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Transmission electron microscopy and transistor characteristics of the same carbon nanotube

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A technique is presented which allows one to combine TEM investigations with transport measurements and potentially a wide range of other investigations on the same nanoobject. Using this technique, we have obtained high-resolution transmission electron microscopy images and transport investigations including transfer characteristics on the same single-walled carbon nanotube. The transfer characteristics show ambipolar transport. This observation is discussed taking into account TEM information on tube diameter, number of tubes in the bundle, and possible tube filling with fullerenes (peapods). © *2004 American Institute of Physics*.
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In investigations on nanometer-sized objects often the problem arises that the true nature of the object is not fully known. The interpretation of such measurements then depends on assumptions. For example, the electronic characterization of an individual carbon nanotube is usually carried out by placing two lithographic contacts onto a nanotube which is adsorbed on a substrate. The diameter of the nanotube is estimated by atomic force microscopy (AFM), but this technique does not allow one to tell whether the measurement is performed on a small bundle or a single tube.

Recently, carbon nanotubes encapsulating fullerenes or endohedral metallofullerenes, so-called peapods, have attracted considerable interest. In the case of filled nanotubes, there is no way to tell whether the particular nanotube on which the electronic transport measurements are performed is filled or not.

It is highly desirable to obtain a transmission electron microscope (TEM) image of the very same carbon nanotube on which the transport measurement has been carried out. A TEM image shows whether there is a single nanotube or a bundle, and it reveals the diameter and filling of the tube. Transmission electron microscopy, however, is not possible on objects on a bulk substrate. As the name implies, TEM requires that the electron beam can travel in a straight line through the sample.

None of the previous approaches for combining TEM and transport[1,2] allowed for an electronic characterization of the nanotube in field-effect transistor configuration. However, the dependence of the current on the gate voltage provides crucial information about the electronic structure of the carbon nanotube.

We present a technique which allows electronic transport measurements (including gate response) and subsequent TEM analysis on the very same single-walled carbon nanotube (SWNT). This method is not limited to carbon nanotubes. It is possible to basically select an object, like a carbon nanotube, on the substrate and bring it into the view of the transmission electron microscope. Moreover, it is a simple way to create arbitrary nanostructures which, in the end, are no longer on a substrate.

The principle behind this method is as follows (Fig. 1): First, the desired structures are created by standard lithographic methods. At this point any measurement which requires the presence of a substrate is possible. The substrate is cleaved close to the structure. Next, the substrate is etched in such a way that the structures are undercut from the side (from the cleaved edge), leaving the structure sticking out over the edge. The resulting free-standing structure can be investigated by TEM and potentially by a wide range of other techniques.

Laser-ablation SWNTs were purified by repeated oxidization and subsequent HCl treatment and filled with Dy@C_{82} endohedral metallofullerenes,[3] yielding so-called metallofullerene peapods.[4,5] TEM investigation on the as-produced material showed that filled tubes were present. These SWNTs were suspended in a 1% aqueous solution of

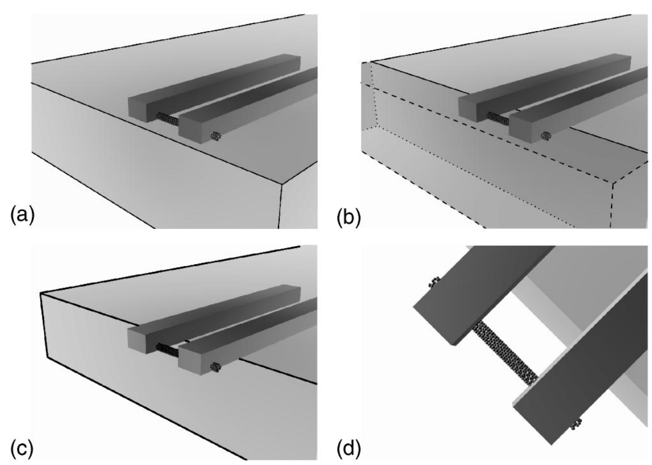

FIG. 1. Principle of creating the free-standing structures. The substrate is cleaved close to the metallic contacts on a carbon nanotube (a). The substrate is etched in such a way that the structure is undercut from the side, removing the shaded volume in (b). This leaves the structure with the nanotube free-standing (c) so that the substrate is not in the line of sight of the TEM [(d), top view].

