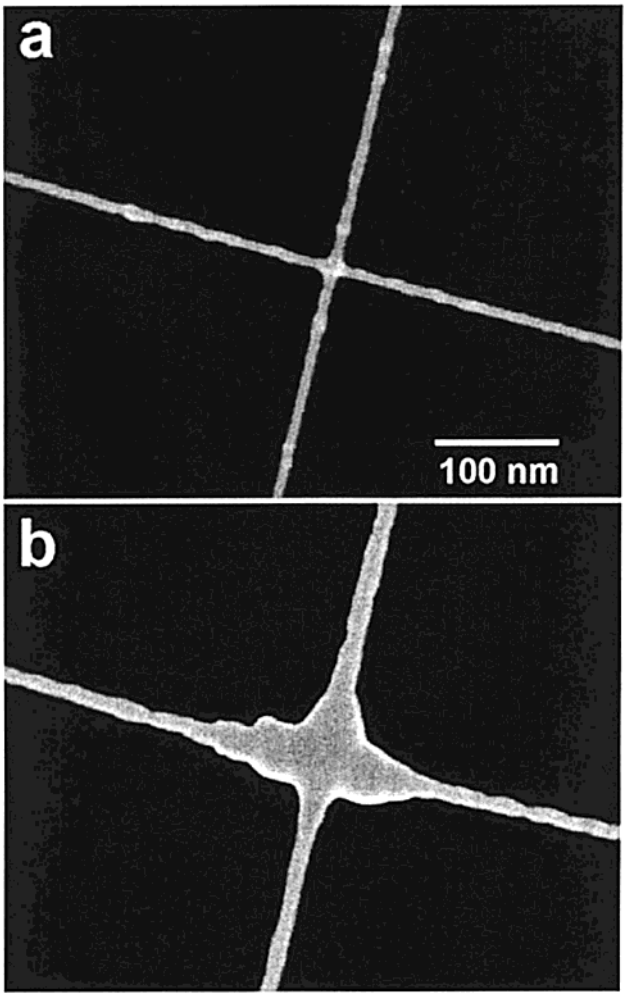

Figure 1. Scanning electron microscopy images of a nanotube junction before (a) and after (b) soldering by deposition of amorphous carbon. Due to a high contamination rate, the deposit at the junction is large. Some contamination is already visible in (a) due to inevitable irradiation during recording of the SEM image (droplets on the tubes).

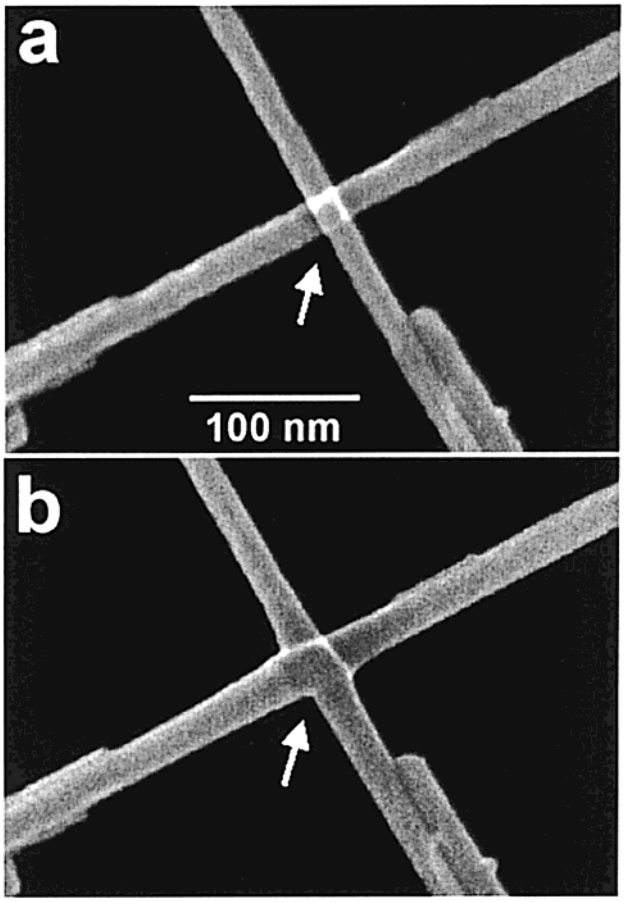

Figure 2. Nanotube junction treated as described in Figure 1 but with a small deposit (low contamination rate).

allow to image the shape of CNTs with almost subnanometer resolution and to manipulate surfaces by depositing contamination selectively. In such a way, a pellet of contamination can be deposited on the junction of two crossing tubes, as is demonstrated in the present study. This is actually a technique of soldering because the tubes do not coalesce; instead, they are held together by a small aggregate of amorphous carbon.

