Length control of individual carbon nanotubes by nanostructuring with a scanning tunneling microscope

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We present a technique to control the length of carbon nanotubes. Individual carbon nanotubes can be locally cut by applying a voltage pulse to the tip of a scanning tunneling microscope (STM). Topographic imaging and STM spectroscopy are subsequently used to investigate the result. The electronic properties of a nanotube can be strongly changed by reducing the size. Current-voltage curves obtained by STM spectroscopy on a 30 nm short tube created from a longer nanotube show a stepwise increase of the current, which is attributed to quantum size effects. © *1997 American Institute of Physics.* [S0003-6951(97)03644-9]

Carbon nanotubes[1,2] are currently being intensively investigated because of their remarkable electronic and mechanical properties. Nanotubes can be thought of as single graphite sheets wrapped into seamless cylinders. They can be either semiconducting, semimetallic, or metallic, depending on the wrapping angle and tube diameter.[2,3] Most nanotubes consist of several concentric layers (multi-wall nanotubes), but single-wall tubes have also been found.[4] Recently a method has been developed to synthesize single-wall carbon nanotubes with high yield and structural uniformity.[5] Metallic single-wall nanotubes are predicted to be truly one-dimensional conductors.[2,3] It is for this reason that these nanotubes are considered as ideal quantum wires. Recent experiments by Tans *et al.*[6] have demonstrated the possibility of measuring electrical transport through individual single-wall nanotubes on nanofabricated electrodes. These measurements, performed at low temperatures, showed that the transport characteristics can be adequately described by taking into account single-electron tunneling and quantum-size energy-level splitting.[6,7]

The quantum transport properties of nanotubes strongly depend on their size and their capacitance to the environment. Control of the size of the nanotubes would allow investigation of the quantum transport properties at different length scales. Up till now it has not been feasible to control the length or diameter of nanotubes. In this letter, we present a technique to cut nanotubes into shorter sections by nanostructuring with a scanning tunneling microscope (STM). STM also allows investigation of the nanotubes before and after the cutting by topographic imaging and STM spectroscopy (STS). We demonstrate the possibility of strongly changing the electronic properties of a nanotube by reducing its length by the use of STM nanostructuring.

Carbon nanotubes are deposited from a dispersion in 1,2 dichloroethane onto single-crystal Au (111) surfaces. The samples are dried in air. The nanotubes were synthesized by a laser vaporization technique as described in Ref. 5 and consist mainly of ~1.4-nm-diam single-wall nanotubes. The nanostructuring experiments have been carried out with an ultrahigh-vacuum Omicron STS at room temperature and a home-built 4 K STM.[8] The latter has been used mainly in combination with STS measurements. All measurements are performed with Pt(90%)Ir(10%) tips, which are mechanically cut in ambient. Individual carbon nanotubes can easily be imaged on the atomically flat Au surface, both at room temperature and at 4 K. On a granular Pt film nanotubes appeared to be too mobile.[9] Figure 1 shows a large-scale image obtained on Au (111) at room temperature. Several nanotubes are visible as well as atomic steps on the gold surface. Figure 2(a) shows a room-temperature image of an individual nanotube together with a line profile through the molecule [Fig. 2(c)]. The apparent full width at half maximum of the nanotube (~5 nm) is determined by the tip size. From the height the diameter of the tube is found to be ~1.4 nm, which is a typical value.

We have found that it is possible to cut nanotubes in a controlled way by STM nanostructuring. Tubes are cut by the following procedure: During imaging, scanning is interrupted and the tip moves to a selected position on the nano-

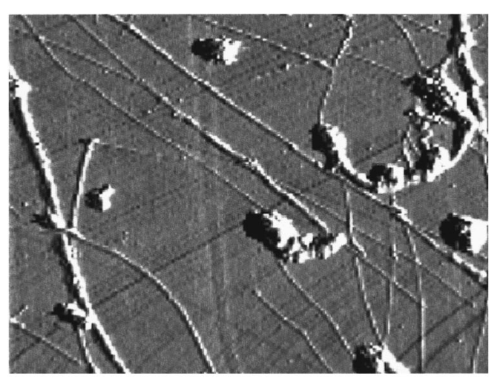

FIG. 1. Large-scale image of several individual nanotubes at room temperature. Monoatomic steps in the gold surface, some amorphous carbon particles, and larger bundles of nanotubes are also visible. Image size is 700 $\times 400$ nm^2.