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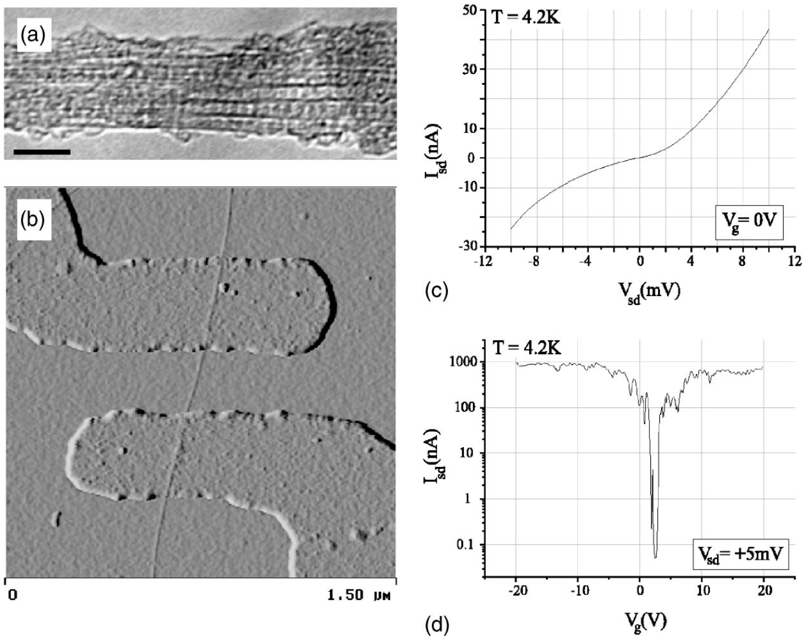

FIG. 2. (a) TEM image showing successful filling of single-walled nanotubes and resistance of the peapods to KOH etching. Scale bar =5 nm. (b) AFM image of a nanotube from the same material with AuPd contacts. (c) Output characteristic of the SWNT bundle for $V_g=0$ at 4.2 K. (d) Transfer characteristic of the bundle for $V_{sd}=+5$ mV at 4.2 K.

sodium dodecyl sulfate and adsorbed onto highly doped ($\rho \leqslant 6$ mΩ cm) silicon substrates with a 200 nm thermally grown silicon dioxide layer. An object suspected to be a single nanotube was located using AFM and a marker system.[6] Contacts consisting of 30 nm AuPd were deposited on top of the SWNTs using electron beam lithography [Fig. 2(b)]. The distance between the contacts was approximately 300 nm. We carried out transport measurements in field-effect transistor configuration at 4.2 K. The dependencies of the current I_{sd} on the source drain voltage V_{sd} and the back gate voltage V_g were measured. The gate voltage was swept within the limits of ±20 V.

After the transport measurements we cleaved the sample, so that the contacted nanotube was approximately 20 μm away from the cleaved edge. It turned out that additional mechanical support for these contacts is required. We created a supporting structure on top of the contacts in a further lithography step, consisting of 3 nm Cr and 110 nm Au. This structure is designed to keep the two contacts which hold the carbon nanotube in a fixed position relative to each other during the following etching step. The sample was etched in 30% KOH solution at 60°C for 7 h, followed by critical point drying. A TEM micrograph of a bundle of $(Dy@C_{82})_n$ @SWNT metallofullerene peapods, which has undergone the etching process described here, indicates that the etching procedure does not remove the fullerenes from the tubes [Fig. 2(a)]. As the silicon is etched much faster than the silicon oxide, the whole structure is undercut mainly from the side of the cleaved edge, leaving the structure reaching out over the edge of the substrate. This free-standing structure, with the carbon nanotube freely suspended between the AuPd contacts, was then investigated by TEM, using a Philips CM200 microscope at 120 kV.

The transport data shown in Figs. 2(c) and 2(d) are retrieved from the very same nanotube bundle that is shown in the TEM images in Fig. 3. The output characteristic $I_{sd}(V_{sd})$ was taken for $V_g=0$ at 4.2 K, the dependence of the current on the bias voltage is nonlinear [Fig. 2(a)]. For small values of V_{sd} a differential resistance of approximately 850 kΩ is obtained.

The transfer characteristic in Fig. 2(b) was measured at 4.2 K for $V_{sd}=+5$ mV. We observe so-called ambipolar transport, i.e., the current I_{sd} through the bundle is suppressed for intermediate values of the gate voltage V_g, whereas large currents are flowing both for high positive and high negative values of V_g. The regime of suppressed current is $\Delta V_g \approx 2.0$ V.

Figures 3(a)–3(c) show several TEM images, connected to span the length of the free-standing nanotubes. The TEM micrographs show a bundle composed of two single-walled carbon nanotubes, both with a diameter of 1.15±0.1 nm. Contrary to our expectation, no fullerene filling is observed. No twisting of the two nanotubes around each other is visible along the entire length. This implies that before etching the two nanotubes were lying parallel and next to each other on the substrate without overlapping or crossing. The substrate was orthogonal to the direction of the electron beam, and correspondingly the nanotubes appear at maximum separation orthogonal to the beam and do not overlap in the projection of the TEM images.

The electron beam exposure of the nanotube, before taking the first image [the one at the right-hand side of the tube, Fig. 3(c)], was only a few seconds. Tests with C_{60} peapods prepared in a similar way and viewed under the same conditions showed that observation of the C_{60} filling is possible before the fullerenes become amorphous due to irradiation damage.

Lee *et al.* have shown by scanning tunneling spectroscopy that filling of SWNTs with endohedral metallofullerenes reduces the band gap significantly.[7] This band gap narrowing makes the observation of ambipolar transfer characteristics likely, as reported in Ref. 8. However, band gap narrowing due to insertion of metallofullerenes can be ruled out for the bundle of tubes investigated within this study. The TEM images reveal that the two carbon nanotubes the bundle consists of are empty, and also that their diameters are too small to allow a filling with $Dy@C_{82}$.