Multiwalled carbon nanotubes were obtained from the deposit on the cathode of an arc-discharge apparatus. The deposit containing nanotubes was prepared on metal support grids for transmission electron microscopy (TEM). The specimens were stored in air for periods between a few hours and several years (some old TEM specimens from earlier work were used). These specimens were studied and irradiated in an SEM (Hitachi S-5200) that was equipped with a field emission gun and an in-lens specimen stage for ultimate resolution. With this instrument, CNTs could be imaged with a resolution of slightly better than 1 nm.

It was found that the amount of contamination depends on the period during which the specimen was exposed to air; whereas newly prepared specimens show almost no contamination even after longer irradiation. Nanotubes in old specimens are covered by a layer of hydrocarbons that leads to rapid accumulation of contamination in the electron beam. Apparently, CNTs strongly attract hydrocarbon molecules from the air. When two crossing nanotubes were found in the specimen material, the beam of the SEM was focused onto the point of contact until the contamination deposit had reached a measurable size. Figures 1 and 2 show two junctions before (a) and after (b) the deposition. Figure 1 shows an example of high contamination rate, Figure 2 of low contamination rate. The soldering effect of the deposit can be clearly seen. To promote the transformation of hydrocarbons into amorphous or graphitic carbon already in the aggregation, a higher SEM voltage (20−30 kV) was used.

To improve the electrical conductivity of the deposited material, graphitization of the initially amorphous deposit was attempted, either by irradiation with an electron beam of higher energy in a TEM or by annealing in a furnace at high temperature. After the generation of junctions in the SEM, some specimens were transferred to a TEM where the junctions were irradiated with electrons of 80 keV energy for several minutes. Because the threshold electron energy for atom displacements in graphitic carbon is around 100 keV,[15] electron energies >100 keV lead to radiation damage of the tubes and are therefore not useful for graphitization. However, as the threshold energy is lower in amorphous

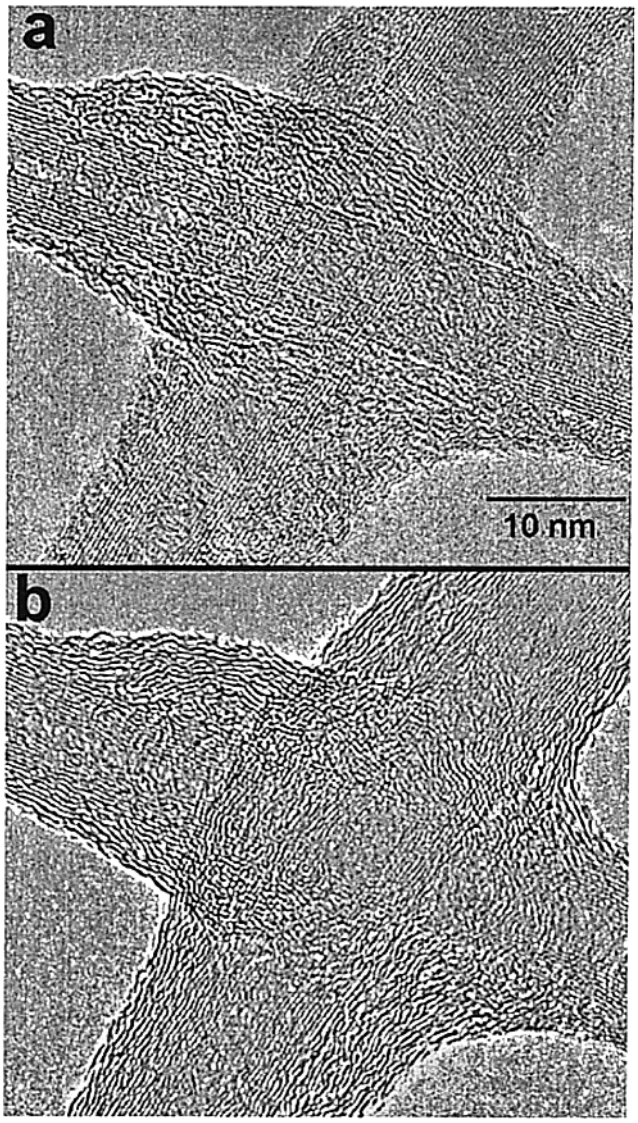

Figure 3. Transmission electron microscopy images of a nanotube junction with a carbon deposit before (a) and after (b) irradiation-induced graphitization. The deposit connects the tubes on the right-hand side of the junction.