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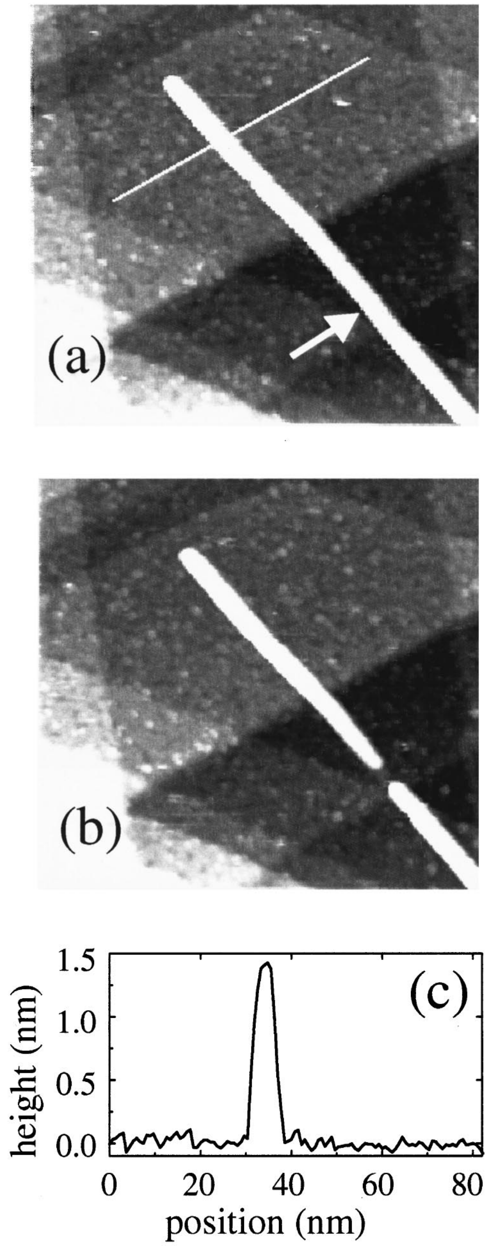

FIG. 2. Room-temperature STM images of a carbon nanotube (a) before and (b) after it was cut at the position on the tube marked with the arrow by applying a voltage pulse of -6.5 V. From the line profile (c), taken along the white line in (a), the diameter of the tube is found to be about 1.4 nm. The image size is 125×125 nm^2.

tube. Feedback is then switched off and a voltage pulse between tip and sample is applied for a specified period. After this voltage pulse, the feedback is again switched on and the tip is moved back to the position where the scanning was interrupted. Scanning is then resumed. A break in the nanotube on the selected position is visible if the cutting has succeeded. Figure 2(b) shows the result of a voltage pulse of -6.5 V on the position marked in Fig. 2(a). It appears that the cutting procedure is a reproducible technique to shorten tubes. Figure 3 shows an example where a nanotube was cut at four different positions. Imaging is typically done at a bias voltage of 100 mV and tunnel current of 20 pA. For all cutting experiments we have used a pulse length of 1 ms, but different voltages of both positive and negative sign. The

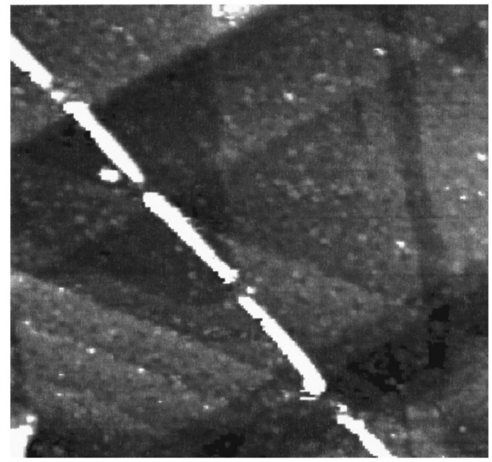

FIG. 3. Room-temperature STM image of a carbon nanotube, which was cut into several smaller tubes to demonstrate the reproducibility of the cutting technique. Voltage pulses of -6.5 V were used. The image size is 140×150 nm^2.

lower limit for the voltage necessary to cut a tube is about 4 V. Voltage pulses of 3.5 V or lower were never successful. With voltages above 5 V, tubes are always cut. The sign of the voltage appears not to be relevant. The determining parameter in the cutting process turns out to be the voltage rather than the current. Applying a very high tunnel current up to 50 nA at low voltages does not result in any change in the nanotube. The same procedure to cut nanotubes was also successful at 4 K.