To estimate the band gap E_g of the investigated SWNT bundle, it is required to know the coupling factor $\alpha = C_g/C_\Sigma$, where C_g is the capacity between the SWNT and the gate

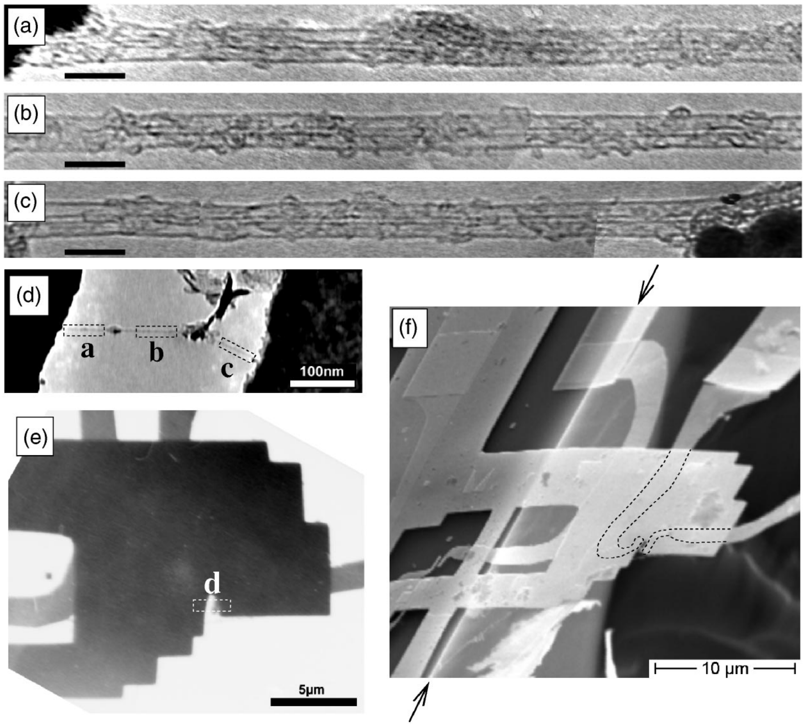

FIG. 3. (a)–(c) High-resolution TEM images of the nanotube segments. Scale bar =5 nm. The images show that the sample comprises two SWNTs, and that they are not filled with fullerenes. (d) The whole nanotube between the AuPd contacts. A piece of debris (dark spot), a contamination from the etching process, induces a kink in the nanotube. The low-magnification TEM image (e) and the SEM image (f) show how the nanotube and the contacts are embedded in the supporting structure which provides mechanical support. This structure is applied after the transport measurements and before etching. In (f), arrows indicate the edge of the substrate after etching. Structures to the left of this line are still on the substrate, while structures to the right of the line are free-standing. The dashed line indicates the location of the AuPd contacts that were used for the transport measurement. They are now covered by the supporting structure except for a small gap around the nanotube.

electrode and C_Σ the total capacity of the nanotube with respect to the metal electrodes and the gate. With a given α the band gap E_g is obtained by $E_g=\alpha\Delta V_g e$. Within this study a carbon nanotube which was not treated with the fullerene filling method exhibited Coulomb blockade behavior at 4.2 K which allowed one to extract $\alpha\approx 0.2$ from the diamond plot. Similar values for α have been reported by other authors.[9] Assuming the same α for the nanotube bundle investigated here results in a band gap of $E_g\approx 400$ meV. Using a nearest-neighbor C–C tight binding overlap energy of $\gamma=2.5$ eV[10] and a tube diameter $d_T=1.15$ one can calculate the gap of our tubes to be $E_g=309$ meV in reasonable agreement with the value deduced from the transport measurements.

Of course, $\alpha=0.2$ is only a crude estimate, and α can be different for different carbon nanotube field effect transistors, even if they are prepared in the same way. The smallest value of α we have found in the literature is $\alpha=0.05$,[11] which would lead to $E_g\approx 100$ meV, too small for the gap of a semiconducting nanotube and too large for a curvature-induced small band gap in a "nearly metallic" SWNT.[12,13]

Another possibility for the observed ambipolar transfer characteristics might be tube–tube interactions in the bundle of SWNTs.[14] Also the nanotube-contact interface may play an important role.[15,16]

We want to note that the number of tubes in a bundle can only be approximately determined from an AFM measurement. In our case, the diameter (i.e., the height) of the bundle was found to be 1.5 nm. Similar diameters have often been associated with single tubes, while our TEM images clearly show two nanotubes.

The above-mentioned results show that accessing selected nanotubes by TEM after transport measurements on the same object provides crucial information for the interpretation of the measurement. The described method makes it possible to bring nanotubes contacted in a widely used way, possibly from existing samples, into the view of the TEM. We envisage correlating TEM with further transport investigations, AFM measurements of mechanical properties on the free-standing tubes, TEM and Raman comparisons, and others. Furthermore, freely designed lithographic structures with carbon nanotubes in the TEM will enable new types of *in situ* investigations.

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