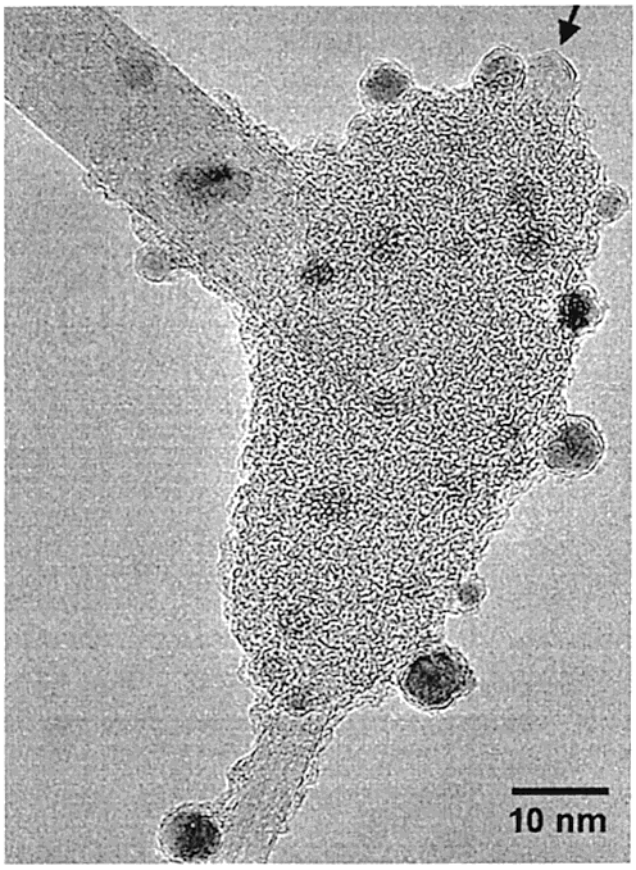

Figure 4. TEM image of a T-junction of two nanotubes after deposition of amorphous carbon and annealing at 700 °C. (The black dots are metal crystals that have condensed on the sample during the annealing procedure in the furnace.)

carbon, grahitization can be achieved by displacements in the amorphous phase at an electron energy of 80 keV. Irradiation-induced graphitization has therefore to be carried out at electron energies between the displacement thresholds for amorphous carbon and graphite. As an alternative approach to graphitization, some other specimens were annealed in a furnace in high vacuum (2×10^{-7}mbar) at 700 °C for about 1 h.

Successive investigation of the nanotube junctions was carried out in a TEM (Philips CM-20-ST). Figure 3a shows a TEM image of a junction of two nanotubes after deposition of contamination in the SEM. The deposit shows amorphous carbon and some disordered graphitic basal layers. Figure 3b shows the result of irradiation with an 80 keV electron beam in the TEM. The graphitization is improved; however, some damage of the tubes appears due to inevitable irradiation with 200 keV electrons during imaging in the TEM. Figure 4 shows another junction after thermal annealing. (Small Cu crystals were unintentionally evaporated during the annealing in the furnace and condensed on the sample but are not of interest here.) Apparently, at temperatures up to 700 °C, the annealing does lead in a small way to improved graphitization. As a result, irradiation with an electron beam of appropriate energy seems to be more effective in graphitization than does annealing at moderate temperatures.

To investigate the usefulness of the present technique for making contacts in a nanotube network, the electrical characterization of such a nanotube junction has to be carried out. In particular, it has to be clarified whether ohmic contacts with a sufficiently high conductivity are created. This was not the subject of the present study but can be undertaken when CNTs are deposited on a substrate patterned with electrodes. The attachment of CNTs to the electrodes and the junctions between the tubes can be made by "soldering" in the SEM. Measurements of the conductivity could clarify whether graphitization after the deposition of contamination is necessary to obtain the desired conductivity. Irradiation-induced graphitization could be integrated into an automatic process (electron beam lithography) because graphitization would already be induced during the deposition when carried out at sufficient electron energy. In a possible fabrication of nanotube devices, the deposition of contamination could be controlled by evaporation of hydrocarbons or polymeric material onto CNTs before soldering in the electron beam.

Although the conductivity of the junctions has not been measured here, it is to be expected from the known properties of carbon material with similar atomic structure (such as glassy carbon) that these amorphous or graphitic carbon deposits have sufficient conductivity. A high conductivity of a contamination deposit is further supported by results from ramified growth of carbon filaments in the Laplace field of charged insulators in an electron microscope.[16,17] However, it should be pointed out that with the technique described here, the contact is established between the *surfaces* of nanotubes. Because the conductivity of graphite is anisotropic (the conductivity is higher within the graphene planes than along the *c*-axis), such a contact should be different from a contact with an open end of a nanotube. A junction of two tubes where the tubes join by coalescence of the lattices would be highly interesting, but this has not, to the author's knowledge, been realized to date.

To conclude, a connection between carbon nanotubes was achieved by depositing carbon contamination selectively at nanotube junctions with an electron beam. Although a SEM was used to deposit the aggregate, inspection of the junctions by high-resolution TEM showed that the surfaces of the tubes are connected with graphitic material that can be expected to be electrically conductive.

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