The gap in the tube which arises after a cutting event is typically in the order of 5–10 nm. During the voltage pulse, carbon material from the nanotube directly under the tip is removed. Occasionally it partly stays in or near the gap, as is observed from STM images. For example in the upper left corner of Fig. 3, two carbon particles are visible as white dots of $\sim$5 nm in and near the gaps in the nanotube. In most cases material is picked up by the tip, which is apparent from a sudden degradation of the imaging quality after a cutting event. By applying a voltage pulse of 6 V on a bare part of the gold substrate the tip can be cleaned again, and the quality of STM imaging restored. It can be confirmed that the tip is indeed free from dirt by carrying out STS on the bare gold substrate. The resulting current-voltage ($I-V$) curve will be linear, as is expected for a metal substrate, only if the tip is clean.

From our observations it can be concluded that the tubes can only be cut by applying a relatively high voltage. We speculate that electrons injected into the nanotubes with a minimum energy of about 4 eV may break up the carbon–carbon (C–C) bonds in the nanotube. The bonding of the hexagonal carbon lattice on the surface of the nanotubes can be described by a sp^2 hybridization with a small admixture of sp^3 character due to the curvature. The bond energies in this lattice will be in between the bond energy of 3.6 eV for a single C–C bond and 6.3 eV for a double C═C bond. The minimum voltage of about 4 V to break up a tube is indeed within this range.[10]

The length control of nanotubes provided by the cutting technique may be used to investigate the electrical properties of very short nanotubes. Here we report an example where

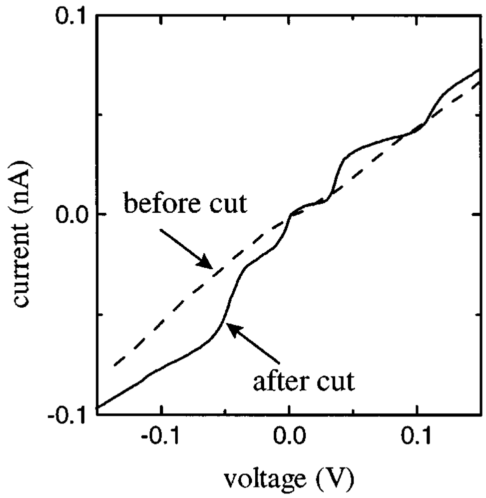

FIG. 4. $I-V$ curves obtained by STS on an individual single-wall nanotube at 4 K. The dashed line denotes the $I-V$ curve before the cutting. The solid line represents the $I-V$ curve after the nanotube was cut into a 30 nm short tube section. The length reduction appears to change the $I-V$ curve from linear to stepwise. This can be explained by the occurrence of quantum size effects.

the $I-V$ characteristics observed by STM spectroscopy at 4 K changed dramatically after a long tube was shortened to a 30 nm tube section (Fig. 4). Before the cutting event, $I-V$ curves taken at different positions on the nanotube were approximately linear. No gap was observed up to ± 1 V, indicating that the nanotube exhibits metallic behavior. By contrast, the $I-V$ curves on the shorter section made from the same tube show a clear steplike behavior of the current. The $I-V$ curves on the bare gold near the tube were linear, indicating that the tip is clean. We attribute these current steps to discrete energy states of the tube which line up with the tip Fermi level at increasing voltage. Discrete energy states result from quantum confinement of electrons in the length direction of the tube. The separation between the energy states (ΔE) scales inversely linear with the nanotube length. In transport experiments ΔE for a 3 μm tube was found to be $\sim$0.4 meV.[6] We thus expect ΔE to be in the order of 40 meV for a 30 nm tube. This corresponds well to the observed step widths which vary between 30 and 75 meV. Single-electron tunneling due to Coulomb charging has been shown to be the dominant low-bias feature in electrical transport measurements.[6,7] In our case, Coulomb charging is expected to be less relevant since the nanotube makes contact to the metal substrate over its full length. This results in a large capacitance of the tube to the substrate and accordingly a small Coulomb charging energy. The $I-V$ curve cannot be explained by a Coulomb staircase because the steps are not equidistant.

Summing up, we have presented a method to control the length and therefore the electrical properties of individual nanotubes by STM nanostructuring. The technique of cutting nanotubes into shorter sections may also be useful for the future development of nanotechnology. Construction of devices on a molecular scale can be envisioned, where structuring and manipulation of individual nanotubes by STM is used.

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